Environmental Security Technology Certification Program (ESTCP)

Field Demonstration and Validation of a New Device for Measuring Water and Solute Fluxes NASA LC-34 SITE

Final Report

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List of Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
CAR	corrective action report
CF	chloroform
CFB	Canadian Force Base
CM	chloromethane
CU	clay unit
CV	coefficient of variation
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FID	flame-ionization detector
FRTR	Federal Remediation Technology Roundtable
FTL	field team leader
GC	gas chromatography
HASP	health and safety plan
IDL	instrument detection limit
IDLH	immediately dangerous to life or health
LSU	lower sand unit
MDL	minimum detection level
MeCl	methylene chloride
MFGU	middle fine grain unit
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
PCE	perchloroethylene
PEL	permissible exposure limit
PPE	personal protective equipment
PSO	project safety officer
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RRF	relative response factors
RRT	relative retention times
SD	standard deviation
SOP	Standard operating procedure

SRM	Standard Reference Materials
SSO	site safety officer
TCE	trichloroethylene
TLV	threshold limit value
TWA	time weighted averages
USU	upper sand unit
VOA	volatile organic acid

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Executive Summary

The use of contaminant flux and contaminant mass discharge as robust metrics for assessment of risks at contaminated sites and for evaluating the performance of site remediation efforts has gained increasing acceptance within the scientific, regulatory and user communities. The Passive Flux Meter (PFM) is a new technology that directly addresses the DoD need for cost-effective long-term monitoring, because flux measurements can be used for process control, for remedial action performance assessments, and for compliance purposes. However, the use of innovative technologies such as the PFM can be slow to gain acceptance in the environmental community. Thus, to gain acceptance it must be shown that the PFM technology possesses a sound theoretical basis accepted widely in the technical circles and that it be field-scale demonstrated 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 Construction Base in Port Hueneme, California; and the Naval Surface Warfare Center at Indian head, Maryland. The projects at Hill, NASA, and Borden include 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 stimulated commercialization. The Port Hueneme project evaluated MTBE flux with similar objectives while the Indianhead project demonstrated the borehole flux meter to measure water and perchlorate contaminant flux.

The focus of the NASA site was to demonstrate and validate a the PFM, for measuring simultaneously the groundwater and contaminant fluxes in contaminated aquifers. More specifically, PFMs were tested 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™.

Site Study Objectives

- Evaluate the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant flux during bioremediation.
- Compile field data in support of an effort to transition the technology from the innovative testing phase to a point where it receives regulatory and end user acceptance and stimulate commercialization.

Methods

To demonstrate the performance of the passive flux meter method at site LC34, groundwater and contaminant flux was evaluated during 4 deployments in order to establish baseline flux during steady water flow, flux during ethanol biostimulation, and flux after application of microbial KB-1 bioaugmentation. Alcohol tracer pre-equilibrated, wet activated carbon was packed into crinoline socks on site at each deployment. During the packing process, field samples were collected to measure the initial concentrations of tracers present on the activated carbon. After exposure, the flux meter was extracted from the well and sub-sampled in vertical sections to vials of isobutyl alcohol. A total of 6 PFMs, 2 per well, were installed on site at each of the 4 phases of the evaluation. Laboratory extraction of the samples involved a two step process: the initial extraction with the isobutyl alcohol followed by a second extraction with an acetone and hexane

mixture. From the extracts, all samples were analyzed for alcohols and contaminants using GC and HPLC analysis.

To estimate groundwater flux, the alcohol tracer mass fraction present on the PFM sorbent was quantified and compared to the initial mass fraction before well insertion. To perform this analysis, Hatfield et al. (2004) presented the theory and quantitative tools required to estimate the water flux using the intercepted alcohol-tracer mass ratios.

To compare PFM measured fluxes with alternative methods of assessment, contaminant concentrations were monitored at 5 multilevel sampler (MLS) wells. Extraction well water samples were also analyzed during each PFM deployment. Both the groundwater flux and contaminant mass flux were calculated from PFM quantification methods (Hatfield et al. 2004) and then compared to contaminant fluxes derived from 1) taking the product of the induced specific discharge in the test cell and contaminant concentrations measured at multilevel samplers and 2) contaminant mass flows measured at the central extraction well.

Groundwater Flux Results

During the first installation, which occurred before ethanol biostimulation, and KB-1 bioaugmentation, the measured ambient groundwater fluxes relied on analyses of the ethanol resident tracer. These results compared favorably with the induced flux. For the second deployment, the ethanol biostimulation stage, resident tracers isopropyl alcohol and tert-butyl alcohol were used successfully, providing results within a 10-15% error range. PFM measurements after bioaugmentation indicated an unexpected 60% increase in flux (based on the ethanol tracer). The bioactivity in the aquifer manifested in pump fouling and the development of a biofilm in the well; these conditions may have contributed to a significant degradation of ethanol tracer on the PFM despite the use of silver-impregnated activated carbon. A loss of ethanol tracer by biodegradation would have resulted in an overestimation of water flux. It is also possible the microbial biofilm protected active bacteria within the matrix from the inhibitory affect of the silver ion. Because ethanol is easily degraded, this would contribute to a reduced ethanol mass fraction on the PFM sorbent. Finally, there is also the possibility that silver's inhibitory activity on bacteria was exhausted in a highly bioactive environment at LC34 (Zhang et al. 2004; Chambers et al. 1962; Russell and Hugo, 1994; Silver, 2003).

Contaminant Mass Flux Results

During the initial background flood, contaminant flux measurements were taken for TCE, dichloroethylene (DCE), vinyl chloride (VC), and ethane. Fluxes were also derived for the same contaminants using concentrations gathered from MLS wells. There were significant differences between the MLS derived and PFM measured fluxes for both TCE and DCE. Vinyl chloride and ethene were not detected in the first phase. During the second biostimulation phase, vinyl chloride appeared due to ethanol enhanced TCE degradation. Again, relative differences between MLS derived and PFM measure fluxes were high. PFMs gave significantly higher integral assessments of VC and DCE fluxes. Differences in trichloroethylene fluxes estimated by MLS versus PFM were even more dramatic after microbial application. Vinyl chloride and ethene fluxes measured by PFM were more than 100% higher than estimates from MLS, while the integral TCE and DCE fluxes from PFM were more than 60% lower; this would suggest

possible TCE and DCE degradation to vinyl chloride and ethene while when TCE and DCE were intercepted retained on the PFM sorbent.

Cost Assessment and Comparison

Costs were 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. 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

Vertical variations in the contaminant flux distribution were visualized using the passive flux meter measurements at NASA LC34. The compared mass discharges at the distinct phases of the project demonstrated dechlorination and mass reduction following biostimulation and KB-1 augmentation. Graphical plots of flux distribution showed the ability of the PFM to characterize vertical contaminant distribution.

Water flux estimates were in good agreement prior to bioaugmentation. After KB-1 bioaugmentation, the accuracy of flux estimates decreased but was within 67%. The site bioactivity appeared to degrade the resident tracer ethanol; as a result, this tracer was no longer suitable for estimating water flux. The less degradable and more highly sorbed alcohols appeared to give more a reliable assessment of the water flux.

During biostimulation and after bioaugmentation, contaminant flux estimates varied significantly with average differences between MLS and PFM measurements ranging from 58% to 189%. PFM measurements indicated significantly higher vinyl chloride and ethene fluxes than those derived from extraction well data and MLS samples. It may be that the PFM sorbent (activated carbon sorbent) functioned as an effective trap for these highly volatile and gaseous compounds (Baumann, 1989; Scamehorn, 1979). It might also be the case that the sorbed TCE and DCE degraded to vinyl chloride and ethene while sorbed on the activated carbon (Browne, 1990).

Recommendations

Based on these results, it appears that the inhibitory activity of the silver on the PFM sorbent is depleted in a highly bioactive environment. More research is needed to understand the nature of the inhibitory function. It may be that the silver ion existed at concentrations lower than expected or that it was in a reduced form. Also, it is possible that the bacteria had developed a resistance to the silver ion (Russell and Hugo, 1994; Silver, 2003). It is recommended that other sorbent materials be evaluated for more effective, longer-lasting bacterial inhibition.

1.0. Introduction

1.1. Background

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

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

The 'flux meter' 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 fluid flux.

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

The location of the field demonstration was the NASA Launch Complex 34 (LC-34) site at Cape Canaveral Florida. Site geology is composed of surficial sand and shell deposits that extend to a depth of 45 feet where clay is encountered. The Clay Unit (CU) is typically 2 feet thick but can be very thin, e.g., 0.5 feet. The surficial unit can be divided into three parts, the Upper Sand Unit (USU), the Middle Fine Grained Unit (MFGU), and the Lower Sand Unit (LSU). The aquifer exists within the MFGU, at a depth 22 to 30 feet below ground surface. The MFGU is a fine-grained sand layer with significant clay content. The top surface of the MFGU is irregular and the thickness of the unit varies significantly over short distances (from 1 foot to 17 feet).

The sediments in the surficial aquifer are relatively permeable. Vertical permeabilities range from 10^{-3} to 10^{-2} cm/s. The hydraulic conductivity ranges from 1.44×10^{-2} to 1.21×10^{-2} cm/s in the USU, from 8.28×10^{-2} to 5.43×10^{-2} cm/s in the MFGU, and 1.21×10^{-2} to 4.10×10^{-2} cm/s in the LSU. The difference between the three upper units and the CU is 4 to 6 orders of magnitude

(CU: 10^{-7}-10^{-8} cm/s). Previous measurements of vertical hydraulic conductivity of the CU range from $1.5x10^{-7}$ to $4.5x10^{-8}$ cm/s with an average of $5.89x10^{-8}$ cm/s.

Sediments and groundwater below the LC34 site contain residual trichloroethylene (TCE), cis dichloroethylene (c-DCE), and vinyl chloride. TCE tends to be associated with silty sand layers in the MFGU and with depressions on the surface of the Clay Unit. The focus of this project was on trichloroethylene (TCE) in the MFGU. Flux measurements were taken in coordination with a bioremediation study conducted by GeoSyntec to address DNAPL contamination cleanup.

The scope of the demonstration project included working with the GeoSyntec and NASA to conduct flux monitoring of the pilot bioremediation study during four phases of the experiment. The test plot consisted of three injection and three extraction wells which were used to produce a steady state flow cell. The first phase of the study, which was the first application of the flux meters, involved assessing conditions under steady water flow. These were employed in 3 fully screened wells located approximately 1.0 m upgradient of the extraction wells (Figure 1-1). Flux measured at these wells was compared to flux measured at the extraction wells and flux based on multilevel samplers located about 0.5 m upgradient of each flux meter well (Figure 1-2). Flux was then monitored during the next three phases of the study which included nutrient injection, microbe injection, and final post-bioaugmentation assessment.

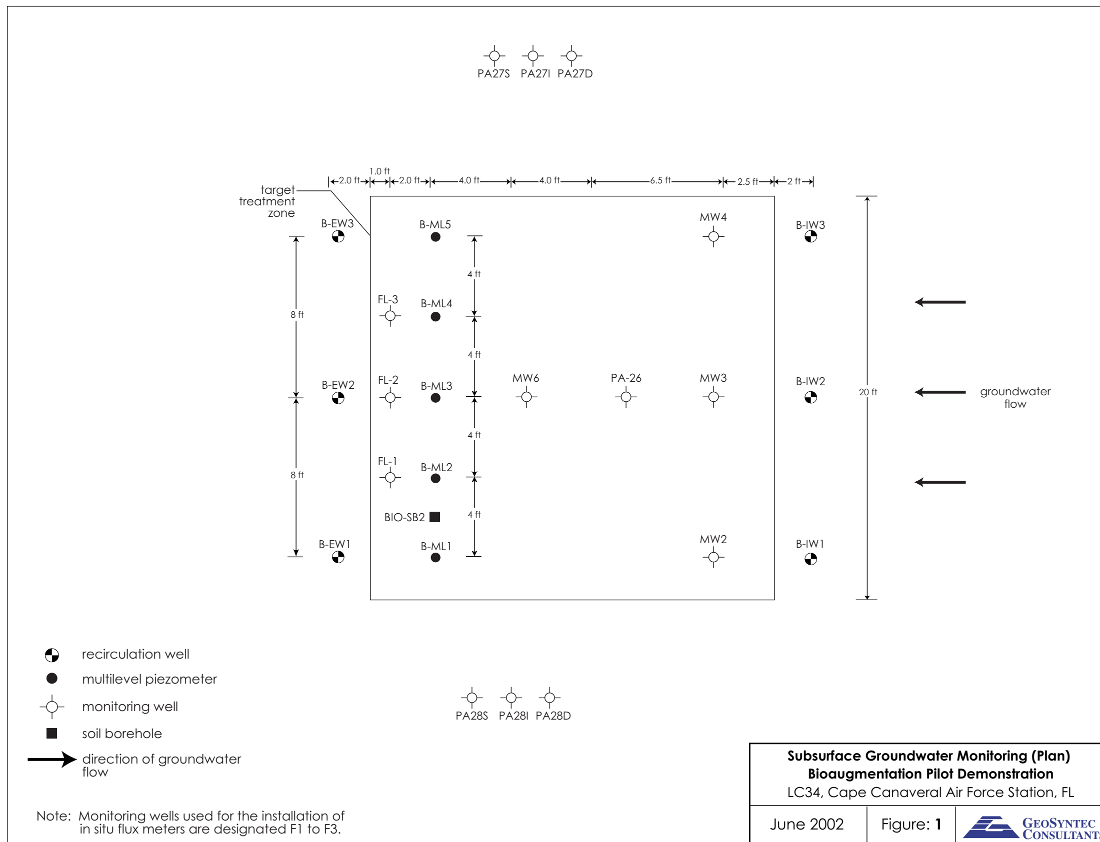


Figure 1-1. Schematic of the test cell constructed at the LC-34 site.

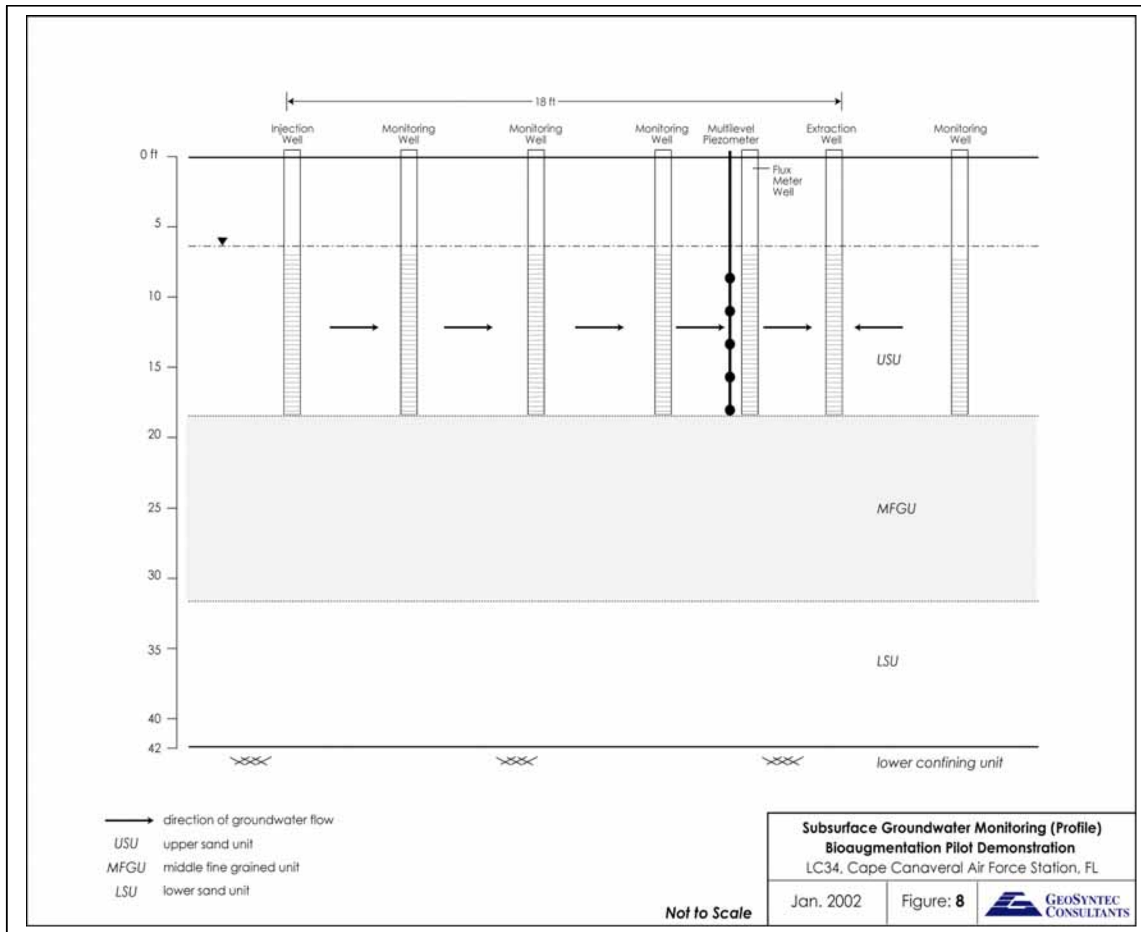


Figure 1-2. Vertical cross-sectional view of the test cell at the LC-34 site.

1.2. Objectives of the Demonstration

The specific objectives of this demonstration project were to:

1) demonstrate and validate the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant fluxes in groundwater,
2) demonstrate and validate a methodology for interpreting source strength from point-wise measurements of cumulative contaminant and water fluxes, 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 receives regulatory and end user acceptance and stimulate commercialization.

1.3. DoD Directives

Since the the Department of Defense (DoD) needs technologies that provide cost-effective long-term monitoring of volatile organic chemicals, petroleum and related compounds, trace metals, and explosives, this project demonstrated such a technology. The project was designed to validate the ‘flux meter’ which is a new technology for direct in situ measurement of both

cumulative subsurface water and contaminant fluxes. These measurements can then 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 flux meter yield correct results?
Issue 2: Can the flux meter yield reliable results in the presence of biodegradation?
Issue 3: Are monitoring costs of the flux meter lower than the costs of traditional technologies?

The demonstration addressed each issue of concern. In regard to the first issue, in situ flux measurements were compared to contaminant fluxes estimated from extraction wells and from multilevel samplers. Concerning the second issue, flux devices were installed under a range of biological stimulation experiments. The third and final issue was addressed through an analysis of costs incurred when traditional monitoring technologies are used to obtain comparable information on water and contaminant fluxes.

2.0. Technology Description

2.1. Technology Development and Application

This demonstration plan outlines the strategy for testing and validating a new method for direct in situ measurement of both cumulative water and contaminant fluxes in groundwater. The new method involves a device, hereafter referred to as a 'flux meter,' 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 flux meter 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 fluid flux.

After a specified period of exposure to groundwater flow, the flux meter is removed from the well or boring. Next, the sorbent is carefully extracted to quantify the mass of all contaminants intercepted by the flux meter and the residual masses of all resident tracers. The contaminants masses are used to calculate cumulative and time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative or time- average fluid flux. Depth variations of both water and contaminant fluxes can be measured in an aquifer from a single flux meter by vertically segmenting the exposed sorbent packing, and analyzing for resident tracers and contaminants. Thus, at any specific well depth, an extraction from the locally exposed sorbent yields the mass of resident tracer remaining and the mass of contaminant intercepted. Note that multiple tracers with a range of partitioning coefficients are used to determine variability in groundwater flow with depth that could range over orders of magnitude. This data is used to estimate local cumulative water and contaminant fluxes.

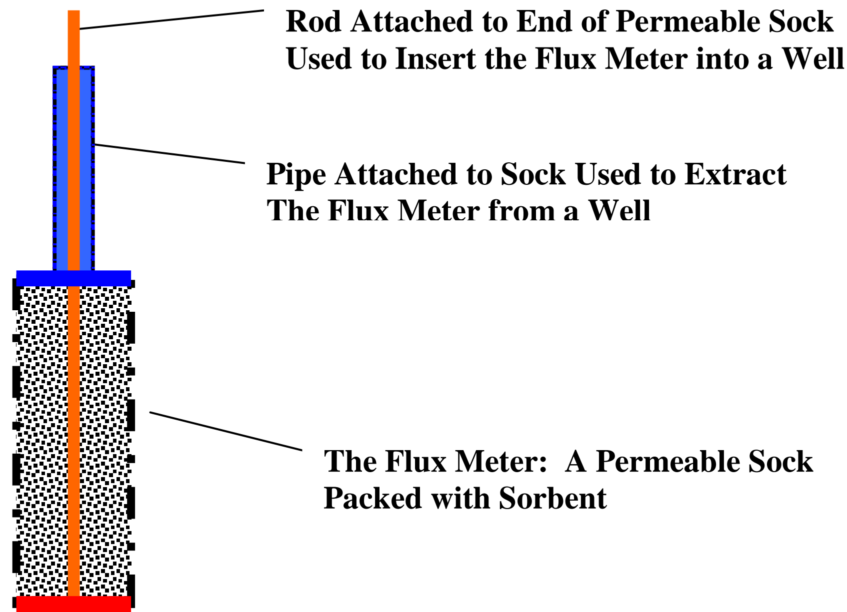


Figure 2-1. Schematic of a Flux meter comprised of a permeable sock filled with a selected sorbent.

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

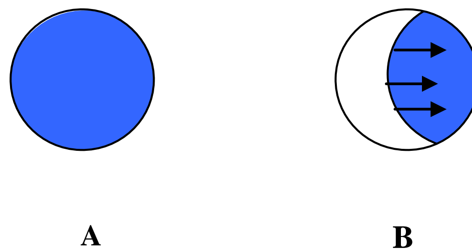


Figure 2-2. Flux meter cross-sections A: initial condition, B: displaced tracer distribution after exposure to a fluid flow field.

The mass of resident tracer remaining within section-B of Figure 2-2, can be used to estimate the cumulative fluid volume intercepted by this section of the meter. Assuming reversible, linear and instantaneous resident tracer partitioning between the sorbent and water, the dimensionless cumulative volume,ξ, of water intercepted by the flux meter at a specified well depth is obtained iteratively using the following Equation 2-1:

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

where M_R is the relative mass of tracer retained in the flux meter sorbent at the particular well depth. The water flux through the sorbent, q [L/T](e.g., m/day), is calculated using Equation 2-2:

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

where, r is the radius of the flux meter cylinder; θ, is the water content of the sorbent; R_d is the retardation factor of the resident tracer on the sorbent; and t is the sampling duration. Since in most field applications, flow is unknown, multiple resident tracers should be used to represent a broad range of tracer retardation factors. Also, providing a suite of multiple tracers designs for flux meters that can be utilized in both long- and short-term sampling durations.

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

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

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

The contaminant mass retained on the sorbing porous matrix can be used to estimate solute flux into the meter. The measured flux is valid over the dimensions of porous medium contributing flow to the device. For example, a meter designed to sample the entire vertical depth of an aquifer could be used to characterize horizontal groundwater and contaminant fluxes continuously over the vertical extent of an aquifer. Assuming reversible, linear and instantaneous contaminant partitioning between the sorbent and water, the contaminant mass flux Jc [M/L^2/T](e.g., Kg/m^2/day) can be determined using Equation (2-4):

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

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

A listing of key criteria used to design a flux meter 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 flux meter can be designed using estimated permeability ranges in the aquifer, the well screen and the sorbent (Klammler, et al. 2006).

Table 2-1. Key Design Criteria for the Flux Meter

Key Design Criteria	
Parameter	**Comments**
Sampling Period	The specified duration of continuous flux measurements
Sorbent	Must be resistant to microbial degradation
Retardation Factors of Resident Tracers	A suite of tracers are needed such that residual mass of one or more exists at the end of the sampling period, given 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

Development of the flux meter and pertinent design criteria evolved from theoretical work initially submitted as part of a patent (Hatfield et al. 2002). Since that time, multiple laboratory experiments have been performed to validate theory and design prototypes of devices that could be demonstrated in the field. Some of the initial investigations were bench scales studies of flux meters 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) devise a design to quantify both the magnitude and the direction of chromium (VI) fluxes.

Several potential applications exist for the flux meter. Simultaneous measurements of water 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 as shown in Equation 2-5.

$$\iint J_C dydz = Load[M/T] \quad (2\text{-}5)$$

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

2.2. Previous Testing of the Technology

Previous testing of the technology was limited to laboratory tests (Campbell et al. 2006; and Hatfield et al. 2001). Recent field scale testing has been conducted at the University of Waterloo test site at Canadian Forces Base Borden, Ontario; Hill AFB in Layton, Utah; Naval Base Construction Base in Port Hueneme, California; and the Naval Surface Warfare Center at Indian head, Maryland.

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 was anticipated that comparable analytical costs would be incurred for each tracer or contaminant analyzed per sample. One cost that is unique to this technology is the cost associated with the flux meter sorbent (i.e., activated carbon or ion-exchange resin).

Another important factor that affects costs is the frequency of sampling. A flux meter provides time-integrated information in a single sample. The same type of information can be obtained through multiple water samples. It was expected that the long-term flux measurements would 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 is greater than with typical groundwater sampling.

As indicated above, the design and therefore the performance of the flux meter depends on several factors. For example, knowing the permeability of the meter and having a good estimate of the aquifer permeability is essential. For example, it is preferable the sorbent have a permeability that is at least 36 times a great as the aquifer. It is also important that the contaminant and some resident tracers have an affinity for the flux meter sorbent that is considered high but reversible; thus, the sorptive characteristics of both the contaminants and resident tracers must be known.

2.4 Advantages and Limitations of the Technology

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

The flux meter possess the advantage of providing a long-term monitoring solution that generates time integrated estimates of both groundwater and contaminant flux. Hence, transient fluctuations in contaminant concentrations and groundwater flows are not an issue of concern, as they are with traditional monitoring methods, because such variations are directly integrated in flux estimates. Field measurements do not require training beyond that currently needed in collecting groundwater samples. However, unlike typical groundwater sampling protocols, the wells used for flux measurements are not purged; thus, disposal of contaminated purge water is not an issue. Note that implementation needed to be long enough so that the initial bore volume perturbation, both chemical and hydraulic, would not significantly influence the measurements. Finally, the flux meter does not require power; thus, it can be used in remote locations and has an advantage over continuous monitoring technologies that require power (such a down-hole flow meter).

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

3.0. Demonstration Design

3.1. Performance Objectives

Established performance objectives provided the basis for evaluating the performance and costs of the technology. These objectives were then designated the primary performance criteria (see sections 4.1 and 4.2) for evaluation. The successful demonstration and validation of the flux meter depended on meeting these performance criteria.

Table 3-1 lists the performance objectives paradigm. With regards to the quantitative performance objectives, the research team understood that future field application of this technology is contingent upon rigorous statistical comparison of solute and groundwater flux data between the flux meter and conventional groundwater measuring devices. Thus, as part of this demonstration, statistics were developed and comparisons were drawn between solute and water fluxes derived from the flux meter and flux data generated through alternative groundwater measurements.

Table 3-1. Performance Objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance
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 Selection of Test Site

The LC-34 site was selected for testing the flux meter in a biologically simulated environment. Pre-demonstration cores were conducted by NASA and GeoSyntec to select a site within the TCE source zone containing significant quantities of DNAPL within the flow cell domain.

3.3. Test Site History/Characteristics

Launch Complex 34 was constructed to support the Saturn I and IB missile launches. Launch operations involved the use of nitrogen, helium, liquid oxygen (LOX) and RP-1 fuel. Furthermore, during this time, Saturn rocket engines were cleaned while on the launch pad with solvents containing TCE. Engine parts were also cleaned with TCE on racks located in the shop situated on the western side of the Engineering Support Building. The area utilized for flux testing was located underneath the Engineering Support Building and contained TCE as a non-aqueous phase liquid.

3.4. Completed Operations

Two additional source zone remediation studies were conducted. These included an enhanced bioremediation study and a zero-valent iron injection test.

3.5. Pre-Demonstration Testing and Analysis

The site was characterized by GeoSyntec to locate the remediation cell in which the flux wells were installed.

3.6. Testing and Evaluation Plan

3.6.1. Demonstration Set-Up and Start-Up

Prior to any experiments of measuring water and contaminant fluxes in the field, several laboratory batch experiments were conducted to select sorbents and tracers. In addition, flow-through-box aquifer experiments were conducted under known flow conditions to characterize the performance of the flux meter in wells with and without sand packs.

Solid-aqueous phase batch partitioning tests were conducted to evaluate sorbents for intercepting contaminants (PCE and TCE) and releasing tracers. Activated carbon was the primary sorbent under consideration, because it is inexpensive, and it can be recycled. Batch tests followed well-established methods for determining sorption and desorption isotherms between solid and aqueous phases. The measured isotherms were used to assess the applicability of each sorbent as a packing media for the flux meter. Using linear isotherms, partitioning coefficients were determined to design specific packing for each application. Non-linear isotherms were also characterized and appropriate models used. Hysteretic and non-equilibrium partitioning behavior was also considered in the sorbent and tracer selection process.

Flow-through-box aquifer experiments were conducted under known flow conditions to characterize the performance of the flux meter. A water-tight container (glass or stainless steel) with dimensions of ~80 cm by ~50 cm and ~40 cm deep was used to create an aquifer model. The two ends of the container were used for flow injection and extraction and packed with coarse gravel. This was done to provide a constant head across the width of the box, and a uniform gradient across the length of the box The main section of the box was packed under water with sand to a height of 16~20 cm. The water used in packing the sand and later used to produce flow through the box aquifer contained surrogate contaminants (i.e., 2, 6-dimethyl-2-heptanol). The water table in the box was set to a height of 16~20 cm.

The model flux meters consisted of activated carbon packed in permeable cotton socks. The activated carbon was pre-equilibrated with several resident tracers. The flux meters were inserted into the well screens. After a known period of exposure the flux meters were pulled from the box and the activated carbon extracted to assess the mass of surrogate contaminants intercepted and the masses of resident tracer loss.

For field site evaluation, flux meters were constructed on-site prior to installation in each well. The tracers used in some cases are volatile and therefore a minimum time between construction and installation was desired. The construction of each flux device involved packing the sorbent

(with tracers) into the socks and including any impermeable dividers to minimize vertical flow. Following construction, the flux meters were installed into the two-inch monitoring wells. The construction and installation time for each meter was approximately 30 minutes. Each flux monitoring event required 6 flux meters of 5 foot length (3 wells of 10 foot well screen).

The flux meters remained in the flow field from 3 days to 2 weeks depending on the sorbent and tracers used. During flux meter retrieval, the device was removed from the well and segmented vertically for sub-sampling. In each interval the sorbent was homogenized and sub-sampled for analysis. The entire process of extraction and subsampling required about 30 minutes.

3.6.2. Period of Operation

The work at the LC-34 site was conducted over a one-year period for a total of four phases of the bioremediation study.

3.6.3. Amount /Treatment Rate of Material

Not applicable.

3.6.4. Residuals Handling

Flux meters generate a minimal amount of waste. An event of 6 flux meters generated approximately 22 liters of sorbent, which contains tracers and contaminants. This waste was stored on-site in drums for later disposal. Efforts were made with NASA to minimize and concentrate the waste generated. All materials brought back to Florida for analysis were disposed of using proper laboratory protocol.

3.6.5. Operating Parameters for the Technology

Operationally the flux meter device is very simple. This is one of the advantages of the technique. A single individual can perform the entire procedure; however, two people is often the most time-saving operation and were used for these NASA PFM deployments. The device can be installed in a number of wells (10 to 20) in a single day. The extraction is quite simple and is usually conducted by a single individual. The method required no electrical utilities and could be performed in remote locations. Measurements including the use of an electronic balance were made prior to leaving the laboratory. During the initial testing phase of the flux meter cost/time saving approaches were identified including complete pre-field assembly and rapid extraction and segmenting procedures.

3.6.6. Experimental Design

The flux meter technology was validated in a flow cell designed to assess bioremediation within a DNAPL source zone at LC-34. Flux was measured under 4 different conditions during the bioremediation study.

The experimental flow cell consisted of three injection wells and three extraction wells and limited monitoring wells within the cell (Figure 1-1). The flux monitoring was conducted in three wells installed up-gradient of the central extraction well (EW-2). Focus was placed on the capture zone for EW-2 because of minimal flow lines from outside the flow domain. The

capture zone for wells EW-1 and EW-3 included mass entering from outside the flow cell and therefore was difficult to interpret. The flux into EW-2 was compared to that measured at the flux wells FL-1, 2, and 3. The flux was also compared to calculations based on the three corresponding multilevel samplers ML 2, 3, and 4. All wells and ML samplers were screened in the interval 16 to 26 feet below ground surface. The ML samplers have 5 sampling locations distributed over this interval.

Flux was calculated with the PFM, ML, and EW samples four times over the course of the bioremediation study. The first deployment took place during water re-circulation after approximately four weeks of steady water flow. This provided the background flux prior to bioremediation. At this point and for all subsequent measurements, TCE and degradation by-products were quantified. The next two flux monitoring events occurred during ethanol injection in order to stimulate biological activity (phase II) with the third event (phase III) occurring after injection of microbes specifically identified as TCE degraders. The final phase occurred after several weeks with no additional treatment in the intervening time. Onsite treatment with activated carbon removed the contaminants from injected water.

3.6.7. Sampling Plan

The flux meter testing experiments used 3 wells with 10 feet of screen interval. Subsamples were taken in intervals of 2 feet (or less) to correspond with the multilevel sampling network. During the period of installation, samples were collected from the multilevel sampler network at the beginning and end of the period. Also, extraction well samples were collected from the three extraction wells. Flow rates and water levels were monitored during the period in order to determine cumulative water flow.

Sample Collection. Two types of samples were collected during this study: groundwater samples from MLS or extraction wells, and sorbent samples from flux meters.

Water samples were collected in EPA VOA vials with zero headspace. Samples were pumped from the MLS wells and collected at outflow lines from the extraction wells. Sampling protocol at the LC-34 site followed guidelines recommended and utilized by the GeoSyntec study protocol in order to have consistency in data collection. These samples were immediately placed in coolers and kept cold during transport to Gainesville. These samples were held for less than two weeks prior to analysis. Samples were analyzed for TCE and degradation byproducts.

Sorbent samples were collected from the extracted flux meters. Approximate 20 cm vertical intervals of the flux meter were segmented and transferred to containers for homogenization. Samples were stirred and subsampled into 40-ml VOA vials containing the extraction alcohol, isobutanol. Approximately 8-10 grams of sorbent were extracted with 20 ml of isobutanol. These samples were then cooled for shipping to Gainesville and analyzed within two weeks. The ability to hold these samples longer was tested in the laboratory; samples stored in alcohol were more stable than the water samples making prompt analysis requisite for error limitation.

Sample Analysis. All samples were analyzed at the University of Florida. Volatile organics, including alcohol tracers, were analyzed by direct liquid injection on Gas Chromatographs.

Details of analytical methods are provided in Appendix D. Detection limits are approximately 1 mg/L. Headspace analysis was used when low concentrations were encountered (detection limits for HS was approximately 50 ug/L).

Experimental Controls. GeoSyntec Consultants monitored flow and collected independent measures of mass flux at the extraction wells and multilevel control plane. This information was compared with University of Florida results.

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 E.

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

Data Quality Indicators. Simple regression analysis was used to assess the quality of data collected at any single well. However, more sophisticated techniques of spatial analysis were also performed with data collected.

3.7. Demobilization
Minimal demobilization was required for the Flux Meter testing. All equipment 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 F.

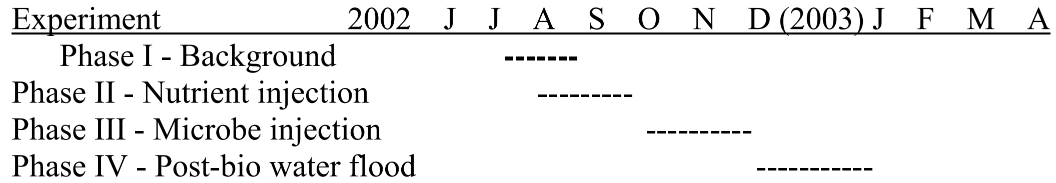
3.9. Selection of Analytical/Testing Methods
Analytical methods are provided in Appendix D.

3.10. Selection of Analytical/Testing Laboratory
No outside laboratories required.

3.11. Management and Staffing
Mike Annable was responsible for field activities at LC-34. Graduate students assisted with field activities. Mike Annable also oversaw laboratory analytical work at the University of Florida

3.12. Demonstration Schedule

A Gantt chart was provided below to show the date and anticipated duration of each phase of the demonstration.



4.0. Performance Assessment

4.1. Performance Criteria

Described in the tabular format below (Table 4-1) are the general performance criteria used to evaluate the performance of the flux meter. 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

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance
Qualitative	*1. Ease of Use*	*Operator acceptance*	***Installed by University personnel***
	2. Acceptability of sample analysis	*Environmental laboratory acceptance*	***University analysis***
	3. Regulatory acceptability of method	*General acceptance*	***NASA submitted document requesting and obtaining approval for tracer release (based on replicate sample analysis)***
Quantitative	*1. Sensitivity*	*+/- 15%*	***Current estimate +/- 10% for local mass flux***
	2. Minimum detection	*< 2 cm/day*	***Lowest value reported 1.0 cm/day***
	3. Accuracy	*+/- 25%*	***Current estimate +/- 20% for local mass flux (based on error propagation through calculations)***

4.2. Performance Confirmation Methods

The quality of groundwater and contaminant flux estimates based on the flux meter installations was compared to alternative measures of these quantities. Future field application of this technology was contingent upon rigorous statistical comparison of solute and groundwater flux data between the flux meter and conventional groundwater measuring devices; therefore, statistics were developed to characterize the "expected" flux and the flux "estimation variance".

The installation and interpretation of the flux meter data was generally the same in all experiments designed to conduct this comparison. Contaminant flux was compared with estimates based on multilevel sampler data and extraction well data collected during the flux meter placement period.

Table 4-2 lists for each performance criterion an expected or a desired value and the method that was used to confirm performance of the flux meter.

Table 4-2. Expected 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*	**Approximately 20 minute installation per 5 foot unit (sampling time approximately 15 min.)**
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Water flux estimates	*Estimated within 20%*	*Comparison to borehole dilution (induced flow rate)*	**Percent differences for pre-remediation ranged from 6 to 19%. Post remediation ranged from 4 to 30% after bio-stimulation differences were up to 67% (see Table 4-14)**
Contaminant flux estimates during background flood	*Estimate within 25%*	*Comparison with MLS based estimates*	**Integral average flux plane differences between flux meters and MLS ranged from 0 to 23%. Point to point TCE flux comparisons differences ranged from 7 to 113%. Average difference for local flux was 41% (Table 4-15)**
Contaminant fluxes during the bioremediation phase	*Estimate within 45%*	*Comparison with extracted volume rates*	**Integral average flux plane differences between flux meters and MLS ranged from 17 to 186%. Point to point TCE flux comparisons differences ranged from 0 to 200%. Average difference for local flux was 125%. Comparison between integrated flux from well and PFM flux plane varied from 32 to 190% (see Tables 4-16,17,18)**
Process Waste - Generated	*25 gallons*	*Observation*	**Approximately 4 gallons of waste activated carbon generated for each deployment. Disposed by NASA.**
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Reliability (CU)	*No failures*	*Record keeping*	
Safety (all) 3) Hazards 4) Protective clothing	*Contaminated sorbents* *Level D*	*Experience from demonstration operation*	**Level of protection similar to ground water sampling methods. Minimal vapor exposure with samples on activated carbon.**
Versatility (all) 1. Short/long term averaging 2. Other applications	*Yes* *Fractured rock, radionuceides*	*Experience from demonstration operation*	**Problems encountered with material integrity. More durable fabrics may be warranted.**

Refer to Appendix B or Appendix D for further details

Qualitative metrics were selected for several performance criteria including: ease of use (a primary criterion), reliability, safety, and versatility. Ease of use is an important performance

criterion and the results of the demonstration verified the level of training required to install/extract and interpret information from the flux meter. Reliability was assessed from records of total device installations versus total numbers of device failures. The performance metrics for the versatility criterion demonstrated that the flux meter can be successfully applied to generate both short- and long-term assessments, and that it can be applied (in theory) to other sorbing (or ion exchanging) contaminants (e.g., metals, radionuclides).

As indicated in Table 4.2, several quantitative performance metrics were identified to assess the performance of the new technology. Because the typical range for contaminant fluxes in the field can be 5 orders of magnitude (for water fluxes the range is 2 orders of magnitude), it is believed that achieving the performance metrics identified would greatly reduce the uncertainty of contaminant flux assessments. Clearly, a significant uncertainty reduction would be valuable to regulators and site managers. For the LC34 experiments discussed above, a successful comparison would results if the contaminant fluxes were estimated within 25% and the comparison between pre- and post-remediation fluxes were within 40%. The higher uncertainty, associated with contaminant flux measurement, is partly due to the nature of the MLS and EW estimates.

4.3. Data Analysis, Interpretation and Evaluation

4.3.1. Laboratory Studies on Biodegradability of Flux Tracers

Remedial groundwater treatments often use nutrients or introduced microbes to enhance chemical degradation. Because of these additives, there is a need to evaluate the integrity of the alcohol tracers used in the flux device over a period of days or weeks depending on the site application. Biodegrading microorganisms are naturally present in a range of subsurface environments and are limited primarily by energy source availability, toxic inactivation, pore space and water.

The biodegradability of alcohol tracers used in the flux device is influenced by the length and branching of the alkyl chain, the number of hydroxyl groups and the presence of other substituent types. Additionally, degradability initiation depends on the required microbial acclimation time as well as concentration effects (Boethling, 1979). Of the aliphatic alcohols evaluated in laboratory studies, methanol and ethanol are easily degraded in both aerobic and anaerobic environments (Pitter and Chuboda, 1990; Pitter, 1975). Isopropanol is expected to be less easily degraded while tetra-butyl alcohol and 2,4-DMP are resistant due to alkyl branching (Dias and Alexander, 1971; Novak et al. 1985; White et al. 1986; Zogorski et al.1996, 1997; Nielsen et al. 1996). Specific alcohol biodegradability rates have also been reported in detail in the Handbook of Environmental Degradation Rates (Howard and Boethling, 1991). This compilation resulted from work by the the Syracuse Research Corporation under EPA auspices to evaluate chemicals of anthropogenic origin in environmental compartments of soil, air and water. Estimates were made for alcohols in which rate data was available from the literature; the transport of a chemical between medias is not accounted for in these rates (Table 4-3).

Table 4-3. Groundwater half-lives based on acclimated aerobic aqueous biodegradation half-lives

Tracer Alcohol	*Aerobic half-life/high*	*Aerobic half-life/low*
Ethanol	52 hrs	13 hrs
Methanol	168 hrs	24 hrs
Isopropanol	336 hrs	48 hrs
Tert-Butyl Alcohol	8640 hrs	1334 hrs
2,4-dimethyl-3-pentanol	Not available – recalcitrant	Not available- recalcitrant

As shown in Table 4-3-1, ethanol is the most readily degraded alcohol; experiments have shown an ethanol aerobic degradation rate of 100 mg/l in 7 days and an anaerobic degradation rate of 100 mg/l in 3-25 days depending on conditions (Corseuil et al. 1998). The structural characteristics of ethanol favor rapid biodegradation; it is a naturally occurring intermediate in anoxic environments and is expected to rapidly biodegrade in essentially all environmental conditions (i.e., temperature, pH, and pressure) since microorganisms capable of metabolizing ethanol are ubiquitous in the environment (Cristensson et al. 1994, Wiedemeir, 1999).

To assess the degradation of the alcohol tracers used in the flux device over a period of days or weeks depending on the site application, 1) batch studies, 2) column studies, and 3) experiments to evaluate preassembly of the PFM in the laboratory were performed.

<u>Batch Studies: Series A and Series B</u>

To evaluate tracer degradation along with controlling environmental factors, batch microcosms were constructed with site specific groundwater and soil under both aerobic (series A) and oxygen-limited (series B) conditions. Both alcohol tracer equilibrated activated carbon and silver impregnated carbons were used in series B experiments in order to assess antimicrobial activity of the silver ion. These affects on activity, reported in the literature (Russell et al. 1994, Matsamura et al. 2003; Silver, 2003), include inactivation of enzymes by thiol S-H group reaction, DNA interaction, structural changes in the cell envelope, cell membrane detachment and formation of silver deposits inside the bacteria. (Liau et al, 1997; Efrima and Bronk, 1998). Site groundwater and soil from a NASA contaminated site, Cape Canaveral Launch Pad LC-34 (Battelle Report, 1999) were used as the source of microbes in the batch tests.

Series A

Methods and materials

Series A (aerobic system) batch equilibrium tests for assessment of alcohol tracer degradation employed four separate batch systems in a low oxygen environment (Figure 4-1). The tracers used in series A were methanol, ethanol, isopropanol, tert-butyl alcohol and 2, 4-dimethyl-3-pentanol. All alcohol tracers used for the study were reagent grade and purchased from Fisher Scientific Company. With these tracers, a solution for equilibrating activated carbon was prepared with resulting alcohol concentrations as shown in Table 4-4.

Approximately 200 grams of Fisher Brand 6-14 mesh activated carbon were added to 1.5 liters of tracer solution and shaken for 24 hours. After equilibration with the tracer solution, 50 grams of wet activated carbon and 300 grams HPLC water were placed into a 500 mL jar which was tightly capped and designated system 1. System 2 was designed to show system response to spiking with NASA site groundwater; both site groundwater and soil were added to system 3; system 4 was set up as a control as shown in Table 4-5.

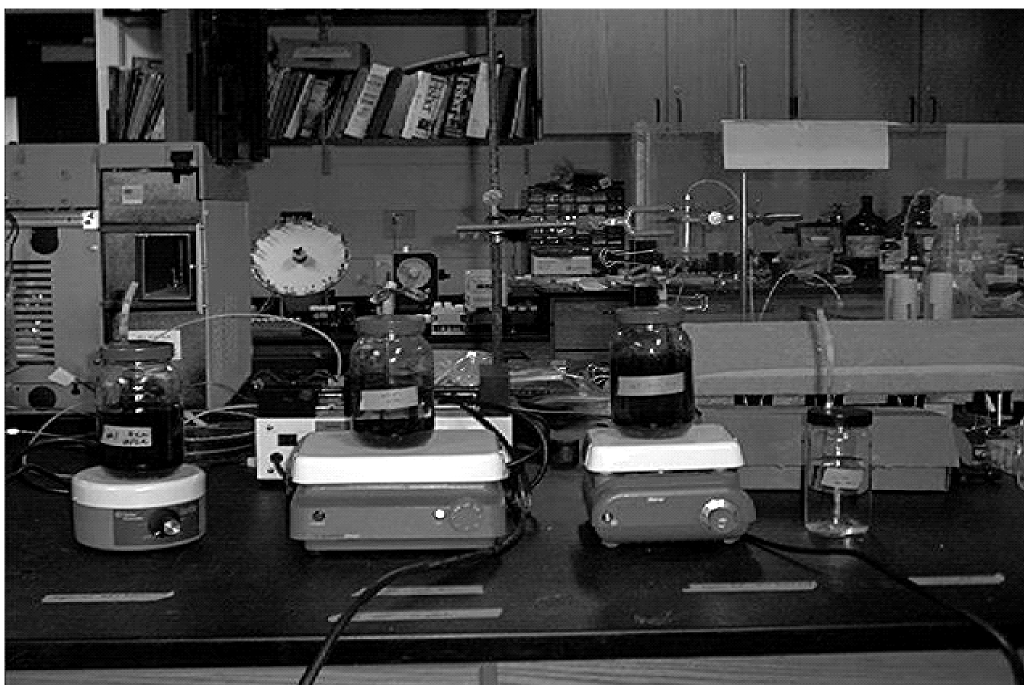


Figure 4-1. Series A aerobic setup, 4 batch systems

The lids on all systems were sealed; the solutions were sampled daily. Systems 1, 2 and 3 were placed on magnetic stirrers at approximately 200 rpm during the course of the experiment. Three hours after initial setup, a 5ml sample was pipetted from each system. This was allowed to settle at least one hour before subsampling into two duplicate 2ml GC vials, which were then tightly sealed with Teflon caps and refrigerated for analysis. The alcohols were then analyzed using a Perkin-Elmer Gas Chromatograph (GC) equipped with automated liquid injection and a Flame

Ionization detector (FID). The experiments for systems 1, 2 and 4 were conducted for 23 days while system 3 was run for 40 days. At day 24, system 3 was spiked with a methanol, ethanol and isopropanol groundwater solution (Table 4-4). From day 23 to day 40, samples were taken every 24 hours and prepared for GC analysis.

Table 4-4. Alcohol Solution Preparation Series A, solution concentrations

	Tracer solution Preparation	*Solution Alcohol Concentration mg/l*
Series A	1.5 mL methanol 1.5 mL ethanol 3 mL isopropyl alcohol 3 mL tertiary butyl alcohol 3 mL 2,4-dimethyl-3 pentanol 3 liters deionized water	395 MeOH 395 EtOH 785 IPA 786 TBA 829 DMP
Series A Spike Solution (Day 24)	60 µl methanol 60 µl ethanol 90 µl isopropyl alcohol 100 ml NASA Groundwater	790 MeOH 790 EtOH 1800 IPA

Table 4-5. Setups for series A

Series A	System 1	System 2	System 3	System 4
	50 g wet AC* 300 g HPLC water	50 g wet AC* 300 g site groundwater	50 g wet AC* 300 g site groundwater 2 g site soil	Control no AC 300 g HPLC water
	22-23°C	22-23°C	22-23°C	22-23°C

(*Designates equilibrated with tracer solution)

<u>Results and discussion batch series A</u>

Figures 4-2 to 4-5 show results for Series A, aerobic system. Systems 1, 2 and 4 showed no activity whereas system 3 with added soil exhibited alcohol degradation. Figure 4-6 shows results of spiking system 3 on day 24. Table 4-6 shows estimated zero order and first-order degradation rates obtained from linear and log scale plots along with estimated acclimation time for microbial growth. In System 3, alcohol degradation initiated in the order 1) ethanol, 2) methanol and then 3) isopropanol. This order was expected as the ethanol has preferential degradation over methanol. As ethanol becomes less available, the bacteria then utilizes methanol. Researchers (Nyberg et al. 1996; Christensson et al. 1994) confirmed in laboratory studies that ethanol is considerably more readily available as a carbon source than methanol. Moreover, a shorter adaptation time was needed. In experiments conducted by Trela et al. 1990, sludge once adapted to ethanol shows an increased activity towards other organic materials such as methanol and acetic acid. System 3, after the alcohol spike, yielded identical degradation rates for ethanol and methanol with no acclimation time required. Note that the 2,4-DMP is

almost non-detect except in control system 4 due to high degree of sorption to the activated carbon relative to the other tracers.

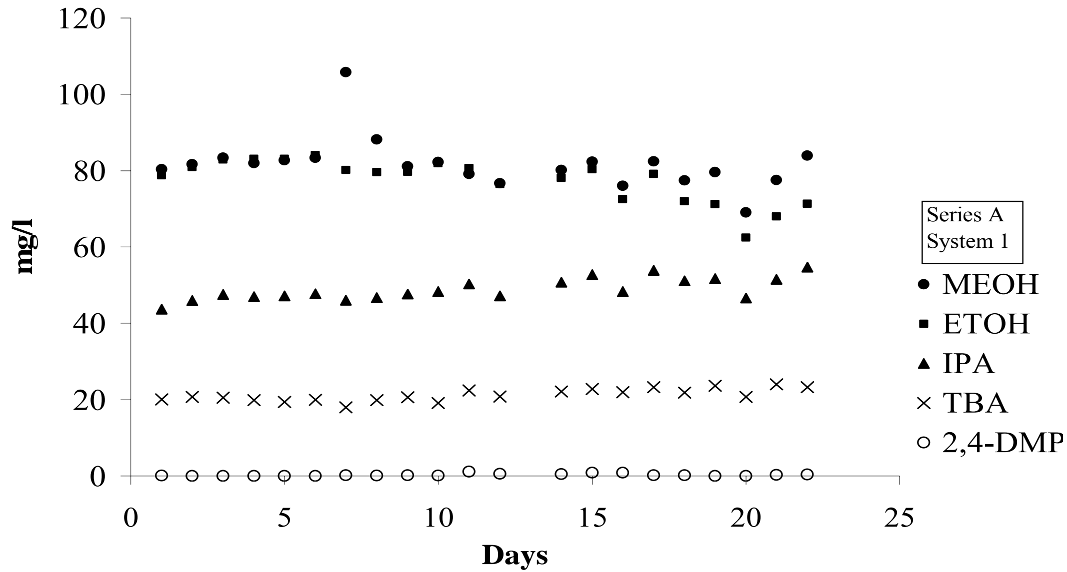


Figure 4-2. Series A Systems 1, 50 g wet AC 300 g HPLC 22-23°C

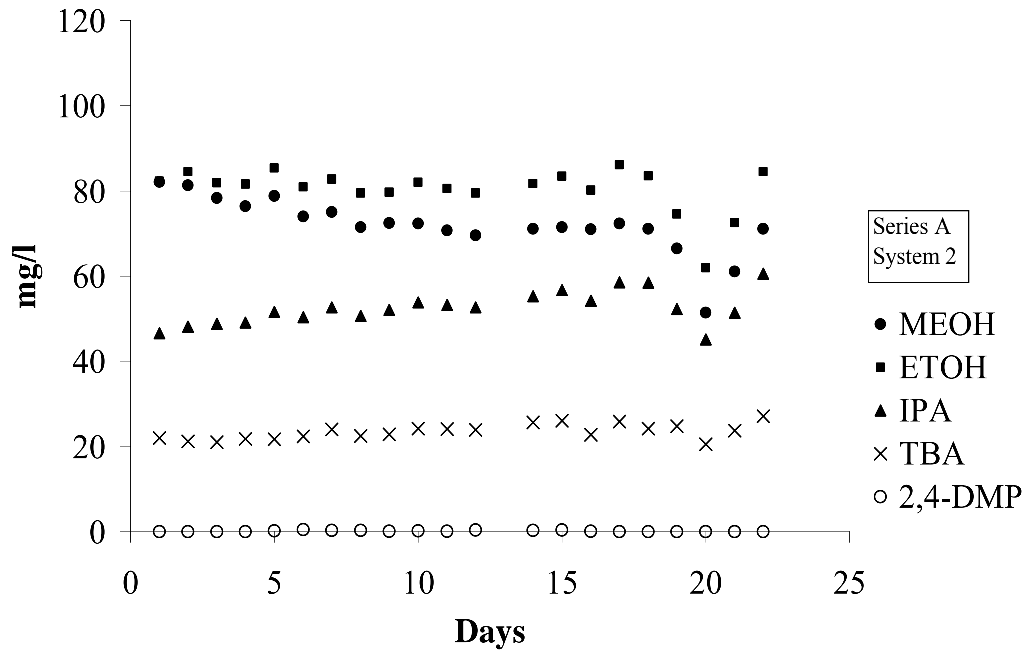


Figure 4-3. System 2: 50 g wet AC 300 g site ground water 22-23°C

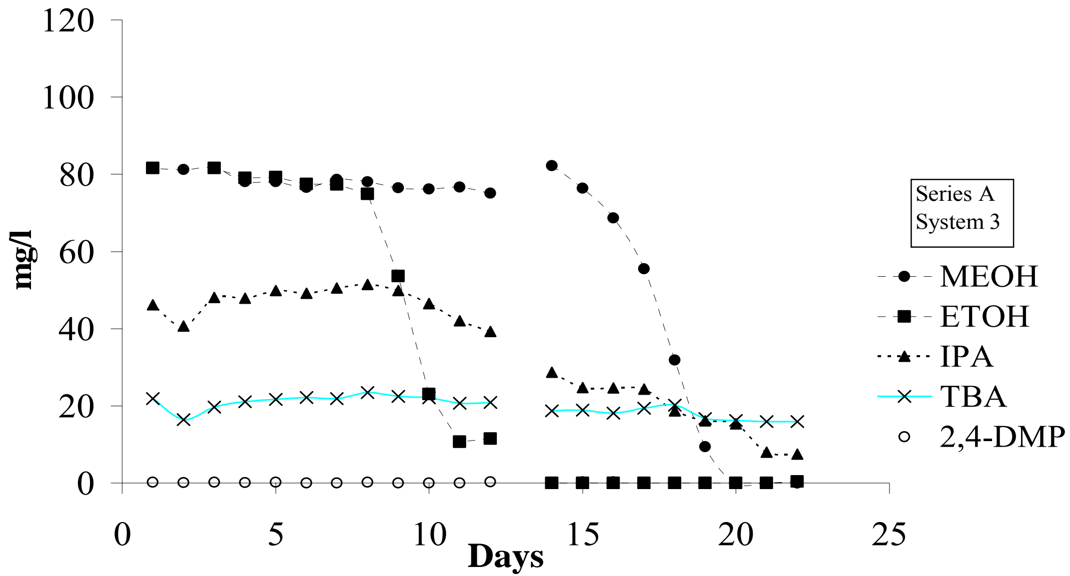


Figure 4-4. Series A System 3: 50g wet AC*300g site ground water 2 grams site soil

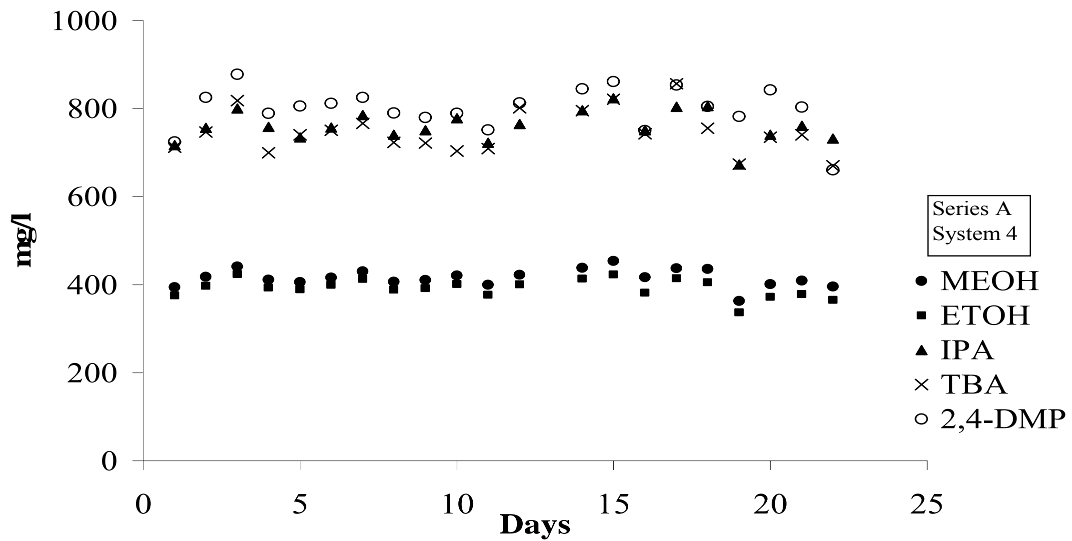


Figure 4-5. System 4: Control no AC 300 g HPLC grade water spiked with tracer alcohol solution

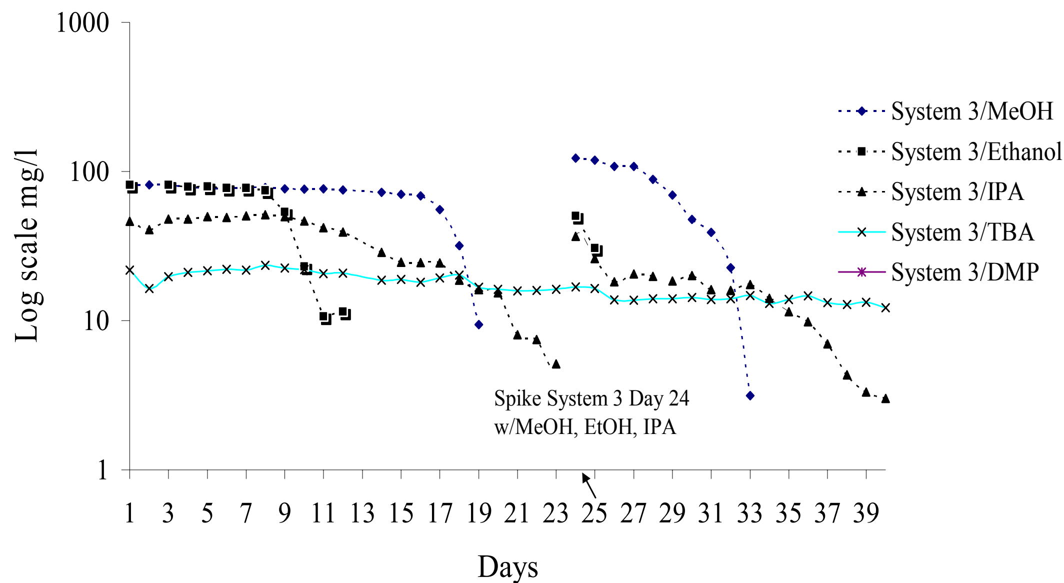


Figure 4-6. Series A System 3: Plot showing effect of alcohol spike at day 24

Table 4-6. Acclimation times and degradation rates based on Series A batch results

	Alcohol	Acclimation time, days	Estd. 0th order K	Est. 1st order K
Series A System 3	MeOH	16	25	1.0
	EtOH	8-9	25	0.8
	IPA	9	4	0.1
	TBA	-	-	-
Series A System 3 Day 24 spiked with alcohol tracers	MeOH	0	25	1.0
	EtOH	0	25	0.8
	IPA	0	4	0.2
	TBA	-	-	-

Series B

Materials and methods batch study: series B (oxygen-limited).

Series B (O_2 limited) batch equilibrium tests employed 8 separate batch reactors (Figure 4-7). The same alcohol tracers were used for both Series A and B. Table 4-7 shows the preparation for spiking the activated carbon and water solution. Approximately 7.5 g Fisher AC was added to 100 g NASA groundwater. In order to minimize dissolved oxygen, the system was then degassed with helium before alcohol tracer addition. Each of the 8 systems (Table 4-8, Series B)

was spiked with 300 µl tracer solution, septa sealed and shaken for several hours. After the systems settled for 24 hours, initial samples were taken. System 6 was prepared with AC impregnated with silver, (Barnesbey Sutcliffe Type 989 12x30 0.026% metallic silver,). 25 mg of lactate was added to System 3 as a nutrient (approximately 100 mg/l as carbon). A 1 mL Teflon syringe was used to sample through septa sealed Systems into 0.4 mL samples, which were then allowed to settle several hours. To avoid possible carbon contamination of the GC equipment, the settled 0.4 mL samples were then subsampled again into 0.2 mL GC vials for chromatographic analysis. System 2 was kept at 15ºC to simulate a representative aquifer environment.

Figure 4-7. Series B oxygen-limited setup, 8 batch systems

Table 4-7. Series B Tracer solution preparation and resulting concentrations

	Tracer solution Preparation	*Solution Alcohol Concentration mg/l*
Series B	40µl methanol 40 µl ethanol 80µl isopropyl alcohol 80µl tertiary butyl alcohol 80µl 2,4-dimethyl-3-pentanol 100 mL NASA Groundwater	350 MeOH 350 EtOH 700 IPA 700 TBA 700 DMP

Table 4-8. Series B Batch System preparation

System 1	**System 2**	**System 3**	**System 4**
7.5 g "dry AC" 100 g NASA GW 0.6 g NASA soil Alcohol spiked 22-23ºC	7.5 g "dry AC" 100 g NASA GW 0.6 g NASA soil Alcohol spiked 15ºC	7.5 g "dry AC" 100 g NASA GW 0.6 g NASA soil 500 μl Lactate soln Alcohol spiked 22-23ºC	7.5 g "dry AC" 100 g NASA GW 0.6 g NASA soil Alcohol spiked 22-23ºC
System 5 100 g NASA GW Alcohol spiked 22-23ºC	System 6 7.5 g "dry Silver AC" 100 g NASA GW 0.6 g NASA soil 500 μl lactate. Alcohol spiked 22-23ºC	System7 100 g NASA GW 0.6 g NASA soil Alcohol spiked 22-23ºC	System 8 Control 100 g Deionized H_20 Alcohol spiked 22-23ºC

Results and discussion: batch series B (oxygen-limited).

The Series B batch experiment employed 7 separate batch reactors using Fisher activated carbon. System 6 was prepared with silver impregnated carbon. Figures 4-8 to 4-15 show the results for systems 1-8. The degradation activity shown for system 1 (Figure 4-8), and for system 3, (Figure 4-10) which was amended with lactate, follow expected results with ethanol and methanol degrading initially followed by isopropanol within a 50 day time period. Tert-butyl alcohol did not degrade. These systems (1, 3) demonstrated prolonged (over 3 weeks) acclimation times. Highly sorbed 2, 4-DMP remained at very low concentrations. System 2 (Figure 4-9) at 15ºC exhibited no degradation activity for the course of the experiment. System 3 received 25 mg lactate in 500 μl solution as nutrient addition; both ethanol and isopropanol exhibit shortened microbial acclimation times, but comparable degradation rates to series A. For a 50 day period system 6 (Figure 4-13), prepared with silver-treated carbon and amended with lactate, exhibited no degradation, an apparent inhibition of microbial activity due to the silver ion (Russell, 1998.). Alcohol degradation occurred in system 7 which included soil but no AC (Figure 4-14). Control system 8 served as a control and showed no activity (Figure 4-15). Estimated zero order and first-order degradation rates obtained from linear and log scale plots are shown in Table 4-9 along with estimated acclimation time for microbial growth.

The ethanol degradation rates for Series B with oxygen limitation had similar degradation rates to series A (Table 4-9). The observed methanol degradation rates were lower in Series B. Lactate addition to system 3 resulted in a slight increase in ethanol degradation rate. The ethanol degradation rate of system 5 which included neither soil nor activated carbon and system 7 which included soil but no activated carbon is similar to systems 1 and 3. However, the acclimation time for ethanol is shortened in these systems (5, 7) without activated carbon; the ethanol exhibited degradation activity within 1-2 days in Systems 5 and 7 as compared 40 days and 23 days in Systems 1 and 3. It appears that the activated carbon inhibits ethanol degradation and increases acclimation time which could be due to alcohol sorption and resultant decreased

availability, a result of concentration effects on alcohol degradation rates (Boethling and Alexander, 1979). Additionally, the carbon matrix could protect sorbed alcohol from bacteria and inhibit enzymatic degradation.

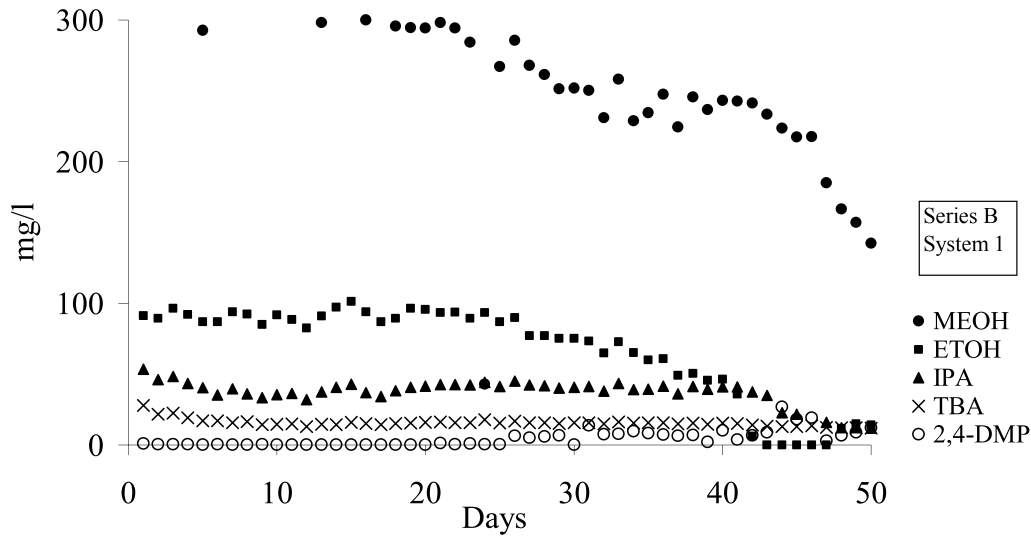


Figure 4-8. Series B System 1: 7.5 g “dry AC”,100 g NASA GW, 0.6 g NASA soil

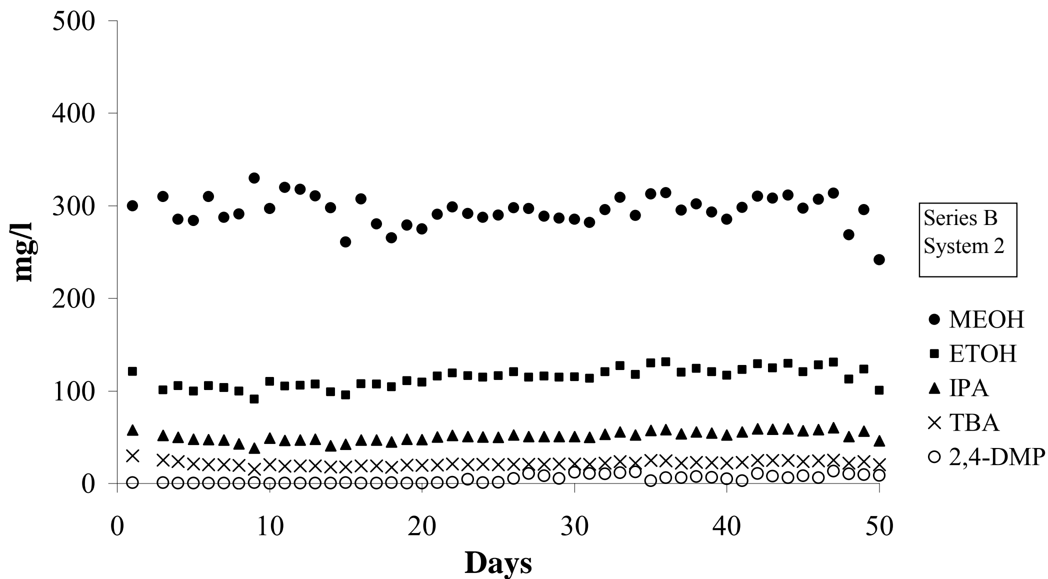


Figure 4-9. Series B System 2:7.5 g dry AC, 100 g NASA GW, 0.6 g NASA soil Alcohol spiked, 15º C

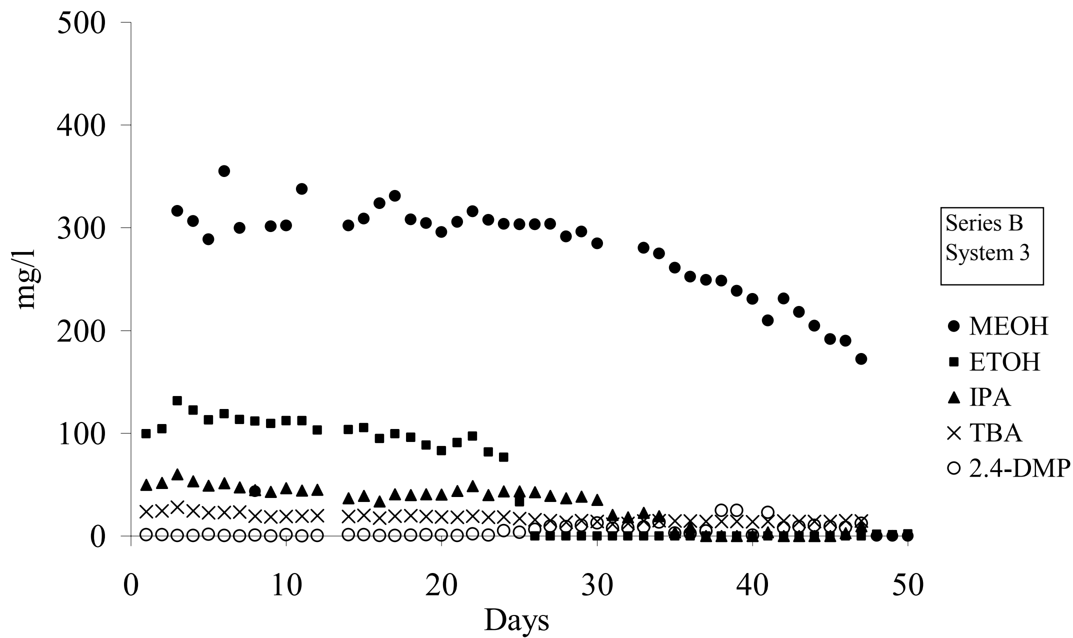


Figure 4-10. Series B System 3 System 3: 7.5 g “dry AC”, 100 g NASA GW, 0.6 g NASA soil, 500 µl Lactate/alcohol spiked

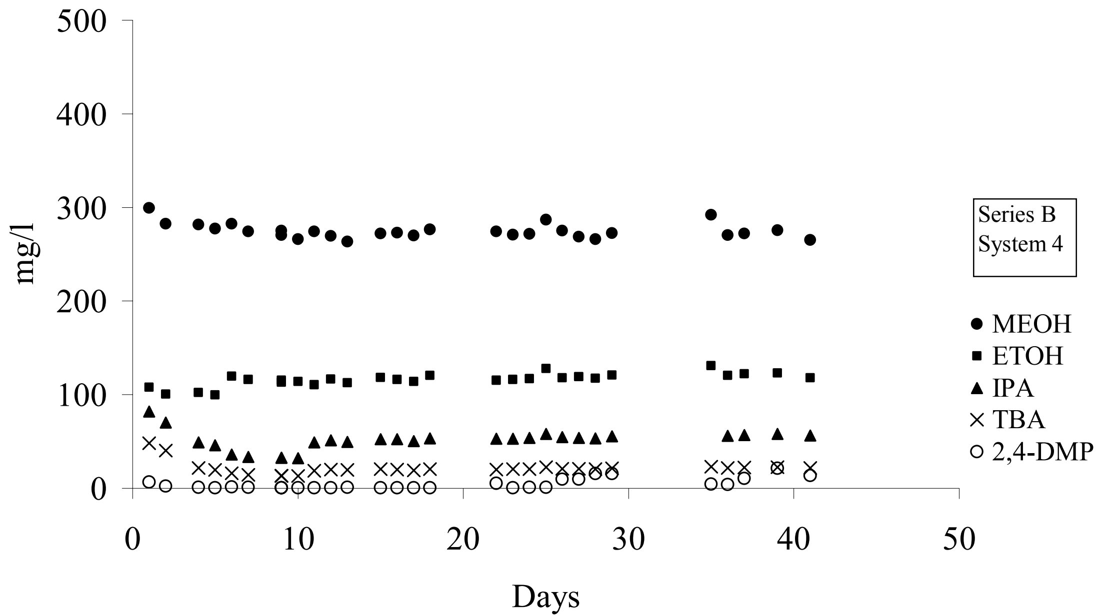


Figure 4-11. Series B System 4: 7.5 g “dry AC”, 100 g water

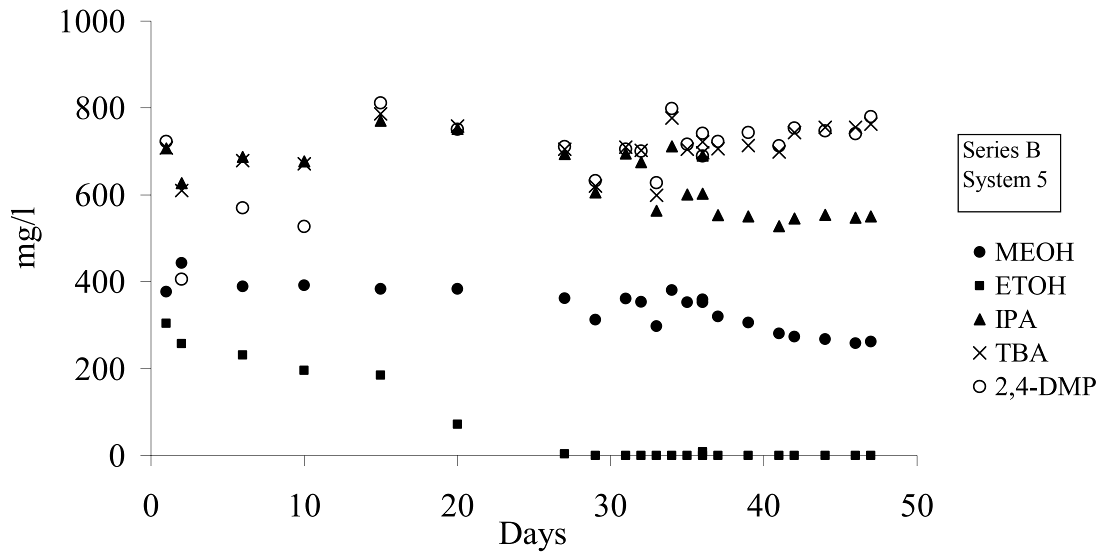


Figure 4-12. Series B System 5: 100 g NASA GW alcohol spiked

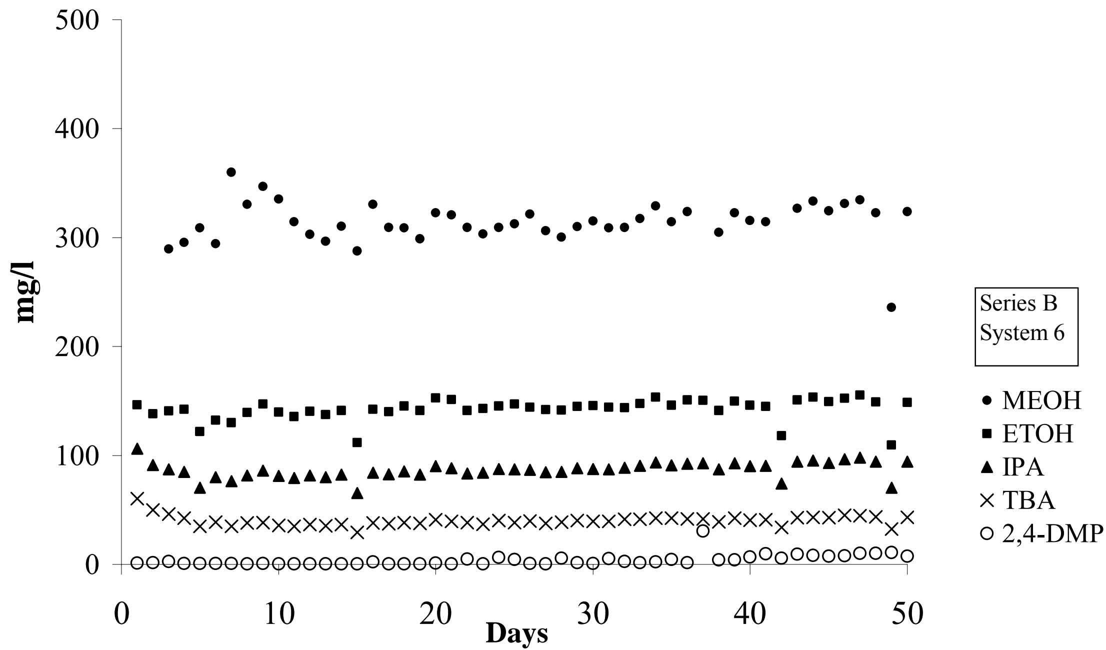


Figure 4-13. Series B System 6:7.5 g silver AC, 100 g NASA GW, 0.6g NASA soil, 500 µl Lact., alcohol spike

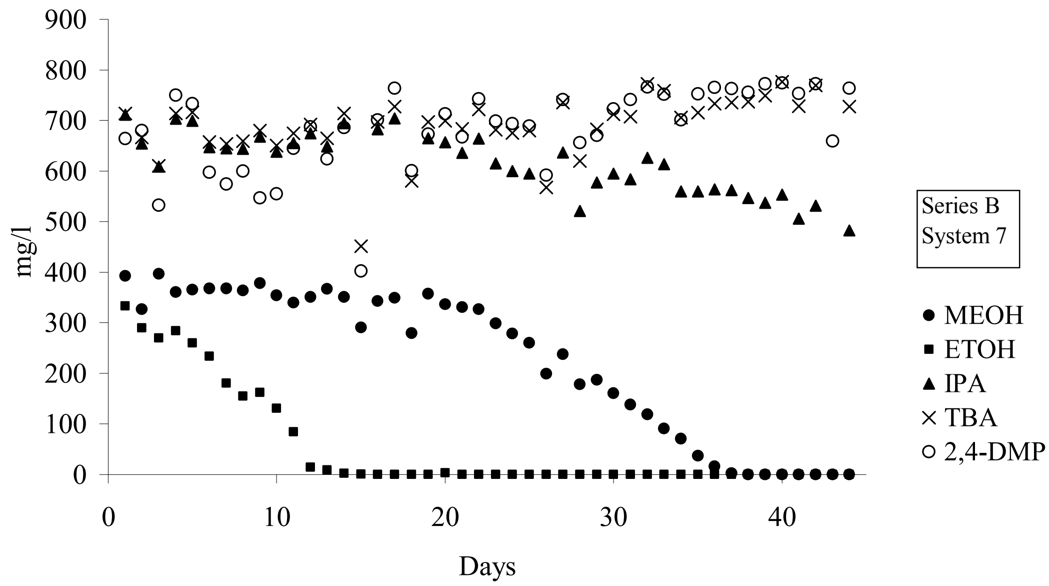


Figure 4-14. Series B System 7: 100g NASA GW. 0.6g NASA soil, alcohol spike

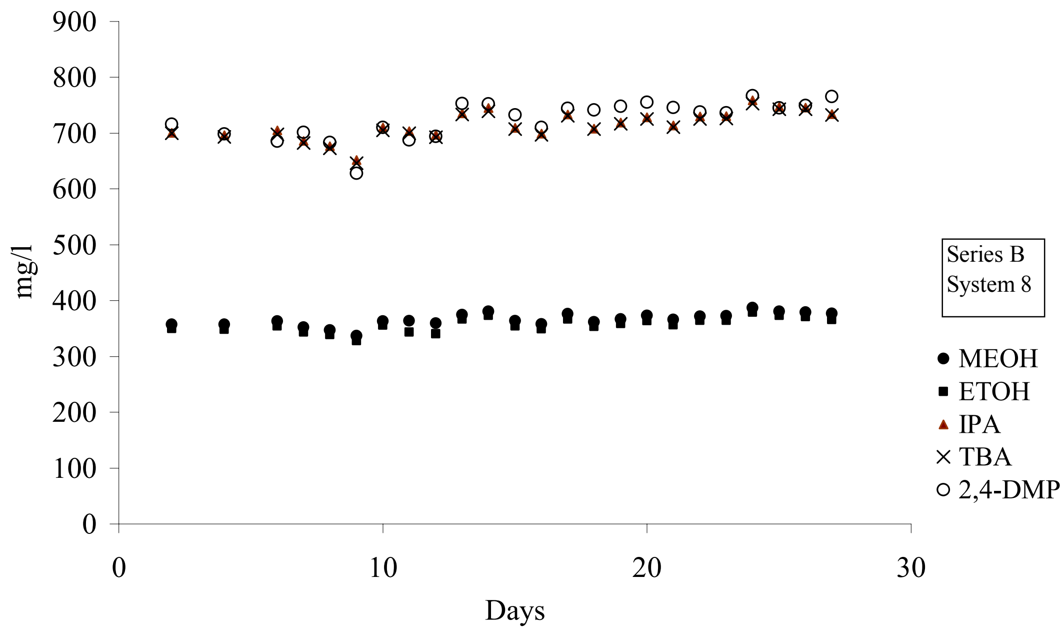


Figure 4-15. Series B System 8: Control, 100 g deionized H_2O, alcohol spike

Table 4-9. Acclimation times and degradation rates based on Series B batch results. Series A results included for comparison

Series B	Description	Alcohol	Acclimation time, Days	Est'd 0 order K mg/l/day	Estd. 1st order K /day
1	AC/NASA GW/soil	MeOH	25	4	0.01
	alcohol spiked at 22-	EtOH	40	20	1.8
	23ºC	IPA	42	5	0.15
		TBA			
2	AC/NASA GW/soil	MeOH	No Activity		
	alcohol spiked at	EtOH			
	15'C	IPA			
		TBA			
3	AC/NASA	MeOH	25	5	0.02
	GW/soil/alcohol	EtOH	23	25	1.0
	spiked/lactate at 22-	IPA	30	5	0.01
	23ºC	TBA			
4	AC/NASA GW/	MeOH	No Activity		
	alcohol spiked	EtOH			
	at 22-23ºC	IPA			
		TBA			
5	NASA GW/ alcohol	MeOH	30	3	0.01
	spiked	EtOH	1-2	12	1.0
	at 22-23ºC	IPA	35	7	0.01
		TBA			
6	SILVER AC/NASA	MeOH	No Activity		
	GW/ soil/alcohol	EtOH			
	spiked/lactate	IPA			
	at 22-23ºC	TBA			
7	NASA GW/ SOIL	MeOH	20	20	0.8
	alcohol spiked	EtOH	1-2	20	1.0
	at 22-23ºC	IPA	35	7	0.01
		TBA			
8	Deionized water/	MeOH	No Activity		
	alcohol spiked at 22-	EtOH			
	23ºC	IPA			
		TBA			
Series A	**Description**	**Alcohol**	**Acclimation time, Days**	**Est'd 0 order K mg/l/day**	**Estd. 1st order K /day**
System 3	50 g wet AC*	MeOH	16-9	25	1.0
	300 g site ground	EtOH	8-9	25	0.8
	water	IPA	9	4	.1
	2 g site soil	TBA			
Spike 3	Day 24 spiked with	MeOH	0	25	1.0
	tracers	EtOH	0	25	0.8
		IPA	0	4	.2
		TBA			

Column Experiments

Activated carbon column experiments were conducted to study porous media flow (Langner et al.1998, Li et al. 2001) and nutrient/electron donor amendment on alcohol tracer degradation rates (White et al. 1986). At NASA LC34 where the University of Florida conducted a PFM evaluation of bioaugmentation, ethanol was used as the amendment. Based on the previous batch studies detailed in Chapter 2, a shortened microbial acclimation time and increased degradation activity could impact PFM tracer alcohol; therefore, it was decided to use an ethanol/groundwater solution as the influent to the sand column. The effluent from the sand column served as the influent to the activated carbon column.

Methods and Materials

Sand Column Preparation. Two small-scale columns (2.5cm x 14cm Kontes chromatography column) were incrementally packed with NASA soil and NASA site groundwater. The caps were screened on both ends with fine mesh and a coarse mesh anodized steel screen. Vibration of the soil increments was performed to improve packing characteristics. NASA groundwater was filtered with 0.45 μm mesh paper and used for influent to the control column. For the experimental column influent, the filtered groundwater was spiked with ethanol at 280 mg/l. This alcohol/groundwater solution was then pumped through the designated experimental column at approximately 0.1 ml/min to simulate NASA field site ethanol flushing of the experimental plot. The second column, the control column, was flushed with ethanol free groundwater at the same rate. These columns were flushed for 9 days to provide adequate time for microbe acclimation based on previous batch experiments. The effluent from the experimental soil column was monitored by gas chromatographic analysis at day 9 to assess ethanol concentration level. At day 9, none was detected confirming the hypothesis that bacteria were now acclimated and degrading ethanol within the sand column. The temperature for all components was approximately 25°C.

Activated carbon column preparation. An alcohol tracer solution was prepared with 45 mL methanol, 45ml ethanol, 90 mL isopropanol, 90 mL tert-butyl alcohol and 45ml 2, 4-dimethyl-3-pentanol for the initial 4 column runs. For the subsequent six runs, 45 mL ethanol was added to the tracer mix. After mixing the tracers, 1.69 mL solution (excluding ethanol) solution was added to 400ml tap water in an 800 mL glass teflon-capped bottle in order to match field PFM activated carbon preparation and resulting alcohol concentrations. To match these concentrations when ethanol was included in the suite, 2.06 mL of ethanol included solution was added. A quantity of 100g Fisher activated carbon (Columbus, Ohio) was added to this water/alcohol solution and rotated for 24 hours. The equilibrated carbon was then drained and incrementally packed and vibrated into two smaller-scale glass columns (2.5cm x 5cm Kontes chromatography column). To mimic field condition inflow to passive flux meter, these columns were then connected to the effluent of the soil columns; the pumping rate of 0.1ml/min was maintained through both setups. This setup was repeated at a range of pumping rates to assess the affect of velocity on degradation kinetics. Immediately after the smaller columns were attached, samples were collected continuing for several days in order to assess tracer desorption from the carbon. Table 4-10 outlines the experimental design and Figures 4-16 and 4-17 show the schematic of the setup for these experiments. For an assessment of effect of silver AC on

activity, silver impregnated carbon was substituted for the Fisher carbon in the initial runs and the experiment run at 0.02 ml/min for approximately 20 pore volumes. The effluent was monitored from both columns approximately every 12 hours in order assess tracer mass loss. The samples were collected in 0.5 mL inserts for 2ml GC vials. All samples were analyzed using a Perkin-Elmer Gas Chromatograph (GC) equipped with automated liquid injection and a Flame Ionization detector (FID).

During the construction of each small column the activated carbon was sampled to establish initial concentrations of the sorbed resident tracers. These concentrations were used in subsequent calculations to ascertain relative mass of each tracer remaining in the activated carbon following a period of exposure to flow in the column. Sampling of the carbon at the conclusion of each run involved extracting the activated carbon with isobutyl alcohol. From the extract, all alcohol tracers and DMP were analyzed using a Perkin-Elmer Gas Chromatograph (GC) equipped with automated liquid injection and a Flame ionization detector (FID). The column was then eluted with water at a flow rate of 0.5 mL/min. Frequent volumetric measurements were taken to develop plots of cumulative elution volume versus time. Whenever the eluent volume was measured, a sample was collected and analyzed to assess transient changes in dissolved concentrations of resident tracers and DMP.

To determine appropriate pumping rates, calculations of water flux were made according to column volumes and pumping rates. The respective volumes of the NASA soil column and smaller AC column were 275 mL (5 cm diameter, 14 cm length) and 25 mL (2.5 cm diameter, 5 cm length). At a pumping rate of 0.1 mL/min or 144ml/day and an effective porosity of 0.4 for the soil column, the resultant pore volume rate is 1.2 pore volumes/day. The AC column volume and porosity results in a rate of over 10 pore volumes/day. Darcy flow through the smaller column is 28.8 cm/day. At the end of the experimental run, mass was sampled from front/entry, middle and end/exit sections (Figure 4-16).

Table 4-10. Experimental Design of Column Tests

Step 1.	Flush “generator” column (2.5 cm x 10.5 cm) packed with NASA soil with alcohol tracer/groundwater solution (NASA groundwater). Flush for 9-10 days to allow microbes’ acclimation time. Monitor effluent to confirm tracer degradation. At same time, flush second column packed with NASA soil with NASA groundwater only, no ethanol. Also flush for 9-10 days. Monitor effluent
Step 2.	Hook up small “fluxmeter”column packed with tracer equilibrated Fisher activated carbon to each large NASA sand column, the “generator column” and control column. Monitor effluent daily to assess tracer mass loss. Continue using alcohol tracer/groundwater solution to flush “generator/baby columns” and groundwater only to flush control setup.
Step 3	At conclusion of each run, sample “fluxmeter” column” at “front, middle, end” (10 mg samples); extract alcohol mass using isobutyl alcohol
Step 4.	Repeat step 2 substituting silver AC for Fisher AC.

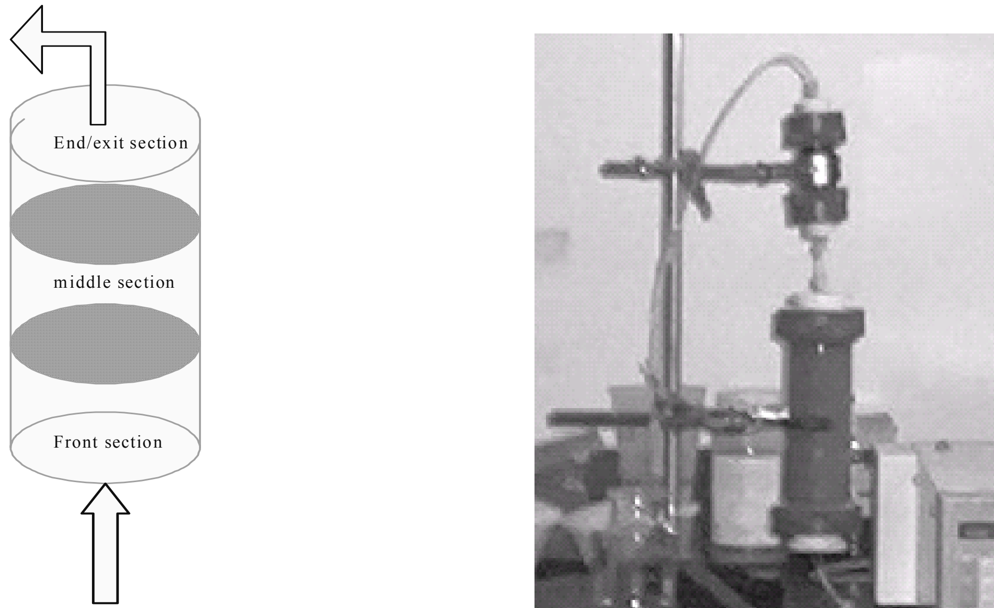


Figure 4-16. Schematic of smaller activated carbon, “fluxmeter column” showing three sampling sections for mass extraction. Photo shows attachment of fluxmeter column to NASA soil column

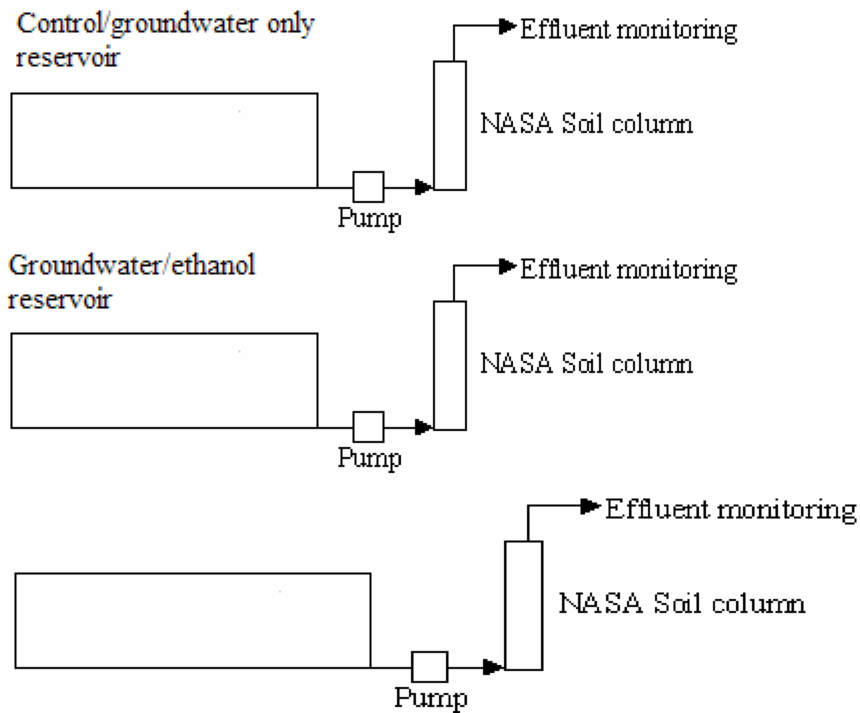


Figure 4-17. Schematic of column setups including control.

Results and Discussion: Column Studies

The effluent concentrations from the activated carbon columns, measured during two runs at 0.02 ml/min are shown in Figure 4-18. The methanol completely degraded within 9 days in both groundwater and groundwater/ethanol column effluents; ethanol was not included in the suite of tracers used for these runs. The desorption rates of methanol, isopropanol and tert-butyl alcohol were consistent with previous bench tests done by the University of Florida (Interim Measure Report, OT-30, Solid Water Management Unit PO41, Patrick Air Force Base, Contract F41624-01-D-8550, 2004).

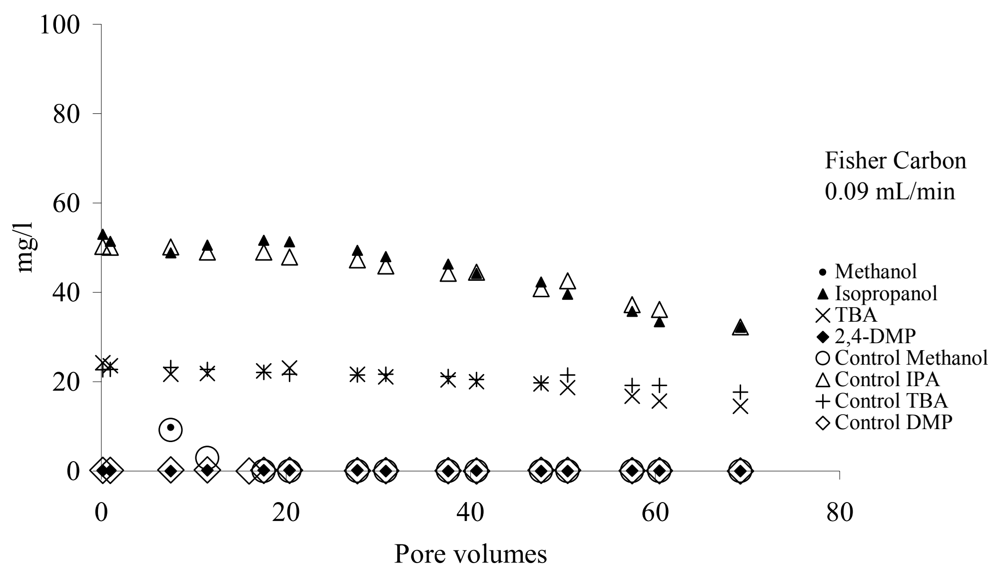
For all subsequent runs, ethanol was included in the tracer suite. The remaining tracer mass after completion of each run, from the extracted column, was visualized with concentration/original concentration (*C/Co*) plots at different total pore volumes and applied flow rates. Several trial runs were necessary to determine the appropriate length of run (number of pore volumes) and pumping rate to assure appropriate (measurable and achievable) tracer removal, for comparison to typical aquifer groundwater flux at PFM field sites.

Figures 4-19 and 4-20 compare the number of pore volumes to the amount of tracer mass (methanol, ethanol, isopropanol, tert-butyl alcohol) remaining using Fisher Carbon. The groundwater only column front, middle, end section mass ratios are plotted along with the ethanol/groundwater column sections. For the specific 9.85 pore volumes flush at 0.02 mL/min, Figure 4-21 illustrates with more detail the tracer alcohol mass remaining on experimental groundwater/ethanol column and groundwater only control columns using Fisher carbon. This mass ratio (C/C_o) was calculated for each AC column section: front/entry, middle, and end/exit. For the isopropanol and tert-butyl fractions, there is no significant difference between masses measured in front/entry, middle and end exit sections. However there is a significant difference in ethanol mass remaining on the groundwater/ethanol influent AC column compared to the groundwater only column. In fact the loss on the ethanol influent column is 10 times greater than the groundwater only column. This same magnitude of loss is found on both middle and end sections. On the ethanol AC entry section, although very little ethanol mass is remaining, the loss appears the same magnitude as the other column subsections.

To assess the effect on silver AC on alcohol degradation, Figure 4-22 includes the results of ethanol tracer mass remaining on the silver AC column extracted after 20.5 pore volumes and compares that to Fisher carbon results extracted at 9.8 and 17.8 pore volumes. (Another experiment was run with silver AC at 43 pore volumes; no ethanol remained on AC after flushing). The ethanol influent column for two runs at 9.8 and 17.8 pore volumes, using Fisher AC, show large decreases in tracer ethanol mass reduction. However, the ethanol influent silver AC column section has significantly less reduction than in the groundwater only silver AC column sections. .

Figure 4-23 shows photos of the experimental setup with a black substance appearing at the entry to the sand column receiving the ethanol influent; the control sand column maintained its original color throughout the experiment. This color change suggested significant bacterial

growth. Indeed, the results for silver AC show that ethanol mass remaining on the extracted experimental (ethanol/groundwater influent) column is significantly higher when compared to the Fisher AC sorbent. However, there is still a significant reduction in ethanol mass in the front and middle experimental sections (94% and 51% respectively) of the silver AC column; only in the end/exit section does all mass remain (compared to control column). It is interesting that the front entry section shows a 94 % reduction in mass for ethanol and apparently no protection from the silver. This may be due to the silver ion flushing out and resulting in silver ion concentrations too low to be bactericidal. However, the middle section had only about a 50 % reduction in ethanol mass whereas the end section showed a slight increase in mass compared to the control. So the end/exit section of the silver AC column appears to have the most protection from bacterial degradation. A white substance was observed on the entry part of the AC column seen upon extraction; this biofilm type substance may protect the bacteria from silver inhibitory activity; there may not only be lower silver ion concentrations but also a biofilm shielding bacteria from silver. In the second section there was a lessened amount of this substance and therefore it is hypothesized that silver ion was better able to transport to the bacterial membrane. At any rate, the ethanol/groundwater influent to the AC column stimulates degradation; it appears the ethanol/groundwater influent biostimulates the microbes so they are growing and acclimated to ethanol degradation of the AC column. In regards to silver leaching from the activated carbon and possibly presenting a regulatory concern, the silver ion tends to form complexes with inorganic chemicals and humic substances in the soil. Furthermore, since it is toxic to soil microorganisms and inhibits enzymes, biotransformation is not considered significant (Boyle, 1968; Domsch, 1984).



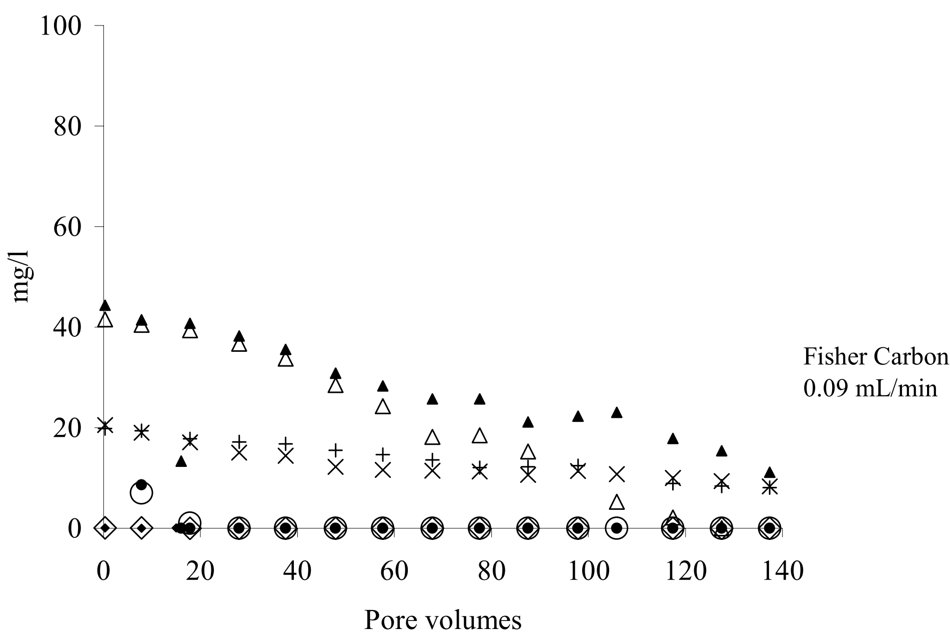
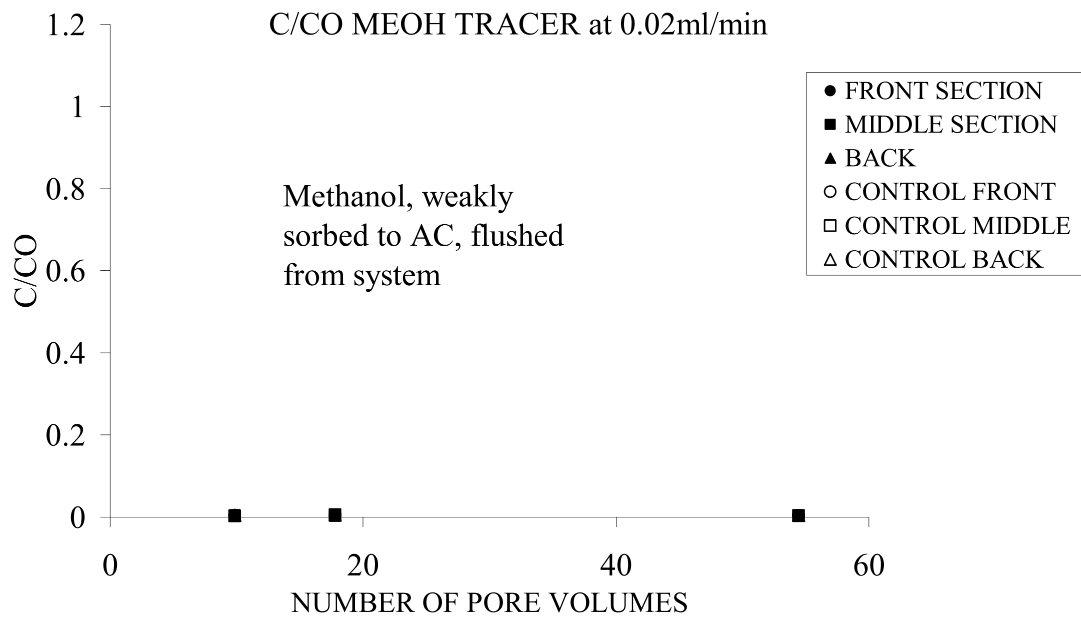


Figure 4-18. Effluent concentrations from activated carbon column runs. A) Experiment 3. B) Experiment 4.



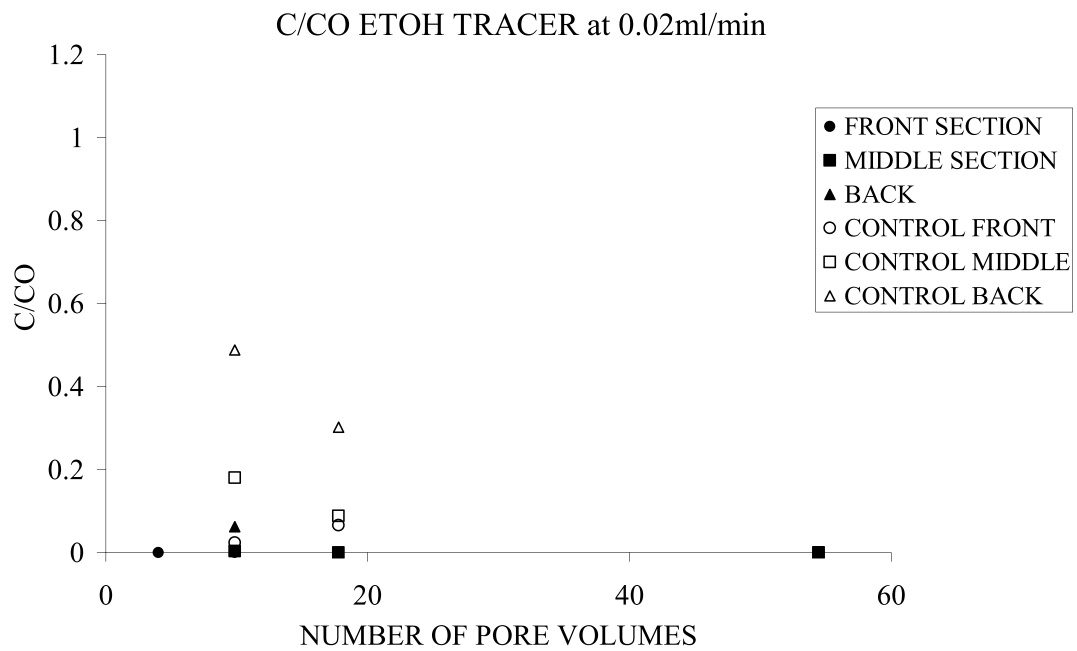
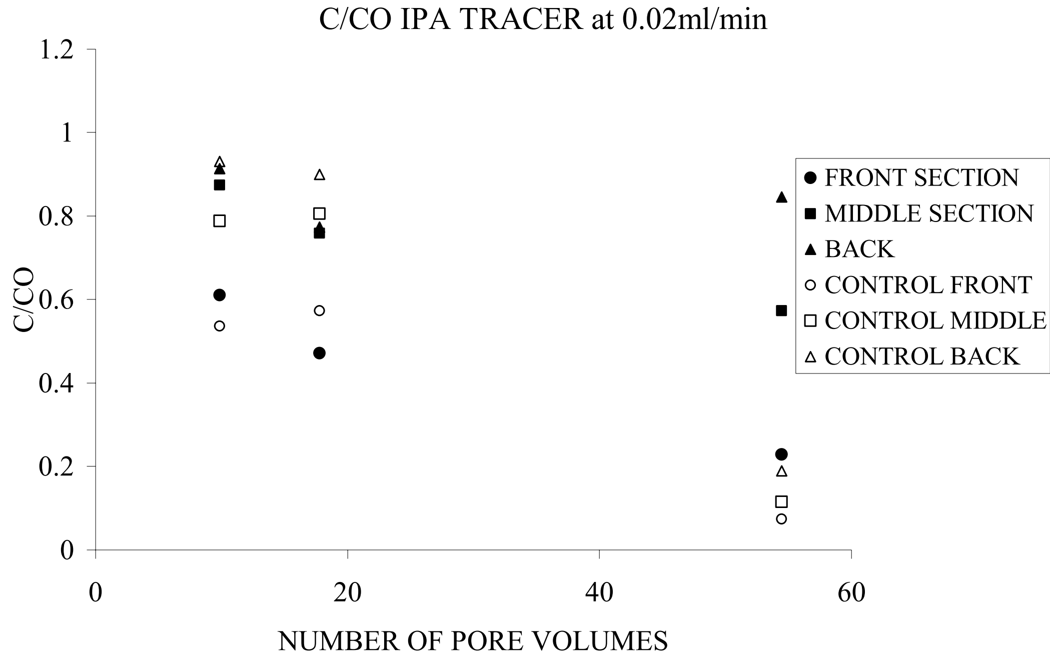


Figure 4-19. Plots alcohol tracer mass remaining after pore volumes flushing. Control is flushed with groundwater only A) Methanol. B) Ethanol



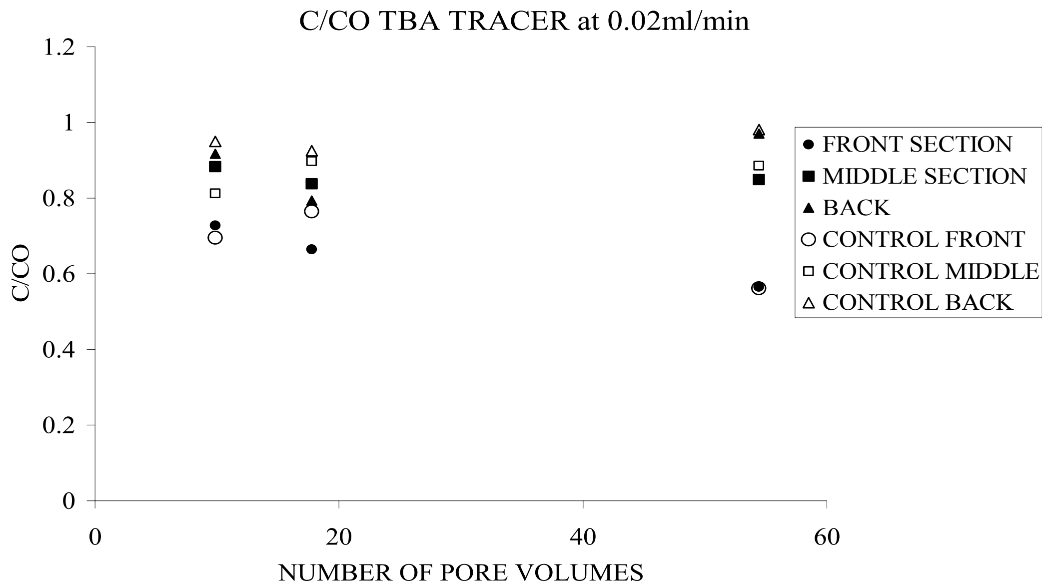
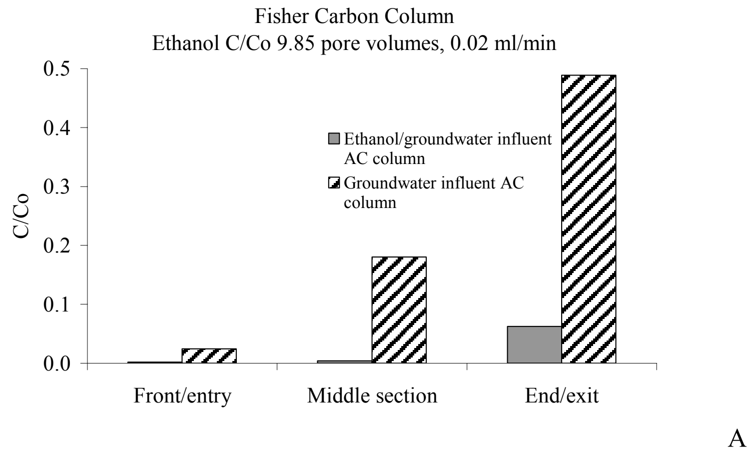
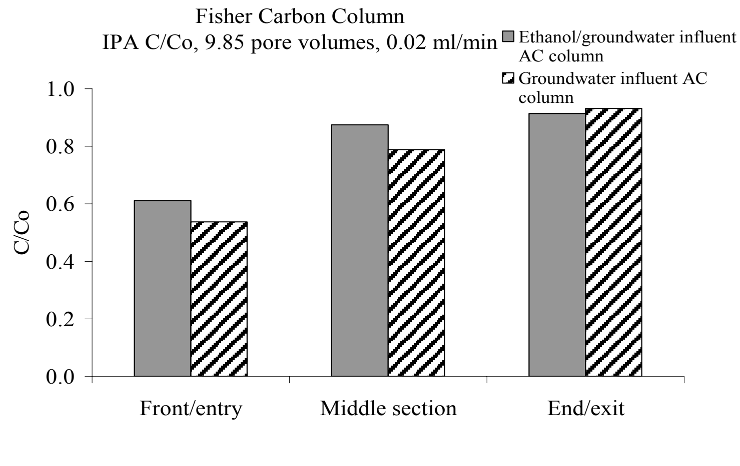


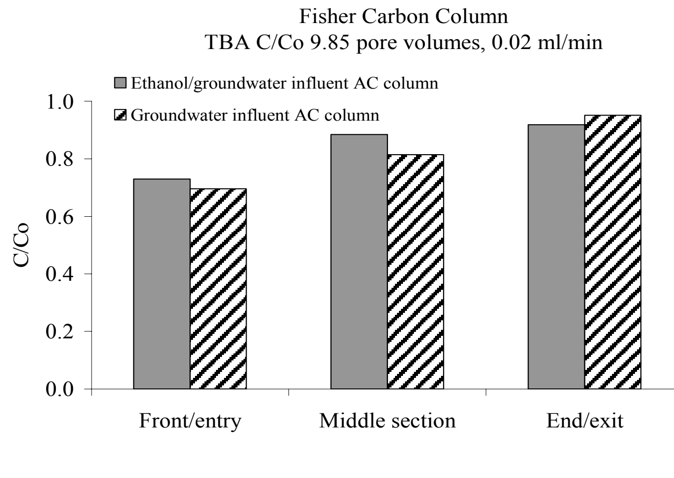
Figure 4-20. Plots alcohol tracer mass remaining after pore volumes flushing. Control is flushed with groundwater only. A) Isopropanol. B) Tert-butyl alcohol.



A



B



C

Figure 4-21. C/Co comparison of alcohol fractions in column sections, 9.85 pore volumes, 0.02 ml/min. A) Ethanol. B) Isopropanol. C) Tert-butyl alcohol.

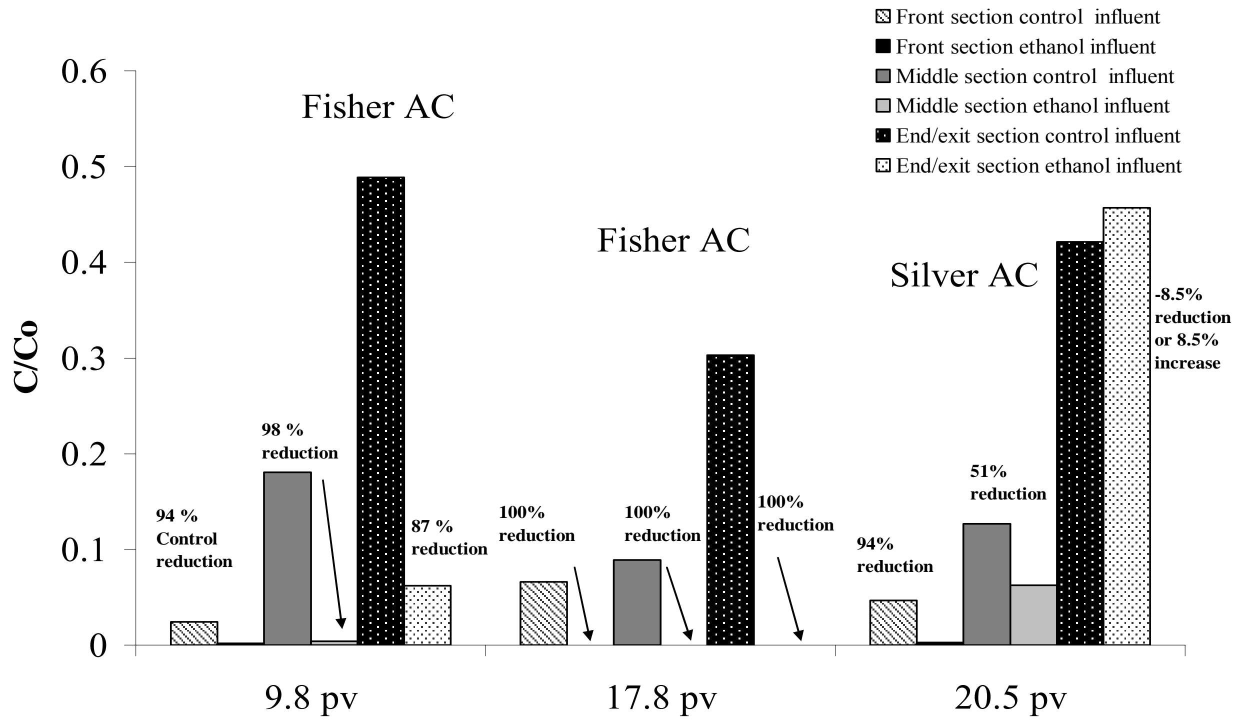


Figure 4-22. Comparison of ethanol mass remaining after determined number of pore volumes flushed through Fisher AC and silver AC. Control is flushed with groundwater only.

A

B

C

Figure 4-23. Photos of control setup. A) Overall setup. B) Sand column, ethanol influent, black substance at the entry to the sand, “generator” column. C) Sand column, groundwater only influent.

Premade Column Experiments

An additional set of experiments was conducted to evaluate possible effects of preassembling flux meters on tracer degradation. Preassembly of flux meters was done for Patrick Air Force Base (PAFB) but preliminary data from the the bioactive site, showed unexpectedly high ethanol degradation, given the low Darcy Flux and time in the aquifer. To evaluate tracer degradation with controlling environmental factors, 4 smaller scale columns were assembled using alcohol tracer equilibrated silver impregnated carbon used in previous batch and column studies. Since a copper tube was used in preassembly of these PFMs, it was conjectured that the unsaturated upper part of the PFM with more exposure to oxygen could, in the presence of copper ion, develop reactive oxygen species resulting in a higher rate ethanol oxidation (Wang et al. 1997). Silver impregnated carbon was used in the preparation of these preassembled PFMs.

Methods and Materials: Premade column experiments

Alcohol Solution Preparation. A tracer solution was prepared with 5ml MeOH, 5ml EtOH, 10ml IPA and 5 mL 2, 4-DMP. A quantity of 11.7 mL of this solution was added to containers containing 1.25 liters of deionized water. The calculated amount of 681 g Barnesbey Sutcliffe Type 989 12x30 0.026% metallic silver was added to each container; the resulting mixture was rotated for 24 hours. After equilibration with the tracer solution, 4 wet carbon samples were taken from each container to determine the initial concentration of the alcohols.

Experimental column preparation. Four downscaled column were prepared using 4 - 30” lengths of 1 ¼” PVC pipe and white crinoline socks as depicted in Figure 4-24. A 3/8” copper rod was inserted into 3 columns (A, B, D) prior to packing to simulate field conditions at PAFB where copper rods were used. To examine any possible affect from the copper, column, “C” was prepared with a 3/8” stainless steel rod. The pre-equilibrated tracer carbon mixture was packed in the PVC columns. Prior to packing 8-10 gram samples of the tracer equilibrated AC were added to IBA to measure the initial mass of alcohol tracers. Saturated and unsaturated zones were designated to simulate the pooling of tracer solution in the activated carbon which might affect bacterial activity and tracer sorption effects.

The columns were unpacked by taking 8-10 gram samples from both the unsaturated and saturated zones. These samples were extracted with IBA to measure the extracted mass and measure initial tracer concentration. Additionally 30 gram samples were taken from both the unsaturated and saturated zones and placed in batch Systems with 180 grams of groundwater and 10 grams of NASA soil. The unpacking and sampling times for the columns were 6 hours (A), 1 day (B and C) and 1 week (D) (Table 4-11). The prepared batch systems were sampled initially to get a *Co* for the alcohols and then every other day to assess remaining alcohol mass.

For the batch System sampling to minimize volatile loss, a 1-mL Teflon syringe was used to sample through septa sealed systems into 0.4-mL samples, which were then allowed to settle several hours. To avoid possible carbon contamination of the GC equipment, the settled 0.4-mL samples were then subsampled again into 0.2-mL GC vials for chromatographic analysis. Table 4-11 outlines the methodology for these batch tests.

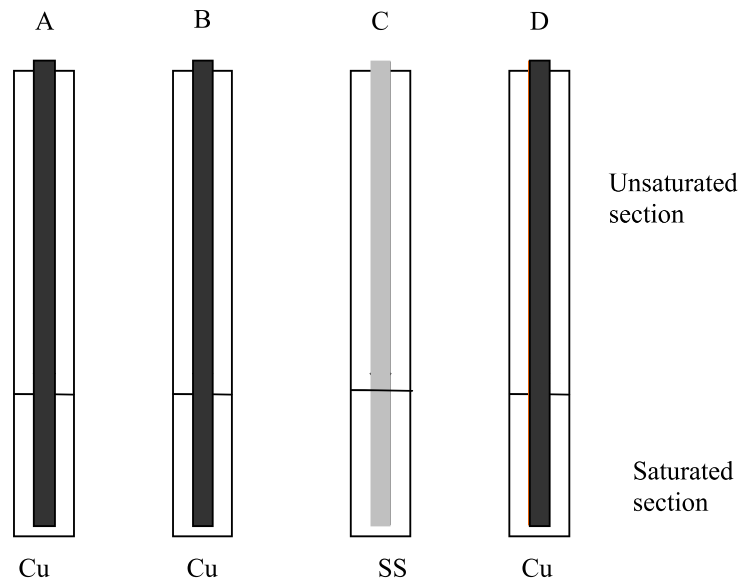


Figure 4-24. Premade Column Setup for saturated, unsaturated zone.

Table 4-11. Premade column preparation, samples collected for extraction, batch analysis

Column	A	B	C	D
Materials	1 ¼” PVCpipe crinoline sock copper rod	1 ¼” PVCpipe crinoline sock copper rod	1 ¼” PVCpipe crinoline sock stainless steel rod	1 ¼” PVCpipe crinoline sock copper rod
Subsample time	6 hour after pack	1 day after pack	1 day after pack	1 week after pack
Samples collected	C_o sample (unsat., sat.) Batch/unsaturated / saturated	C_o sample (unsat.,sat.) Batch/unsaturated/ saturated	C_o sample (unsat.,sat.) Batch/unsaturated/ saturated	C_o sample (unsat.,sat.) Batch/unsaturate d/ saturated
Extraction and batch procedures				
Co/ column extractions	Add 8-10 g Co AC, unsaturated/saturated column AC after unpacking to 20 mL IBA			
Column sample batch jar preparation	Add 30 g unsaturated/saturated column AC to 180 g groundwater and 10 g soil			

Results and Discussion; Premade column studies.

There was no observably significant difference in unsaturated and saturated column samples after unpacking the columns and comparing extracted mass to that in the original mass packed. Figure 4-25 compares the mass ratios for methanol and ethanol after extraction as well as initial concentrations in the batch systems made with AC unpacked from columns. Also, no difference was apparent in the copper rod column (D) when compared to the stainless steel rod column (C). Furthermore, no significant differences were seen in alcohol concentration of column samples after unpacking and placing in batch Systems (Figure 4-26). Figures 4-27 to 4-30 show the concentrations of alcohols in the batch systems plotted over several weeks. The degradation activity shown for the four columns sampled from upper unsaturated and lower saturated (total 8 batch systems) shows ethanol degrading initially followed by methanol. The isopropanol activity was minimal. Table 4-12 shows the acclimation times and degradation rates for all systems prepared with unpacked column AC. No significant difference was seen between these systems.

Of importance is the fact that degradation occurred after an acclimation time in batch systems compared to the previous batch series B (oxygen limited) system 6, which was prepared with silver AC also. One possible explanation is the exposure to oxygen in the laboratory; when unpacked and sampled in the batch systems. System 6 was a sealed system with minimal oxygen exposure. Furthermore, the tracer alcohols were spiked into system 6 which included silver AC only; the preassembled columns were prepared as with field PFMS where the tracers are pre-equilibrated on the AC. Perhaps this additional oxygen stimulated activity that exhausted the bactericidal affect of the silver (Silver, 2003). Another concern is the silver ion concentration. (Chambers et al. 1962). Other factors such as minerals in the water (Woodward, 1963) can impact effectiveness. Research has shown that the concentration of silver ion may affect its bactericidal ability

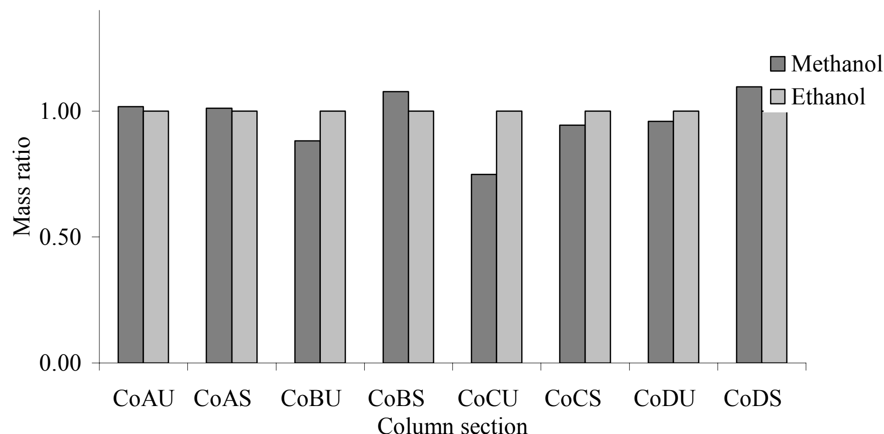


Figure 4-25. Tracer alcohol mass Co and mass after unpacking (6 hrs, 1 day, 1 week). Upper unsaturated, lower saturated A, B, C, D

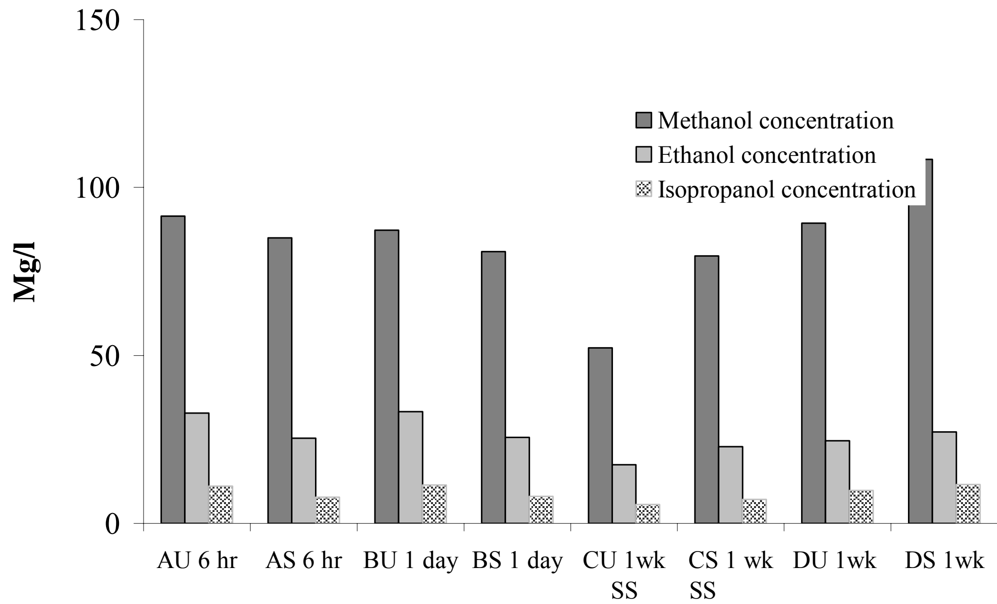


Figure 4-26. Initial tracer alcohol concentrations in batch systems after premade column disassembly. Upper unsaturated, lower saturated A, B, C, D.

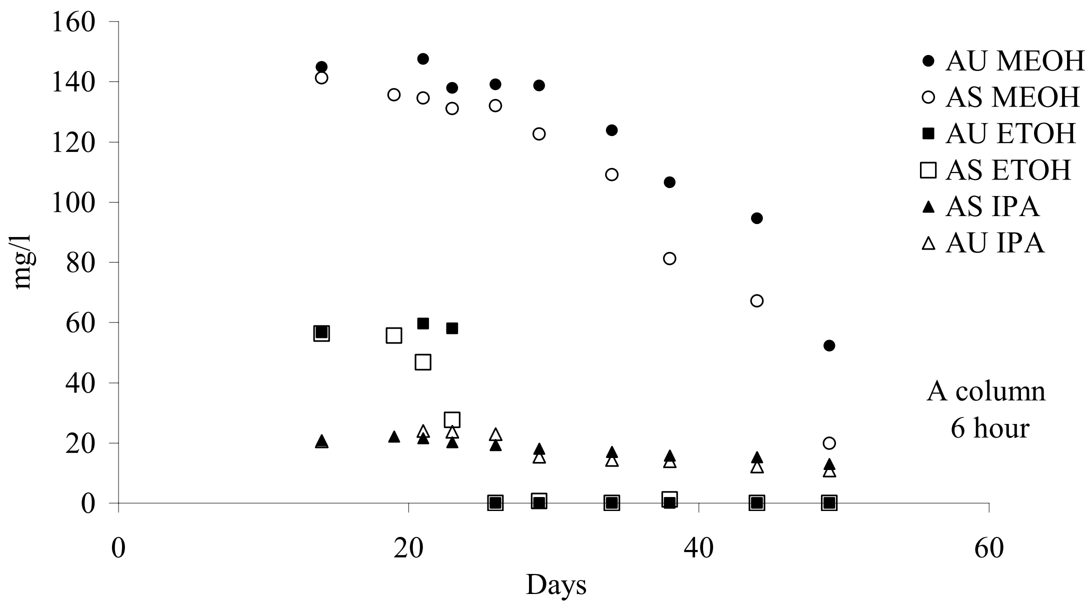


Figure 4-27. 6 hour batch for column A, alcohol concentration

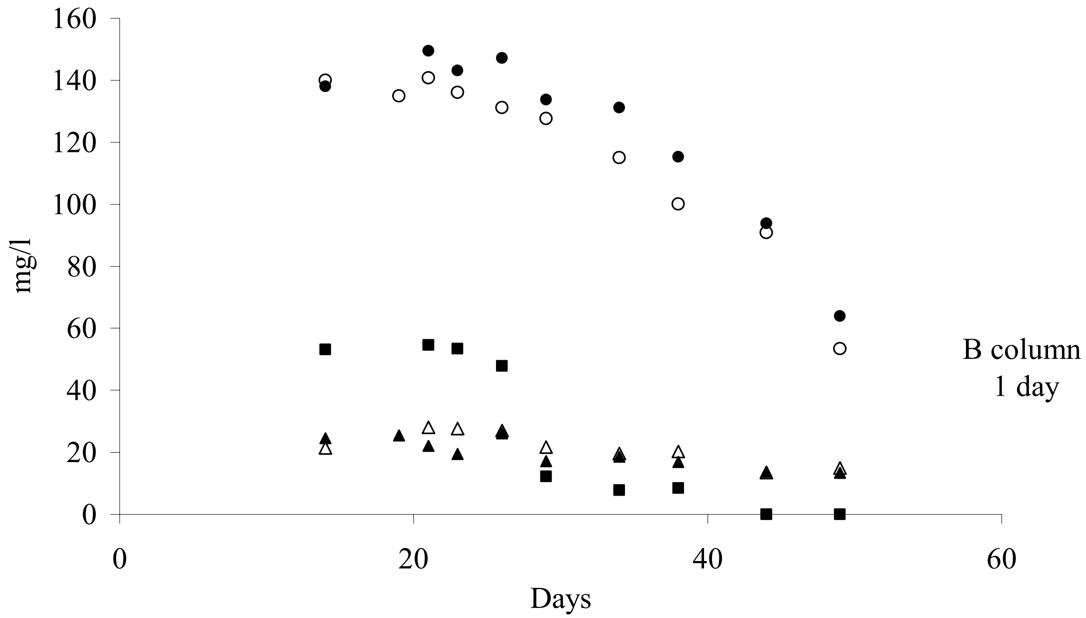


Figure 4-28. 1 day batch for column B (copper rod), alcohol concentration.

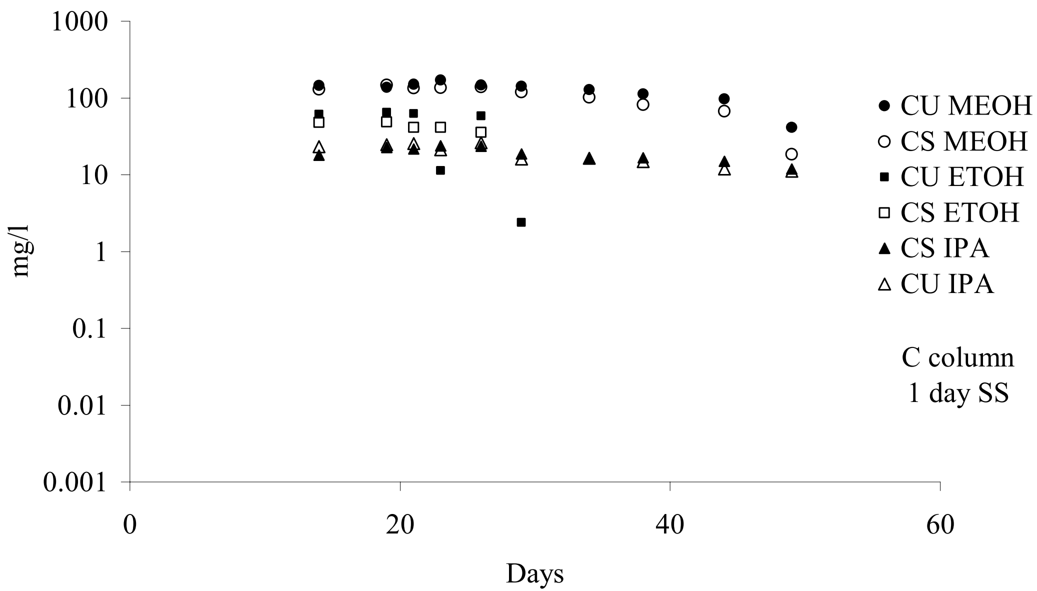


Figure 4-29. 1 day batch for column C (stainless steel rod), alcohol concentration.

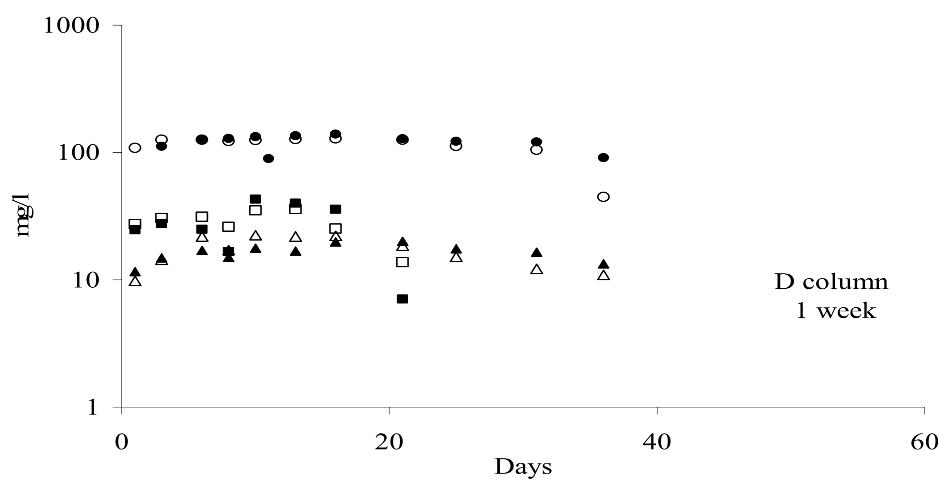


Figure 4-30. 1 week batch D column alcohol concentration.

Table 4-12. Acclimation times and degradation rates for unpacked alcohol equilibrated AC (premade columns) added to aqueous batch Systems

Column	Description	Tracer	Acclimation days	Estimated 0 ord. K	Estimated1[st] ord k
A unsat	1 ¼" PVCpipe crinoline sock	Methanol Ethanol	28 22	5 mg/l/fday 20 mg/l/day	0.1 /day 0.2/day
A sat	copper rod 6 hrs after pack	Methanol Ethanol	28 23	5 mg/l/fday 20 mg/l/day	0.05 /day 0.4day
B unsat	1 ¼" PVCpipe crinoline sock	Methanol Ethanol	28 22	5 mg/l/fday 23 mg/l/day	0.1 /day 0.2/day
B sat.	copper rod 1 day after pack	Methanol Ethanol	28 22	5 mg/l/fday 24 mg/l/day	0.1 /day 0.2/day
C unsat.	1 ¼" PVCpipe crinoline sock	Methanol Ethanol	28 22	5 mg/l/fday 25 mg/l/day	0.1 /day 0.2/day
C sat.	stainless steel rod 1 day after pack	Methanol Ethanol	28 22	5 mg/l/fday 25 mg/l/day	0.1 /day 0.2/day
D unsat.	1 ¼" PVCpipe crinoline sock	Methanol Ethanol	22 15	5 mg/l/fday 20 mg/l/day	0.2 /day 0.2/day
D sat.	copper rod 1 week after pack	Methanol Ethanol	22 15	5 mg/l/fday 25 mg/l/day	0.2 /day 0.2/day

Conclusions: Batch Studies, Column and Preassembled Column Studies

Batch Studies

Alcohol degradation rates derived from aqueous batch studies illustrated the inhibitory affect of both temperature and silver on microbial activity. The batches prepared in Series A (aerobic) and B (oxygen-limited) batch studies with Fisher AC and soil exhibited similar ethanol degradation rates although the oxygen limited B series did show longer acclimation times for both methanol and ethanol. Additionally, the methanol degradation rates were lower for oxygen-limited B series. Again no degradation occurred in system 6, the only system of A and B series which used silver AC. However, the batches prepared with silver AC unpacked from the preassembled columns did degrade, although at lower first order rates than observed in Series A and B using Fisher AC. The sequence of degradation activity is consistent with Series A, B and premade/unpacked column batch tests.

It is apparent that the silver AC did not entirely inihibit activity in the premade column batch tests. As disussed previously, the concentration of silver ion may affect its bactericidal ability. Also, the amount of oxygen exposure could increase bacterial activity which could overwhelm the inhibitory effect of the silver ion present.

Regarding alcohol kinetics, Bekins et al.(1998) compared the use of zero order and first order rates and found that concentration levels as well as the range of those levels, can affect the degradation rates. It was discovered that under some field conditions, first-order kinetic models can be poor representations of biodegradation; zero-order kinetics may better model the kinetics if concentrations are higher than the half-saturation constant, K_s, used in Monod kinetics.

Column Studies.

The column studies illustrated the effect of electron donor amendment on microbial growth and activity which resulted in increased alcohol degradation as well as visual evidence of microbial activity with the formation of biofilm. The preassembled column study using silver AC showed no tracer mass loss due to preassembly; however when placed in batch systems after unpacking, degradation did occur after an acclimation period and thus illustrates the importance of acclimation time to the initiation of degradation activity of the alcohol. Also, questions remain about the efficacy of the silver AC in different concentrations and environments.

The results of the ethanol/groundwater influent column studies using silver AC especially reveal the possible affects of microbe/biofilm growth on silver ion transport to the bacterial cell. The silver ion concentration levels and resultant activity may be significantly reduced due to blockage by biofilm substances.

4.3.2. Flux Meter Evaluation at LC34 During Enhanced Bioremediation

As part of EPA's Superfund Innovative Technology Evaluation (SITE) Program, NASA conducted a demonstration of bioaugmentation with KB-1™ to enhance the removal of TCE DNAPL at its LC-34 demonstration site. KB-1™ was developed by GeoSyntec and the University of Toronto (Harkness et al. 1999; Major et al. 2002). To demonstrate the performance of passive flux meters under enhanced bioremediation, groundwater and contaminant flux was measured with the passive flux meter (PFM) during 4 developmental phases: 1) induced gradient pumping, 2) ethanol flushing for biostimulation, 3) post KB-1 injection at 3 months, and 4) post KB-1 at 8 months.

Objectives

- Evaluate the flux meter as an innovative technology for direct in situ measurement of cumulative water and contaminant fluxes in groundwater during bioremediation.
- Evaluate methodology for interpreting DNAPL source strength from point-wise measurements of cumulative contaminant and water fluxes, and
- Compile field data in support of an effort to transition the technology from the innovative testing phase to a point where it receives regulatory and end user acceptance and stimulate commercialization.

Project Scope

The scope of the demonstration project included working with GeoSyntec and NASA to conduct flux monitoring of the pilot bioremediation study during four phases of the experiment. The test plot consisted of three injection and three extraction wells which were used to produce a steady state flow cell. The first phase and application of the study involved assessing conditions under steady water flow. The flux meters were employed in 3 fully screened wells located approximately 1.0 m upgradient of the extraction wells. Measured flux at the PFMs was compared to flux measured at the extraction wells and flux based on multilevel samplers located about 0.5 m upgradient of each flux meter well. Flux was then monitored during the next three phases of the study which involved nutrient injection, microbe injection, and final water flow assessment.

Background

NASA LC34 was a launch site for Saturn rockets from 1960 to 1968. Historical records suggest that workers cleaned rocket engines on the launch pad with organic solvents including TCE. Additional rocket parts were cleaned on racks at the western portion of the engineering support building (ESB) and inside the building. A significant amount of solvents ran off to the surface or discharged into drainage pits, and NAPL source characterization efforts suggest that up to 40,000 kg of solvents are present in the subsurface near the ESB at LC34 (Eddy-Dilek et al. 1998).

Site description

This site, LC34, is located at Cape Canaveral Air force Station (CCAS) along the eastern coast of central Florida. The Cape Canaveral Peninsula is a 1- 2-mile-wide barrier island bordered by the Atlantic Ocean to the east and the Banana River to the west. LC34 is immediately adjacent to the Atlantic Ocean (Figure 4-31). The site elevation is about 0 to 15 ft above mean sea level.

Figure 4-31. Aerial view of LC34. Engineering Support Building, bottom of photo.

Site Geology

The barrier island complex overlies coastal sediments composed of sands and shells with layers and lenses of clay and silt. Limestone bedrock exists at a depth of 145 to 190 ft below ground

surface. The surficial aquifers are unconfined or semi-confined in the LC34 area and consist of mostly sand with portions of clay, silt, and shells or coquina. The aquifers are often isolated and do not form a regional aquifer. Recharge for the surficial aquifer infiltrates directly from the surface to the water table; the aquifer discharges into wetland areas or surface water bodies (Battelle Report, 1999). The surficial aquifer extends from the water table to approximately 43 to 45 ft bgs in the LC34 area.

The aquifer is sub-classified in terms of an upper sand unit (USU), a middle fine-grained unit (MFGU), and a lower sand unit (LSU) (Eddy-Dilek et al. 1998). The surficial aquifer is unconfined above the MFGU and semi-confined below the MFGU. Water levels in this aquifer are about 4 to 5 ft bgs. The USU extends from ground surface to approximately 25 ft bgs. It consists of unconsolidated light brown fine sands and shell fragments. Well logs indicate that up to 70% of the unit consists of shell fragments.

High permeability sediments extend from the ground surface to the water Table, suggesting that precipitation infiltrates directly into the aquifer through the unsaturated zone. A layer of fine-grained silty/clayey sand, termed the MFGU, exists at about 25 to 30 ft bgs. This layer consists of greenish-gray clay, silt, and fine sands. It ranges in thickness from 1 ft to 17 ft and is thicker to the north of the ESB. Below the MFGU is the LSU, which consists of gray silty sand with shell fragments and isolated fine-grained lenses of silt and/or clay. Water levels from wells screened in this unit are usually higher than the water levels from the USU or the MFGU. A 1- to 3-ft-thick confining layer exists at approximately 45 ft bgs in the LC34 area. The layer consists of greenish-gray sandy clay and appears to be pervasive at the LC34 site. However, the unit is fairly thin (1 ft or less) in areas. Figure 4-32 is a schematic of the aquifer cross section.

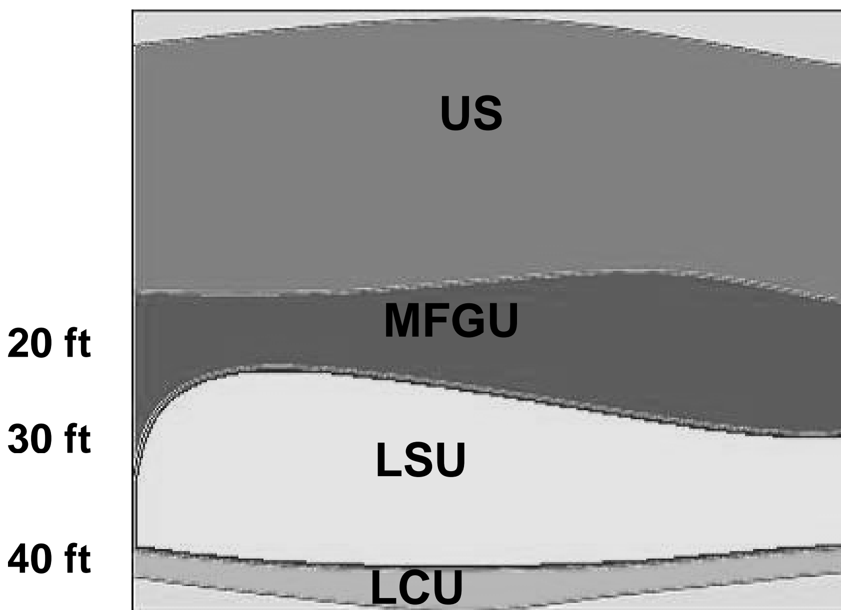


Figure 4-32. Aquifer cross section of LC34 hydrogeology.

Materials and Methods

Establish Baseline, Biostimulation, and Bioaugmentation Flux.

The project included 4 separate PFM installations as shown in Table 4-13.

Table 4-13. Treatment Description for PFM Deployments 1-4

PFM Deployment	Installation Treatment Stage	Installation Dates
Phase 1	Pretreatment with pumped gradient only	7/09-7/12/ 2002
Phase 2	Ethanol Amendment	1/30-2/06/2003
Phase 3	Post KB-1 application (Feb.2003), continued ethanol treatment	4/22-5/02/2003
Phase 4	Post KB-1 application, discontinued ethanol.	9/30-10/07/2003

During Phase 1, prior to ethanol flushing of the bioaugmentation plot, passive flux meters were installed in each of the three flux borehole wells so that baseline measurements of cumulative water and contaminant fluxes could be made. Granular activated carbon (Barney-Sutcliffe silver impregnated, Columbus, OH) was used as the sorbent in the passive flux meters (PFMs). Isopropyl alcohol, tert-butyl alcohol and 2, 4-dimethyl-3-pentanol served as resident tracers pre-equilibrated on the activated carbon. No ethanol was included in the Phase 2 alcohol mix due to concurrent ethanol treatment at the site. Since subsequent laboratory analysis yielded low background ethanol concentrations during Phase 2, ethanol was included in Phases 3 and 4.

Activated Carbon Sorbent Preparation.

In preparation for PFM deployment, one (1) 20-liter Nalgene jug was filled with 14.5 L water, 163 mL of tracer mixture and capped tightly. The water/alcohol solution was shaken for at least one hour for complete mixing. Then approximately 7900 g of dry silver impregnated carbon was slowly added to this mixture. After sealing tightly, the jug was rotated with a 55 gallon drum rotator for 24 hours. The prepared alcohol/AC equilibrated carbon mixtures were refrigerated and drained prior to filling of the mesh sock used in PFM preparation. The amounts of tracer mix and the pre-equilibrated activated carbon for phase/trip 1 as well as the subsequent 3 trips are shown in Table 4-14.

Table 4-14. Alcohol tracer mix and activated carbon, sorbent preparation

	Alcohol tracer mix	Tracer mix proportions	Total silver AC
Trip 1 7/09-7/12/02	90ml MeOH 90ml EtOH, 180ml IPA 180ml TBA	14.5L H20 163 mL tracer mix 20 liter jug	7900 g
	90ml 2-4, DMP	1.5L H20 19.7 mL tracer mix 2 liter jug	817 g
Trip2 1/27-1/30/03	45ml MeOH 0ml EtOH, 90ml IPA 90ml TBA	14.5L H20 163 mL tracer mix 20 liter jug	7900 g
	45ml 2-4, DMP	1.5L H20 19.7 mL tracer mix 2 liter jug	817 g
Trip 3 4/22-4/30/03	45ml MeOH 45ml EtOH, 90ml IPA 90ml TBA	14.5L H20 163 mL tracer mix 20 liter jug	7900 g
	45ml 2-4, DMP	1.5L H20 19.7 mL tracer mix 2 liter jug	817 g
Trip 4 9/30-10/07/03	45ml MeOH 45ml EtOH, 90ml IPA 0ml TBA	14.5L H20 163 mL tracer mix 20 liter jug	7900 g
	45ml 2-4, DMP	1.5L H20 19.7 mL tracer mix 2 liter jug	817 g

To ensure sufficient supply of carbon, an additional 3 - 2.0 L bottles were prepared with 1.5L water, 19.7 mL tracer mix and 817 g carbon. These were also rotated for 24 hours. The equilibrated carbon mixture was subsequently refrigerated and drained prior to filling of the PFM on site.

Passive Flux Meter Preparation and Onsite Deployment

The pre-equilibrated, wet, activated carbon was packed into crinoline socks on site at each deployment. The cotton crinoline socks were pre-washed in water. Each sock, closed on one end, was attached to a threaded rod (8-32 tread or 1/4 inch) between two rubber washers

tightened using two steel washers and nuts. The threaded rod extended up through the center of the sock and was used to slide (pull from the bottom) the flux meter into the well.
The socks ware packed by transferring a measured volume of activated carbon to a funnel entering the top of the sock. The pipe and sock were vibrated to facilitate packing. After each lift, a viton washer was inserted onto the threaded rod and pushed down to the packing depth using a narrower PVC pipe to compact the material in place. The viton washer had an inner opening the diameter of the threaded rod and an outer diameter matching the well screen This washer minimized vertical flow within the flux meter. Each sock was packed in 6 to 7, 20cm sections to contain a total of approximately 1400 grams dry activated carbon: this produced a PFM with a dry carbon bulk density of 0.55 g/cm^3 as established from gravimetric testing.

During the packing process, field samples were collected to measure the initial concentrations of tracers present on the activated carbon. These concentrations were used in subsequent calculations to ascertain the relative mass of each tracer remaining in the PFM following a period of exposure to flow in the fluxmeter plane.

After packing all lifts, the top of the sock was attached with a band clamp to a short section of 3/4 inch PVC pipe which had a rope attached. The rope was used for retrieval of the flux meter by pulling (or sliding) the sock out of the well. Due to the interior ridges in the stainless steel well screen, flexible plastic cylindrical mesh was used to encase the filled flux meter socks and ease insertion and removal from the wells. The socks were than placed in PVC pipes the same diameter as the well screens (2 inch).

Insertion of the flux meter was performed by placing the packing pipe directly over the top of the well and pushing the flux meter in place using the threaded rod. Additional threaded rods were attached as needed to position the flux meter in the desired screen interval.

After a specified period of exposure, the flux meter was extracted from the well using the rope. The flux meter was extracted into a PVC pipe to minimize volatile losses during sampling. The bottom end of the flux meter was then pulled from the pipe and the section of sock cut for sampling. The entire section of activated carbon was transferred to a bowl and mixed vigorously for a few seconds to homogenize. A subsample (approximately 10-g) was transferred to pre-weighed vials containing 20-mL of isobutyl alcohol. The interval length was then recorded prior to sampling the next interval.

A total of 6 PFMs, 2 per well, were installed on site at each of the 4 phases of the evaluation. The flux measuring wells were of direct push 2 inch stainless steel with 10 feet of 0.010 slotted screen installed to approximately 26 ft. below ground surface The well construction is shown in Figure 3-3. Figure 3-4 shows onsite photos of PFM preparation and pumps inside the ESB. The left hand photo shows the sock encased in the flexible plastic mesh to ease well insertion. Figure 3-5 illustrates the field retrieval method for the PFM assembly.

Direct Push 2 inch Flux SS Well Construction

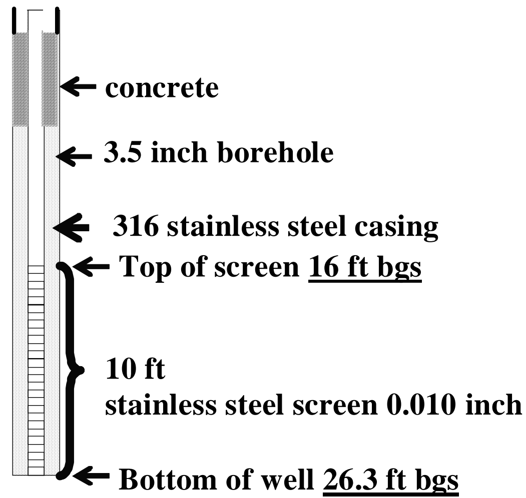


Figure 4-33. Construction of flux wells at NASA LC34, Engineering Support Building.

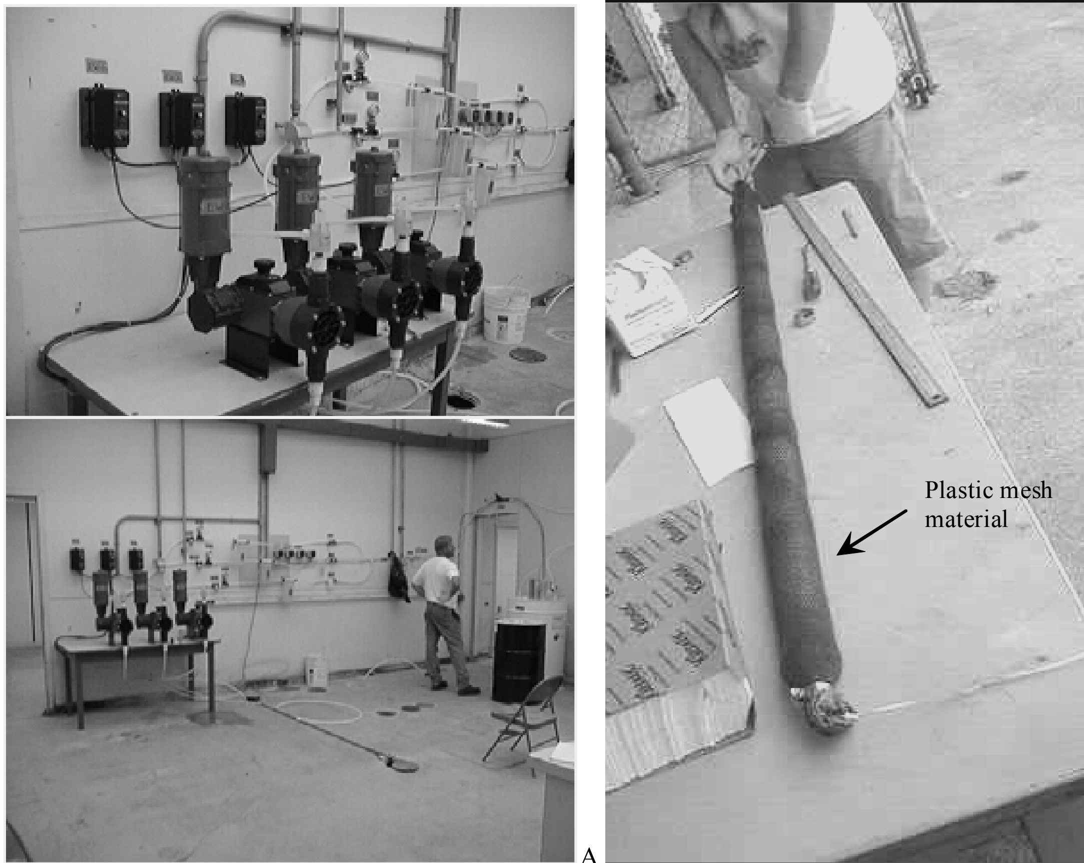


Figure 4-34. Onsite photos at LC34. A) Extraction wells inside ESB. B) PFM preparation and encasement in plastic mesh for ease of insertion.

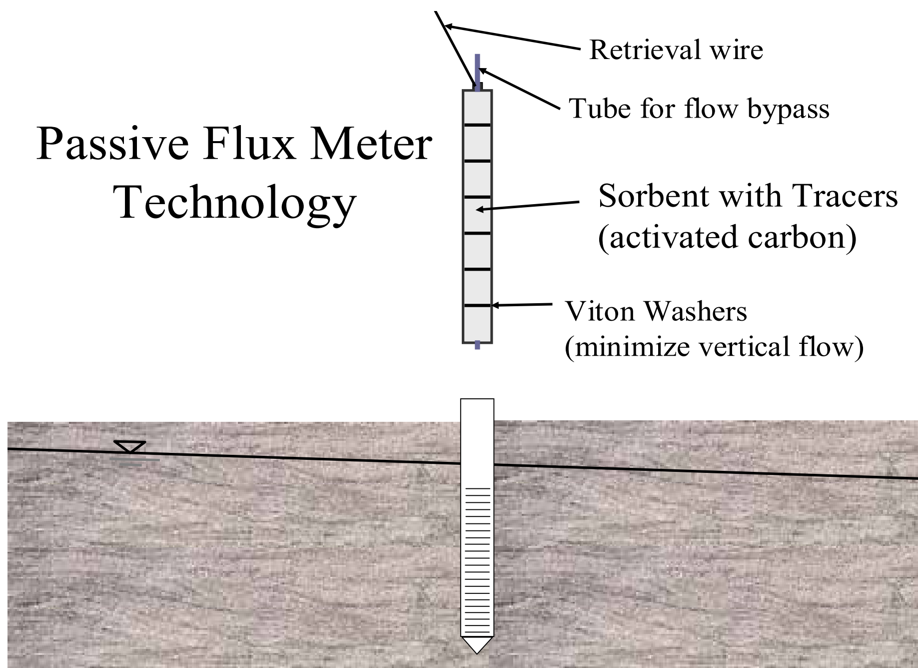


Figure 4-35. Retrieval method with wire (rope, cord) for onsite Passive Flux Meter.

The laboratory extraction of the samples involved a two step process: the initial extraction with the isobutyl alcohol followed by a second extraction with an acetone and hexane mixture. Table 4-15 outlines the extraction procedure. From the extracts, all samples were analyzed for alcohols and contaminants using a Perkin-Elmer Gas Chromatograph (GC) with FID; TCE, 1, 2-dichloroethylene, vinyl chloride and ethene were also analyzed using high performance liquid chromatography (HPLC) with a reverse phase column (C-18, Supelco).

Table 4-15. Flux Meter Sample Extraction Procedure

	Extraction Procedures
a.	Remove from refrigeration vials containing 10 g samples wet AC + 20ml of IBA.
b.	Rotate samples 24hrs, and then allow to settle several hours.
c.	Subsample twice from the supernatants of each 20ml vial
d.	Analyze one sample for tracers and vinyl chloride using GC and the other for TCE and byproducts using HPLC and GC
e.	Decant IBA/water mixture from the vials
f.	Add 25ml of acetone and 7ml of hexanes
g.	Rotate the samples 24hrs.
h.	Subsample twice from the supernatants of each 20ml vial
i.	Analyze the samples for TCE, DCE, VC and Ethene using HPLC, GC

Multilevel and extraction well water sampling methods

Multi level samples were taken at each of 5 multilevel sampler (MLS) wells, 5 levels per well. Extraction well water samples were also taken at each deployment. Both the groundwater flux and contaminant mass flux was calculated from PFM quantification methods and then compared to flux based on the multilevel samplers as well as at the central extraction well. Figure 4-36 shows the well locations at the test plot.

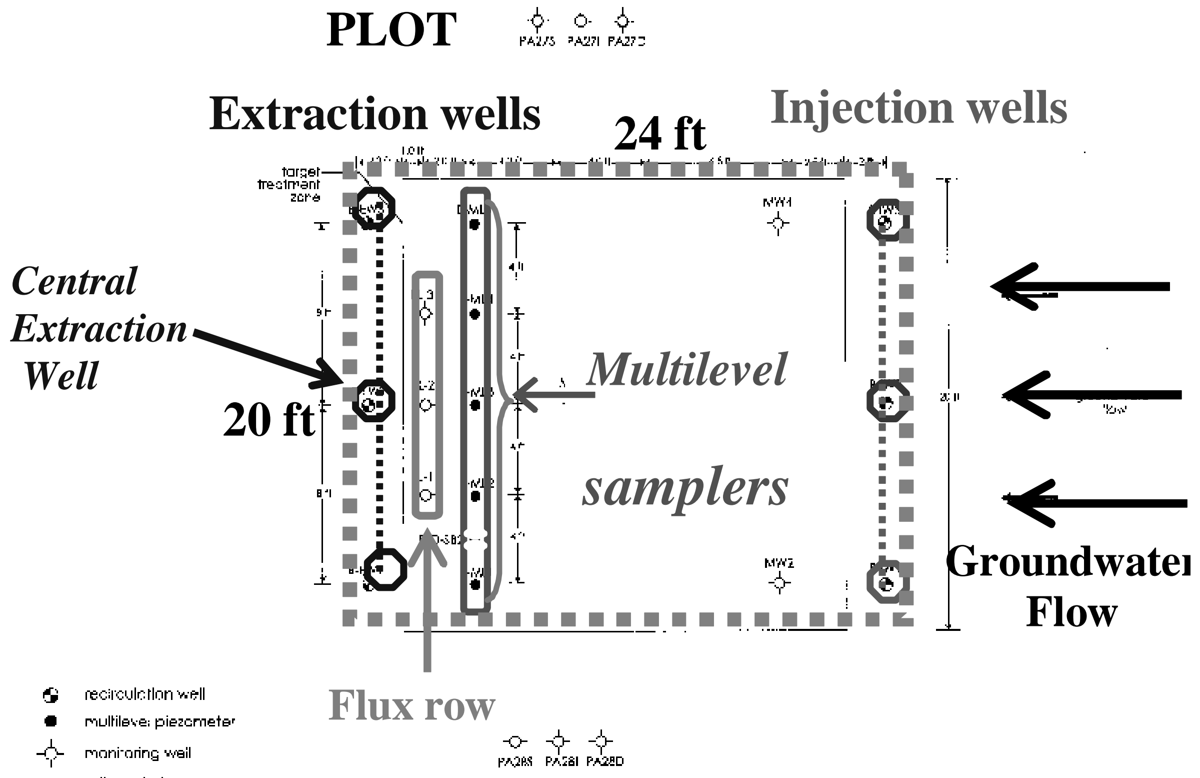


Figure 4-36. Location of 3 extraction wells, central extraction wells, 5 multilevel samplers.

Method for Groundwater Flux Quantification

As outlined in the previous section on theory for quanitification of PFM flux, in order to estimate groundwater flux, the alcohol tracer mass fraction was analyzed in the PFM pre and post groundwater flux exposure for each field deployment. Since 2, 4-dimethyl-3-pentanol (2, 4-DMP) has very high aqueous/activated retardation factor relative to other shorter chain alcohols, it behaves as a non-desorbing reference tracer as compared to the other alcohols: Table 4-16 lists their respective retardation (R) values.

Table 4-16. Retardation factors (R) of tracer alcohols used in PFM

Tracer alcohol	Retardation factor
Methanol	4.9
Ethanol	19.7
Isopropyl alcohol	120
Tert-butyl alcohol	295
2-4 dimethyl-3- pentanol (2,4-DMP)	(estimated) >1000

Therefore, 2-4 DMP was used as an internal standard whereby changes in the mass ratios for methanol, isopropyl alcohol, and ethanol were assessed from measured changes in tracer mass ratios with respect to the 2-4 DMP remaining mass. Measured values of the tracer mass fraction, Ω_R were then applied to the mathematical analysis to determine local water fluxes for comparison to pumped flux based on pumping logs.

As ethanol was included in the alcohol tracer group used for the initial installation (prior to biostimulation) and the mass fraction remaining was within the recommended range, this ethanol mass ratio was used in the Darcy flux calculation. In the second installation, during ethanol stimulation, ethanol was not included in the tracer mix due to biodegradation concerns during the ethanol biostimulation period and subsequent interference with tracer mass fraction results. In this case, isopropanol and tert-butyl alcohol were both used since some samples had mass fractions outside of the recommended range for tracer elution. In the third installation, ethanol was included in the tracer suite; ethanol as well as isopropanol and tert-butyl alcohol were used for groundwater flux analysis. Pumping had been discontinued prior to the fourth installation so the PFMS would represent natural gradient flow.

Flow Field Description.

The forced gradient system included three extraction wells and three injection wells each screened from a depth of 16 to 26 ft. bgs. The bioaugmentation treatment plot covered by the pumping gradient measured approximately 20 x 20 feet and is shown in Figure 4-37. The pumping wells were operated at a combined rate of 1.5 gpm (0.5 gpm each). Flux was monitored in 3 flux wells located upgradient of the central extraction well (EW 2) and immediately downgradient of the multilevel samplers.

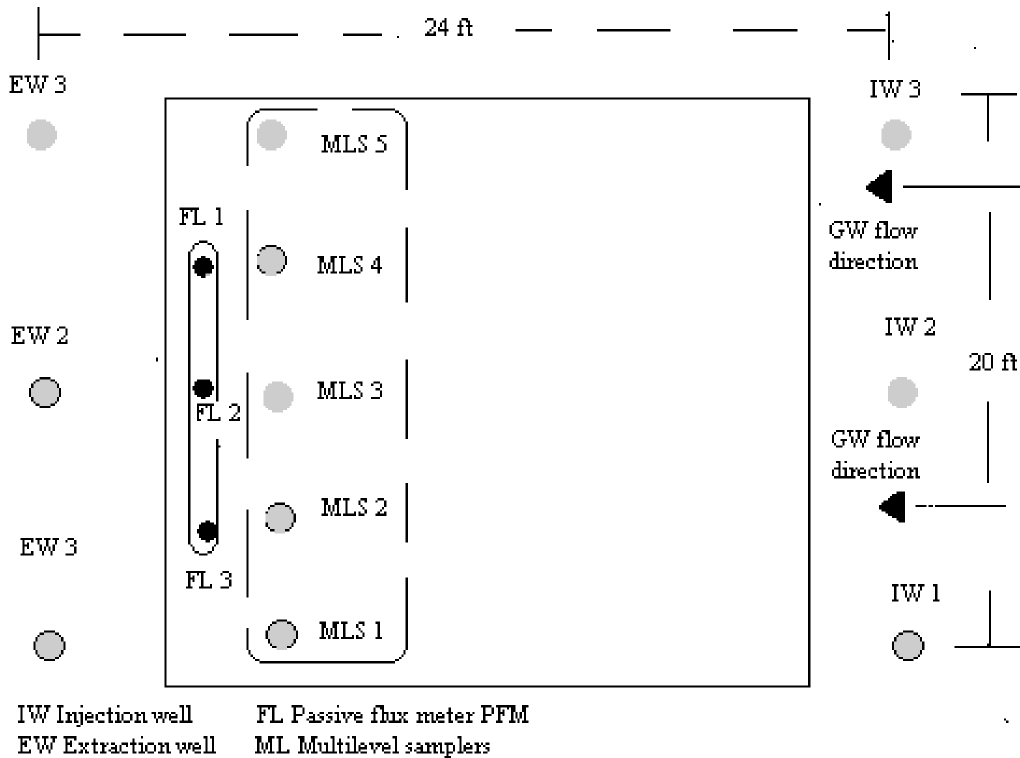
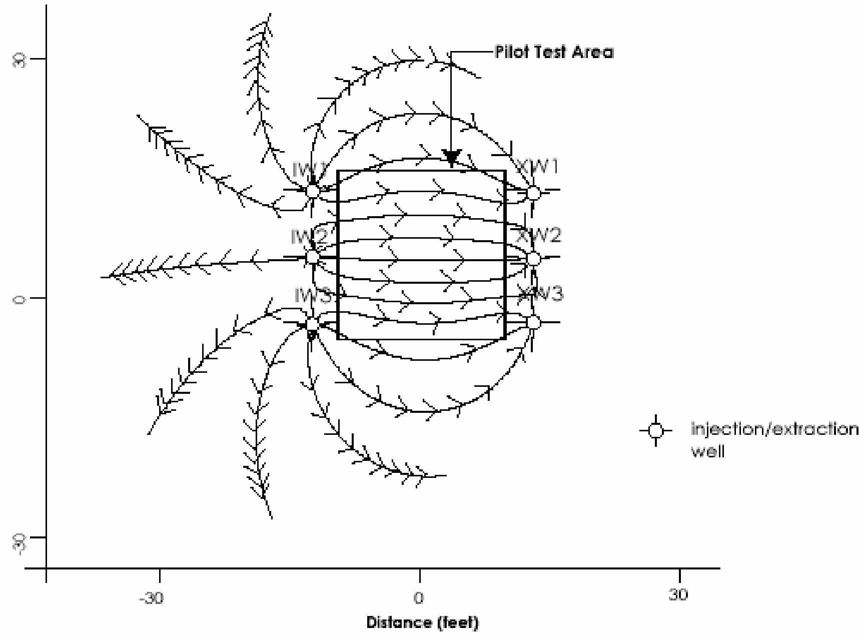


Figure 4-37. Well layout at NASA LC34.

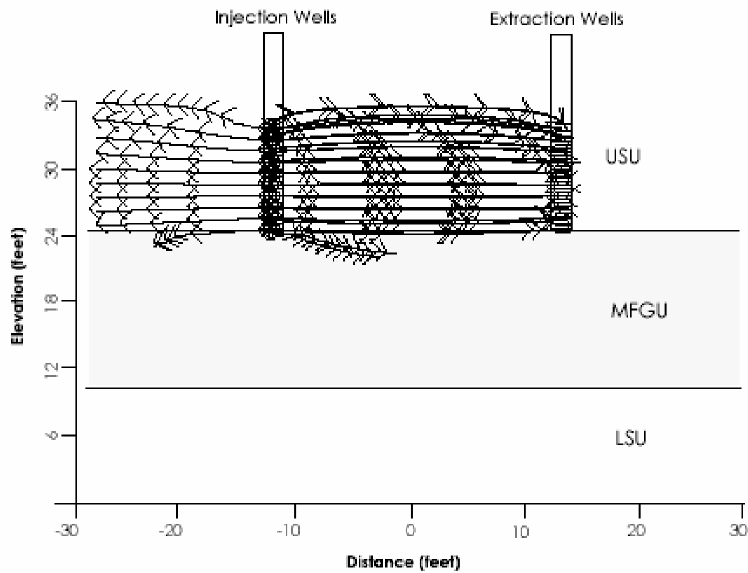
GeoSyntec conducted a bromide tracer test of the recirculation system including the injection and extraction wells; the analysis of breakthrough curves using the method of first moments estimated an average linear groundwater velocity along the centerline of the treatment zones of 0.75 ft/day, resulting in a residence time of 24 days (GeoSyntec Consultants, 2003). Using the average tracer arrival time and the mean hydraulic conductivity of the USU, MODFLOW was used to simulate steady-state groundwater flow and estimate groundwater residence times in the pilot test area (PTA). Preliminary hydro geologic characterization indicated relative homogeneity within the layers; anisotropy was not considered in the modeling.

The surficial aquifer was modeled as a three- layer system using hydraulic conductivities of 4.6, 3, and 2.7 meters/day, for the USU, MFGU, and LSU, respectively, a constant porosity of 0.33, and a regional gradient of 0.0001 m/m (Battelle, 1999). The clay unit is assumed to act as a no-flow boundary for the model. Constant head boundaries were assigned on all fours sides of the model grid to simulate the observed regional hydraulic gradient of 0.0001 and induce groundwater flow from north to south. The static water level in the pilot test area (PTA) due to these boundary conditions resulted in an undisturbed saturated thickness of approximately 36 ft. Zero recharge was specified in the model since the treatment zone is relatively small and entirely contained within the Engineering Services Building (ESB). Figure 4-38 shows the particle trajectories of the simulated groundwater flow in the pilot test area. The particle trajectories for the calibrated groundwater flow model at recirculation rates of 1.5 gpm result in typical residence times for groundwater in the PTA of 24 days through the centerline to 32 days both

flow lines along the sides of the PTA. Based on this, it was calculated that that the average groundwater velocity was 0.25 ft/day or 7.6 cm/day in the 24 ft long pumping zone and within the width of the area monitored. Note that the pumping system was automated and checked on site only when the system indicated a problem; therefore, accuracy in pumping rate records could not be assured.

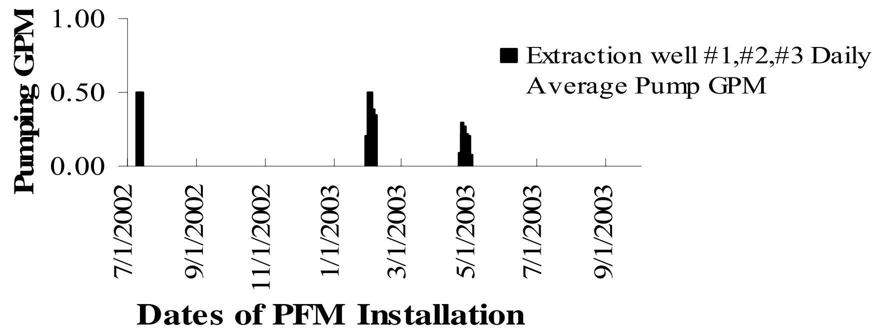


A



B

Figure 4-38. Simulated Groundwater Flow at pilot test area (PTA), 0.5 GPM per pump, 1.5 GPM total. A) Plan view. B) Lateral view



PFM Deployment Date *	Daily flow rate gallons per minute, GPM		
Deployment #1	Extraction rate #1	Extraction rate #2	Extraction rate #3
7/9/2002	0.50	0.50	0.50
7/10/2002	0.50	0.50	0.50
7/11/2002	0.50	0.50	0.50
7/12/2002	0.50	0.50	0.50
Average	0.50	0.50	0.50
Deployment #2			
1/30/2003	0.30	0.01	0.30
1/31/2003	0.20	0.20	0.20
2/1/2003	0.50	0.50	0.50
2/2/2003	0.50	0.50	0.50
2/3/2003	0.44	0.36	0.44
2/4/2003	0.50	0.14	0.50
2/5/2003	0.44	0.15	0.44
2/6/2003	0.39	0.26	0.39
Average	0.41	0.27	0.41
Deployment #3			
4/22/2003	0.01	0.00	0.03
4/23/2003	0.00	0.00	0.27
4/24/2003	0.17	0.17	0.32
4/25/2003	0.30	0.30	0.30
4/26/2003	0.26	0.26	0.26
4/27/2003	0.22	0.22	0.22
4/28/2003	0.22	0.22	0.22
4/29/2003	0.18	0.18	0.18
4/30/2003	0.20	0.20	0.20
5/1/2003	0.20	0.19	0.20
5/2/2003	0.07	0.07	0.07
Average	0.17	0.16	0.21

*Pumps turned off during deployment #4.

Figure 4-39. GeoSyntec pumping record for NASA bioaugmentation plot.

Results and Discussion

Comparison of water flux estimates

Table 4-17 compares the induced Darcy velocity to the flux calculated with the PFM groundwater equation, $q_o = \frac{1.67(1-\Omega_R)r\theta R_D}{\alpha t}$ where q_D is the time-averaged specific discharge through the PFM; Ω_R represents the mass fraction of initial tracer remaining on the sorptive matrix after exposing the PFM to groundwater flow for period t; r is the radius of the flux meter; R_d is the dimensionless retardation factor; and θ is the dimensionless volumetric water content of the sorptive matrix. The dimensionless parameter α characterizes the convergence or divergence of groundwater flow in the vicinity of the PFM.

. As discussed above, the groundwater flux equation is based on the tracer alcohol mass remaining on the PFM sorbent, in this case, activated carbon. Based on modeling results, the groundwater flow indicated a less than 5% variation across width of the flow field. To provide an estimate on the divergence or convergence factor α in the vicinity of the PFM, comparison of the first deployment PFM calculated velocity was made to the estimated velocity based on induced flow modeling. Based on this comparison, an alpha value equal to 1.0 was then applied to all PFM deployments.

Table 4-17. Comparison of induced flow to PFM calculated Darcy flux.

Flux meter deployment		PFM1		PFM2		PFM3	
Date	Darcy Flux measure	q cm/day	% diff.*	q cm/day	% diff. *	q cm/day	% diff. *
07/09-7/12/02	a. induced flow	7.62		7.62		7.62	
	b. PFM tracer/EtOH	7.12	7.0	9.1	-19	7.16	6
1/27-1/30/03	a. induced flow	5.52		5.52		5.52	
	b. PFM tracer/IPA	4.08	30	4.75	15	4.54	19
	b.PFM tracer/IPA-TBA	4.85	13	5.09	8	5.76	-4
4/22-4/30/03	a. induced flow	2.74		2.74		2.74	
	b. PFM tracer/EtOH	5.39	-65	5.52	-67	5.52	-67
	b. PFM tracer/IPA		No data	3.78	-32	2.71	1

*% diff. (percent difference) is calculated (a-b)/ ((a+b)/2), where a =induced flux, b = PFM flux

During the first installation, which occurred prior to ethanol biostimulation and KB-1 bioagumentation, the pumping records indicated continual operation. The derived flux, calculated with ethanol tracer mass, compared favorably with the induced flow; the percentage difference ranged between -19% to +7%. At the second deployment, the ethanol biostimulation stage, ethanol was not used as a tracer alcohol. Therefore, based on remaining mass ratios, either isopropanol or tert-butyl alcohol were used to calculate groundwater flux. Quantifying with isopropanol only, derived groundwater flux was 15% to 30% higher than the modeled water flux; selecting ispropanol or tert-butyl alcohol to minimize laboratory errors in quantified mass ratios, the difference ranged from -4.3% to 13%. As there is higher residual mass (where intercepted mass fraction > 0.32 and is used for calculation of groundwater flux) for isopropanol and tert-butyl alcohol on the activated carbon and these alcohols are less degradable, there may be less subsceptibilty to site bioactivity. The third deployment occurred 11 weeks post KB-1 application. Calculations showed significantly higher PFM derived water flux using ethanol with an over 60% increase in flux. The bioactivity in the aquifer, manifest in pump fouling and biofilm presence in the well, may have contributed to a significant degradation of ethanol despite the use of silver impregnated activated carbon. Also, as in the column experiments with silver AC, this biofilm could have protected the bacteria within the matrix from the inhibitory affect of the silver ion. And as ethanol has high biodegradation rates in water, this would contribute to the reduced ethanol mass fraction. There is also the possibility that silver's inhibitory activity on bacteria was exhausted in a highly bioactive environment at LC34 (Zhang et al. 2004; Chambers et al. 1962; Russell, 1994; Silver, 2003). As in the second deployment, using isopropanol with a larger tracer residual mass reduced the magnitude of the Darcy flux error by more than 50%.

Comparison of Contaminant Flux Estimates

Table 4-18 compares contaminant mass flux results, during the background flood for both MLS derived and PFM measurements (45 cm depth intervals). There are significant differences between the MLS and PFM measurements for both TCE and DCE mass flux. Using an average over the entire screened section and across the entire flux plane (10 ft depth x 24 feet width), the difference is within 25%. The DCE absolute error ranges from 44% to 50%; TCE ranges from 20% to 61%.

Table 4-19 lists the comparisons between MLS and PFM samples for the biostimulation phase. Again, relative error for MLS and PFM measurements is high, with integral flux comparison showing a negative bias for the vinyl chloride and DCE measurements, while the TCE has a positive bias comparing MLS and PFM estimates.

Finally, Table 4-20 shows the results for the bioaugmentation phase (third deployment). Differences are even more dramatic as TCE and DCE show positive bias while VC and ethene results reveal a very high negative bias (more than 100% average for all points).

Table 4-18. Background flood phase comparison of contaminant flux estimates using passive flux meter and multilevel well samples.

Flux#1	Multilevel well flux		Passive flux meter flux		Percent Diff.%*	
Feet above bottom	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	DCE	TCE
8 (no data)						
6.5	0.004224	0.205064	0.001936	0.061412	74	108
5	0.00352	0.095578	0.003872	0.135685	-9.5	-35
3.5	0.00244	0.041415	0.003333	0.087067	-31	-71
1	0.003713	0.228044	0.007094	0.168683	-63	30
Average flux	0.003474	0.142525	0.003954	0.113212		
Std.deviat.	0.000751	0.088791	0.002182	0.048128		
Coeff. Var.	0.216095	0.622987	0.551704	0.425115		
Avg.difference					-7.2	8.0
Avg. Abs.difference					44	61
	Multilevel well flux		Passive flux meter flux		Percent Diff.%	
Flux#2	DCE	TCE	DCE	TCE	DCE	TCE
6.5	0.004904	0.238522	0.006022	0.265653	-20	-11
5						
3.5	0.003975	0.177523	0.008196	0.259151	-69	-37
1	0.003046	0.242127	0.008347	0.420659	-93	-54
Average flux	0.003975	0.219391	0.007522	0.315154		
Std.deviat.	0.000929	0.036303	0.001301	0.091427		
Coeff. Var.	0.233618	0.165472	0.172959	0.290103		
Avg.difference					-61	-34
Avg. Abs.difference					46	26
	Multilevel well flux		Passive flux meter flux		Percent Diff.%	
Flux#3	DCE	TCE	DCE	TCE	DCE	TCE
6.5	0.003273	0.077352	0.004179	0.097465	-24	-23
5	0.014061	0.095205	0.009442	0.169865	49	-40
3.5	0.006516	0.174362	0.01247	0.198411	-113	-7
1	0.003379	0.32435	0.007181	0.346194	-15	-10
Average flux	0.027768	0.175061	0.023762	0.245408		
Std.deviat.	0.005065	0.112549	0.003508	0.104501		
Coeff. Var.	0.18239	0.642914	0.147646	0.425824		
Avg.difference					-29	-23
Avg. Abs.difference					50	20
Integral flux plane average	0.011739	0.178992	0.011746	0.224591	0	-23

* percent difference is calculated (a-b)/((a+b)/2) where MLS flux = a, PFM flux = b.

Table 4-19. Second Installation, Ethanol Biostimulation Phase. Comparison of local mass flux estimates from Passive Flux Meters and Multi-level samplers during the ethanol injection phase. 1/27-1/30/2003

Flux#1	Multilevel well sample calculated flux			Passive flux meter measured flux			Percent difference %*		
Feet above Bottom	VC $mg/cm^2/h$	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	VC $mg/cm^2/h$	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	VC	DCE	TCE
8	0.0063	0.0182	0.0005	0.0151	0.0325	0.0016	-83	-56	-107
6.5	0.0032	0.0272	0.1150	0.0115	0.0344	0.0178	-112	-23	146
5	0.0043	0.0494	0.0112	0.0094	0.0520	0.0316	-74	-5	-95
3.5	0.0042	0.0378	0.1453	0.0090	0.0631	0.0899	-74	-50	47
1	-	-		-	-	-			
Average flux	0.0045	0.0035	0.1425	0.0113	0.0040	0.1132	-86	-1	57
Std.dev.	0.0013	0.0135	0.0730	0.0028	0.0146	0.0384			
Coeff. Var.	0.2835	3.8896	0.5119	0.2469	3.7071	0.3396			
Avg relative difference							-86	-34	-2
Avg. Abs.difference							86	34	99

Flux#2	Multilevel well sample calculated flux VC	DCE	TCE	Passive flux meter measured flux VC	DCE	TCE	Percent difference %* VC	DCE	TCE
8	0.0063	0.0203	0.0030	0.0132	0.0346	0.0012	-70	-52	89
6.5	0.0041	0.0250	0.1323	0.0126	0.0370	0.0127	-102	-39	165
5	0.0040	0.0282	0.0175	0.0094	0.0295	0.0079	-81	-5	76
3.5	0.0034	0.0283	0.0624	0.0083	0.0255	0.0042	-85	10	175
1	-	-		-	-	-			
Average flux	0.0044	0.0255	0.0538	0.0109	0.0317	0.0065	-84	-21	157
Std.dev.	0.0013	0.0038	0.0581	0.0024	0.0052	0.0050			
Coeff. Var.	0.2873	0.1477	1.0796	0.2184	0.1627	0.7640			
Avg relative difference							-84	-21	126
Avg. Abs.difference							84	26	126

Table 4-19. Continued.

Flux#3	Multilevel well sample calculated flux			Passive flux meter measured flux			Percent difference %*		
Feet above bottom	VC $mg/cm^2/h$	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	VC $mg/cm^2/h$	DCE $mg/cm^2/h$	TCE $mg/cm^2/h$	VC	DCE	TCE
8	0.0054	0.0228	0.0000	0.0118	0.0369	0.0037	-75	-47	-200
6.5	0.0045	0.0208	0.0000	0.0076	0.0223	0.0060	-51	-7	-200
5	0.0020	0.0393	0.0147	0.0058	0.0305	0.0143	-97	25	3
3.5	0.0034	0.0344	0.1201	0.0068	0.0451	0.0014	-66	-27	196
1	-	-		-	-				
Average flux	0.0038	0.0293	0.0337	0.0080	0.0337	0.0063	-70	-14	137
Std.dev.	0.0014	0.0089	0.0580	0.0026	0.0097	0.0056			
Coeff. Var.	0.3776	0.3044	1.7222	0.3301	0.2881	0.8893			
Average relative difference							-72	-14	-51
Average absolute difference							72	27	150
Integral flux	0.00423	0.01943	0.07666	0.01006	0.02313	0.042	-82	-17	58

* % diff. (percent difference) = (a-b)/((a+b)/2), Multilevel Well Sample (MLS)=a, Passive Flux Meter (PFM)=b

Table 4-20. Post KB-1 bioaugmentation phase comparison of contaminant flux estimates using PFM and multilevel well samples

Flux#1	Multilevel well sample calculated flux				Passive flux meter measured flux				Percent difference %*			
Feet above bottom	Ethene mg/cm^2/h	VC mg/cm^2/h	DCE mg/cm^2/h	TCE mg/cm^2/h	Ethene mg/cm^2/h	VC mg/cm^2/h	DCE mg/cm^2/h	TCE mg/cm^2/h	Ethene	VC	DCE	TCE
8	0.0010	0.0047	0.0016	0.0000	0.0091	0.0100	0.0005	0.0000	-160	-73	110	
6.5	-	0.0059	0.0180	0.0207	0.0126	0.0150	0.0012	0.0000	-	-87	176	197
5	0.0003	0.0035	0.0135	0.0048	0.0111	0.0166	0.0027	0.0000	-191	131	133	197
3.5	0.0003	0.0034	0.0201	0.0072	0.0083	0.0121	0.0014	0.0000	-188	-113	174	200
1	0.0000	0.0013	0.0265	0.0373	0.0055	0.0055	0.0055	0.0055	-	-123	132	149
Avg.mass flux	0.0004	0.0037	0.0159	0.0140	0.0093	0.0118	0.0022	0.0011				
Std. Dev.	0.0004	0.0017	0.0093	0.0151	0.0027	0.0044	0.0020					
Coeff. Var.	1.1312	0.4569	0.5830	1.0796	0.2941	0.3698	0.8783					
Average relative difference									-180	-105	145	109
Average absolute difference									180	105	145	189

Flux#2	Multilevel well sample calculated flux Ethene	VC	DCE	TCE	Passive flux meter measured flux Ethene	VC	DCE	TCE	Percent difference %* Ethene	VC	DCE	TCE
8	0.0008	0.0037	0.0083	0.0006	0.0108	0.0139	0.0020	0.0000	-173	-116	121	187
6.5	0.0003	0.0032	0.0140	0.0058	0.0092	0.0158	0.0056	0.0003	-188	-133	87	183
5	0.0003	0.0029	0.0144	0.0041	0.0071	0.0274	0.0091	0.0002	-186	-162	45	185
3.5	0.0002	0.0021	0.0099	0.0025	0.0078	0.0514	0.0282	0.0012	-190	-184	-96	72
1	0.0002	0.0024	0.0093	0.0097	0.0082	0.0571	0.0399	0.0012	-188	-184	-125	157
Avg.mass flux	0.0004	0.0029	0.0112	0.0046	0.0086	0.0331	0.0170	0.0006				
Std. Dev.	0.0002	0.0006	0.0028	0.0035	0.0014	0.0200	0.0163	0.0006				
Coeff. Var.	0.6613	0.2138	0.2518	0.7653	0.1662	0.6055	0.9636	1.0257				
Average relative difference									-185	-156	6.5	157
Average absolute difference									185	156	95	157

Table 4-20 Continued

Flux#3	Multilevel well sample calculated flux				Passive flux meter measured flux				Percent difference %*			
Feet above bottom	Ethene mg/cm^2 /h	VC mg/cm^2 /h	DCE mg/cm^2 /h	TCE mg/cm^2 /h	Ethene mg/cm^2 /h	VC mg/cm^2 /h	DCE mg/cm^2 /h	TCE mg/cm^2 /h	Ethene	VC	DCE	TCE
8	-	-	-	-	-	-	-	-	-	-	-	-
6.5	0.0002	0.0055	0.0091	0.0087	0.0137	0.0091	0.0005	0.0005	-194	-150	181	180
5	0.0003	0.0036	0.0153	0.0141	0.0060	0.0153	0.0002	0.0000	-182	-124	195	200
3.5	0.0002	0.0029	0.0164	0.0414	0.0202	0.0164	0.0017	0.0067	-196	-139	163	145
Avg.flux	0.0004	0.0041	0.0104	0.0161	0.0120	0.0104	0.0006	0.0018				
Std. dev.	0.0003	0.0011	0.0071	0.0178	0.0063	0.0071	0.0007	0.0032				
CV	0.7149	0.2689	0.6757	1.1094	0.5275	0.6757	1.2318	1.8096				
Average relative difference									-185	-46	178	141
Average absolute difference									185	110	178	141
Integral Flux .00036		0.0036	0.01252	0.0116	0.0010	0.0185	0.006599	0.001155	-186	-135	62	164

* % diff. (percent difference) = (a-b)/((a+b)/2), Multilevel Well Sample (MLS)=a, Passive Flux Meter (PFM)=b

To illustrate these differences more clearly, plots were made of the interval contaminant estimates The resultant log scale plots for each PFM well interval and MLS level show TCE, DCE, VC and ethene flux ($mg/cm^2/hr$) according to vertical height. Figures 4-40 through 4-48 show the PFM 1, PFM2 and PFM3 measurements as well as the derived flux measurements for the respective multilevel wells at each PFM deployment. The velocities used for calculating MLS contaminant flux at each phase were: deployment #1 0.32 cm/hr, #2 0.23 cm/hr, #3 0.18 cm/hr, and #4 0.05 cm/hr.

The plots comparing PFM with MLS samples associated with the respective PFM well for the first deployment show good agreement between both DCE and TCE fluxes. The fluxes reveal similar distributions with height. The plot of Trip1 PFM#3 shows similar flux distribution for both MLS and PFM measurements; all 3 plots for Trip 1 exhibit decreases in flux as depth decreases. This agrees with the denser than water characteristics of these compounds as well as initial contaminant distributions characterized by Battelle (Battelle Report 1999).

The second deployment plots of Figures 4-43, 4-44 and 4-45 show results during ethanol biostimulation. A substantial increase in DCE flux occurred with a concurrent decrease in TCE flux. The TCE levels are much higher at the lower level by 1 to 2 orders magnitude. The DCE distribution is more uniform suggesting an efflux of DCE from biodegraded TCE. For the first time, vinyl chloride appeared in the water samples and flux meters with distribution throughout the vertical profile. The spatial distribution of the MLS derived flux and PFM measured flux appears to follow similar patterns

The third deployment plots of Figures 4-46, 4-47 and 4-48 show results about 3 months after bioaugmentation. A further increase in DCE flux occurred PFM measured TCE flux. The MLS estimated TCE levels are much higher than the PFM measurements. Vinyl chloride levels are higher in MLS and PFM levels; PFM measures higher than MLS flux estimates. The DCE distribution is further decreased and ethene flux is measured with the PFM; water samples do not show ethene

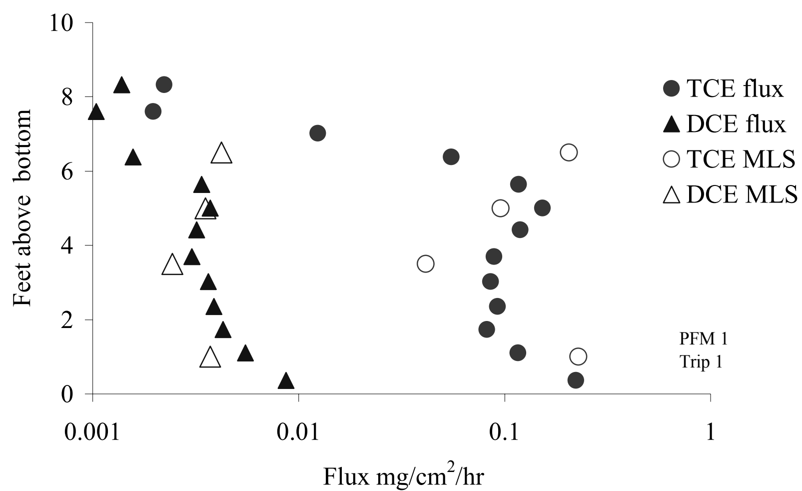


Figure 4-40. Phase 1 PFM#1 TCE, DCE measured PFM Flux, calculate MLS Flux

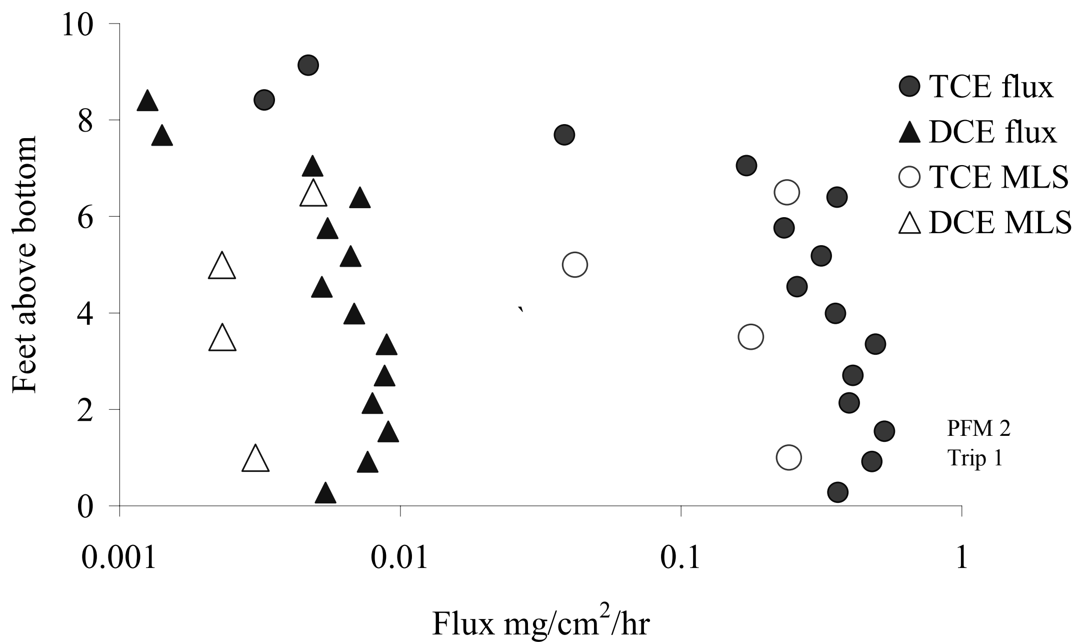


Figure 4-41. Phase 1 PFM#2 TCE, DCE measured PFM Flux, calculate MLS Flux

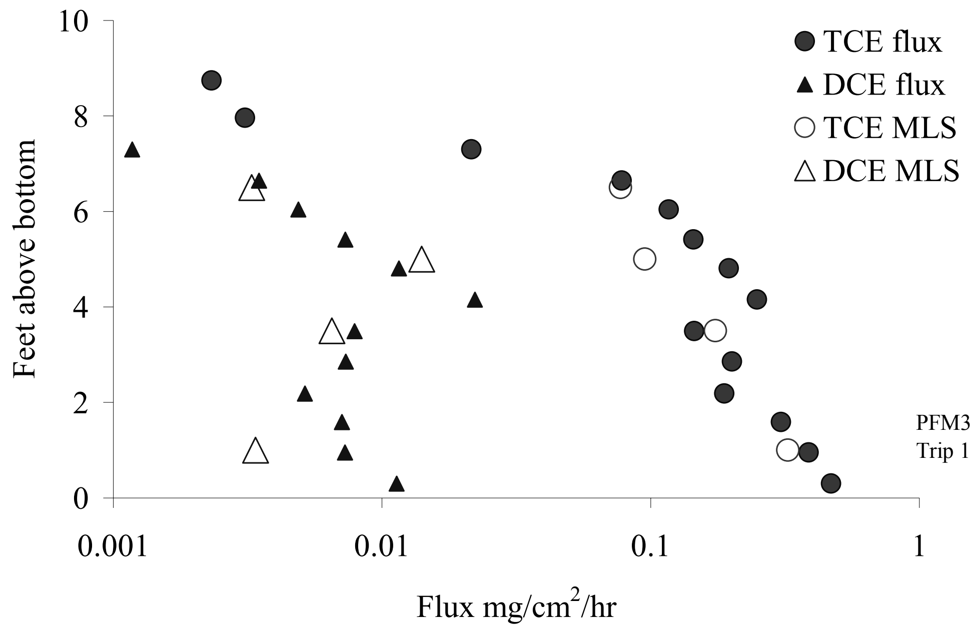


Figure 4-42. Phase 1 PFM#3 TCE, DCE measured PFM Flux, calculate MLS Flux.

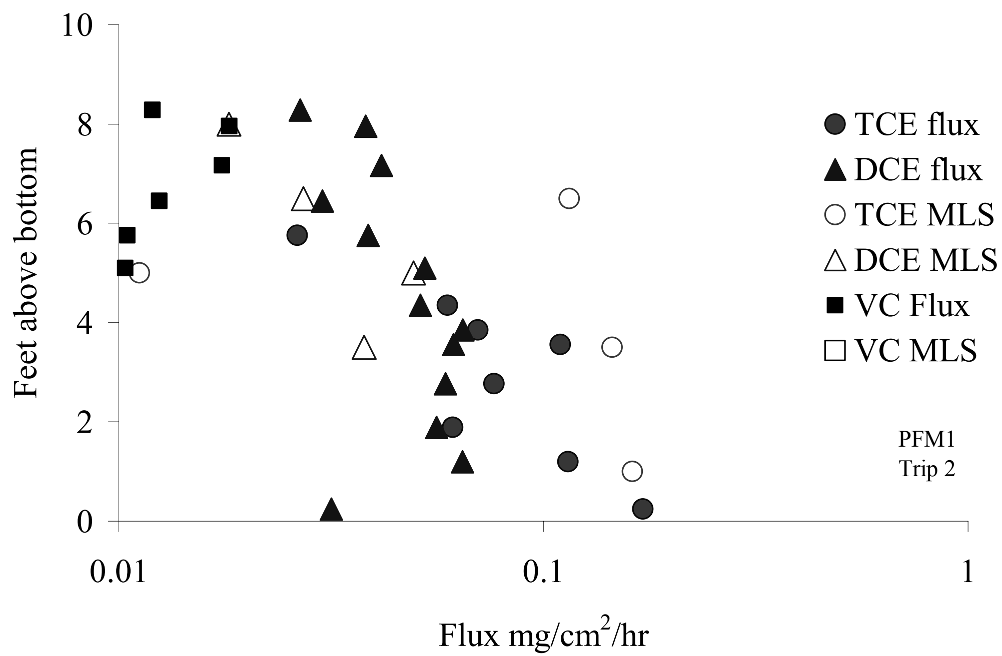


Figure 4-43. Phase 2 PFM#1 TCE, DCE measured PFM Flux, calculate MLS Flux

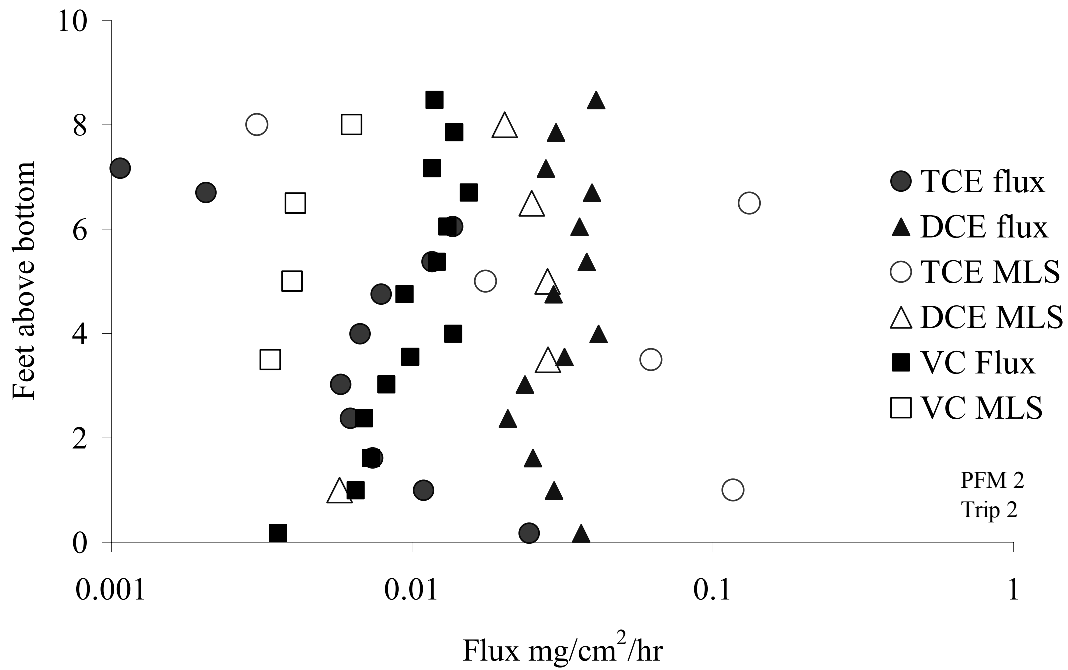


Figure 4-44. Phase 2 PFM#2 TCE, DCE measured PFM Flux, calculate MLS Flux.

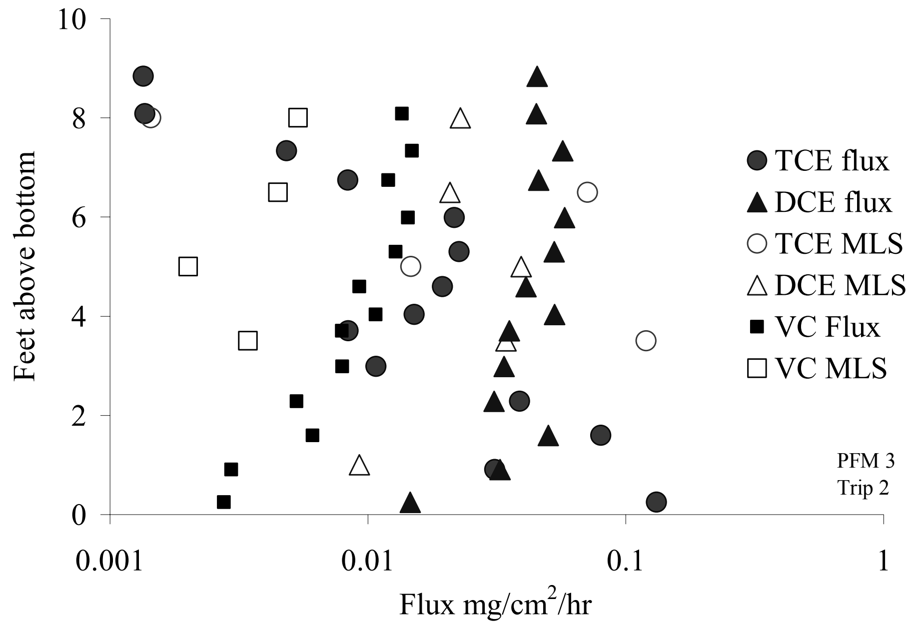


Figure 4-45. Phase 2 PFM#3 TCE, DCE measured PFM Flux, calculate MLS Flux.

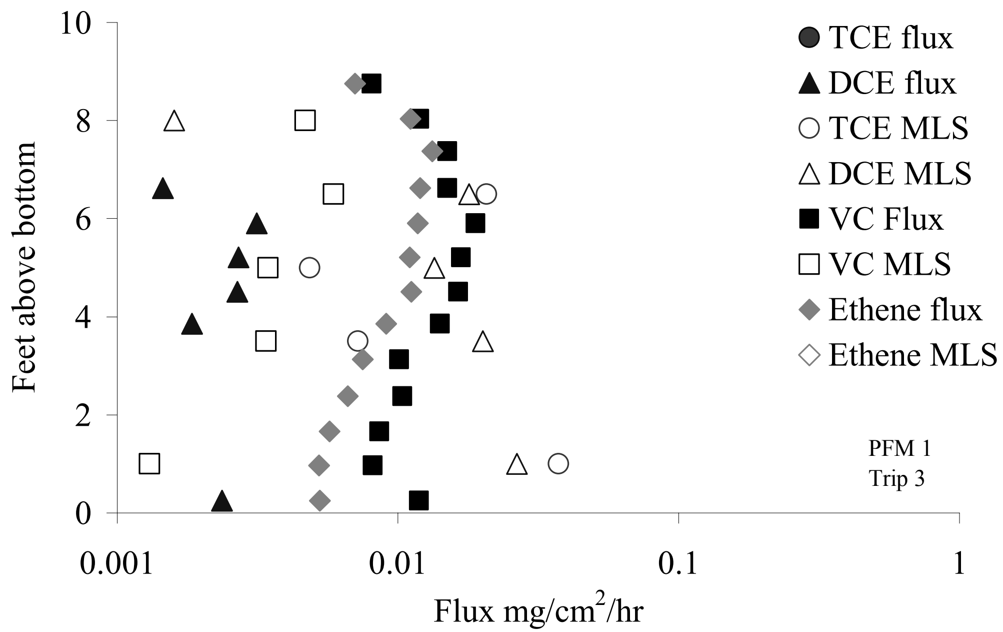


Figure 4-46. Phase 3 PFM#1 TCE, DCE measured PFM Flux, calculate MLS Flux.

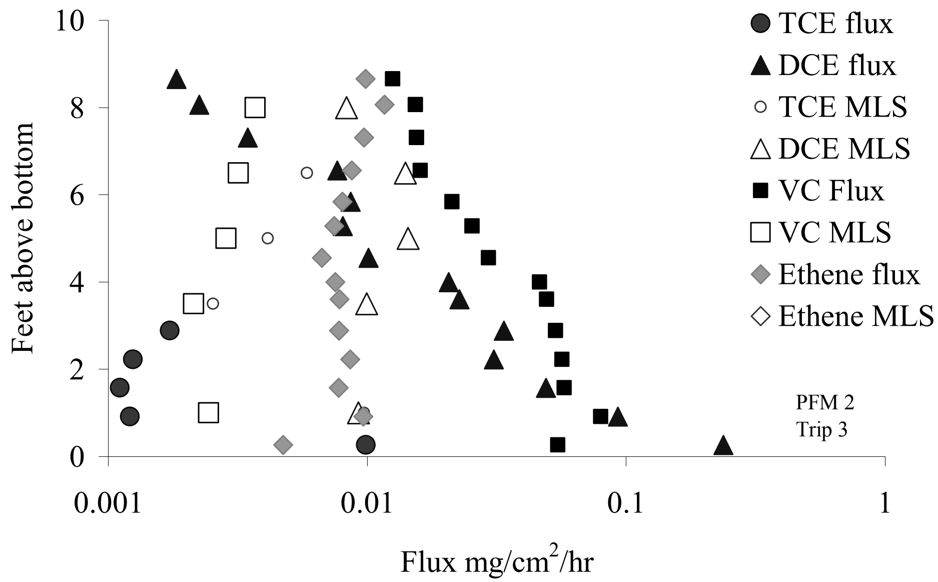


Figure 4-47. Phase 3 PFM#2 TCE, DCE measured PFM Flux, calculate MLS Flux.

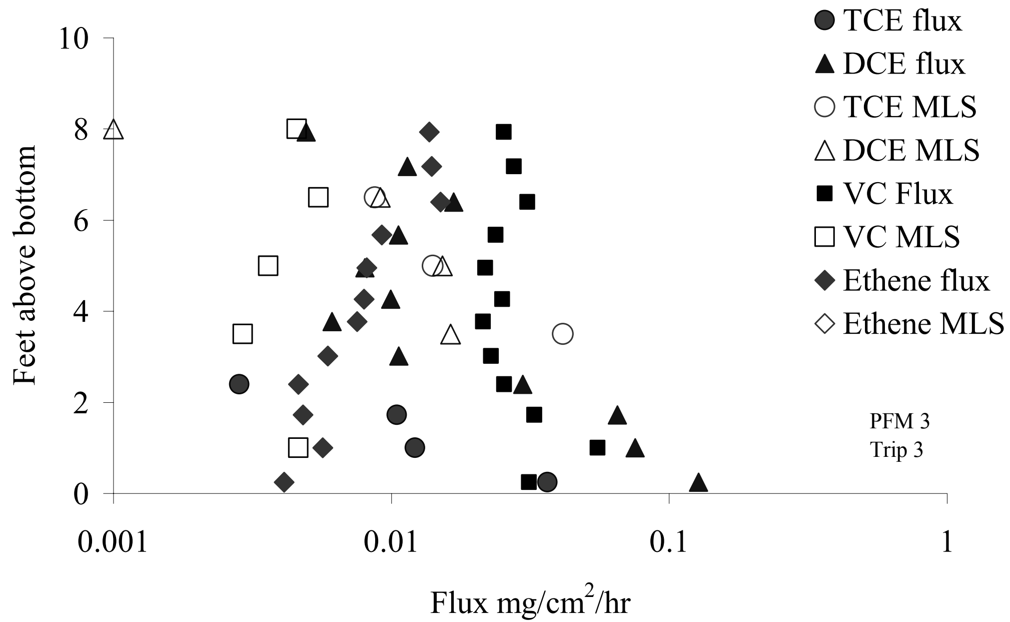


Figure 4-48. Phase 3 PFM#3 TCE, DCE measured PFM Flux, calculate MLS Flux.

The fourth plots of Figure 4-49, 4-50 and 4-51 show results 11 months after KB-1 bioaugmentation. Ethane levels measured by PFM are lower than in the previous deployment; vinyl chloride levels are also lower. Note that pumping had stopped prior to this deployment. In order to estimate flux and show the presence of VC and ethene, a velocity was assumed based on the previous month's pumping log. The natural gradient onsite, based on historical data (Battelle, 1999) ranges from 0.0001to .0007. During full pumping, the gradient was about 0.015. At the fourth deployment, the gradient used was approximately 0.005.

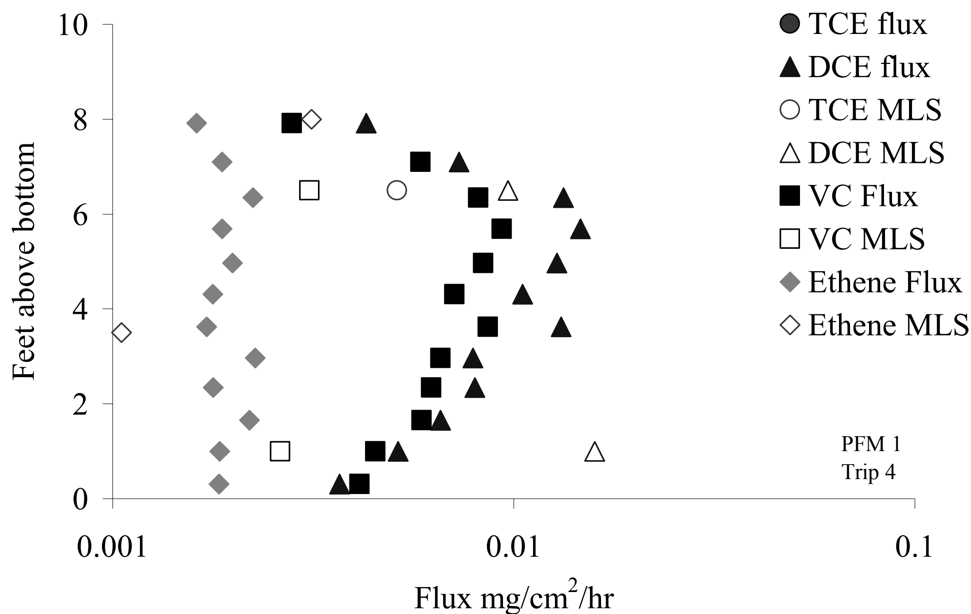


Figure 4-49. Phase 4 PFM#1 TCE, DCE measured PFM Flux, calculated MLS Flux

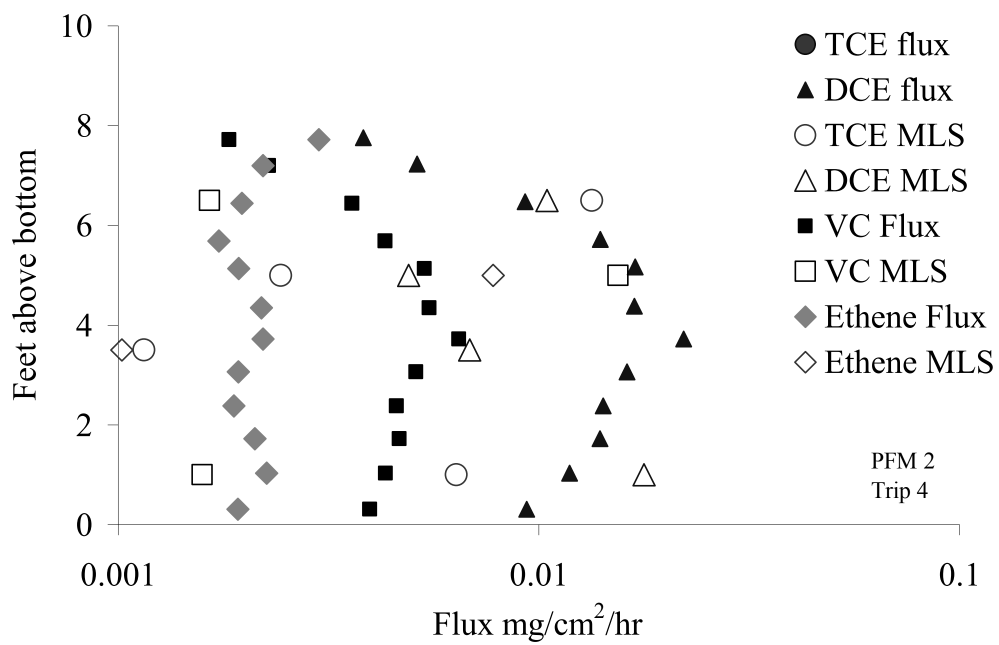


Figure 4-50. Phase 4 PFM#2 TCE, DCE measured PFM Flux, calculated MLS Flux.

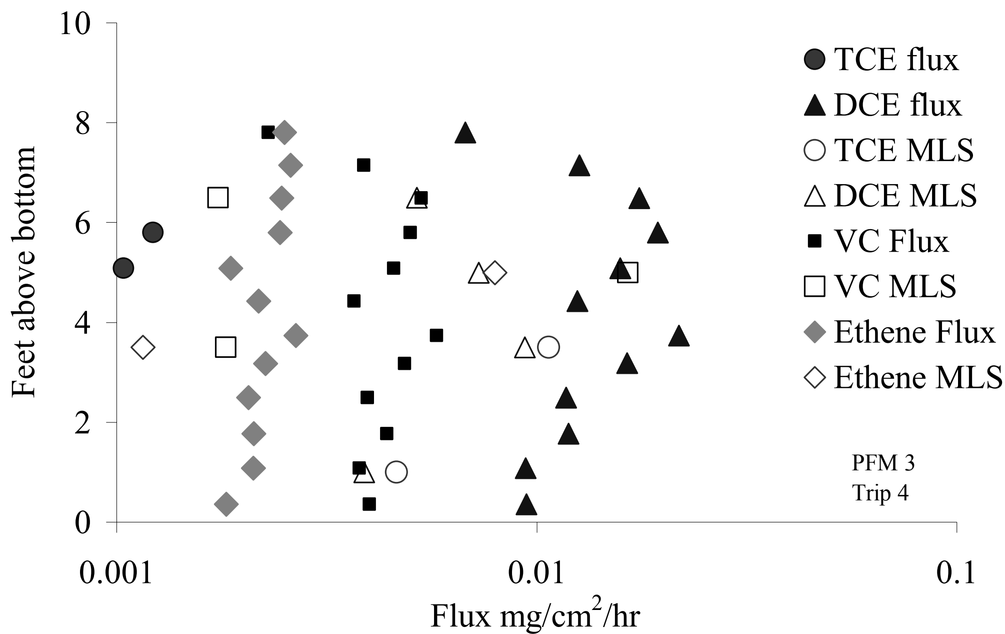


Figure 4-51. Phase 4 PFM#3 TCE, DCE measured PFM Flux, calculate MLS Flux.

<u>Comparison of integral contaminant mass flux estimates from Passive Flux Meters, multilevel samples and the central extraction well.</u>

Using a uniform Darcy velocity across the entire flux plane for all multilevel values, the contaminant mass discharge was calculated using multilevel sample concentrations. Each level was integrated over the vertical interval assuming the sample concentration was an average for that interval. Central extraction well samples were similarly integrated over the flux plane. The flux plane was estimated 10 feet depth and 8 feet width for both MLS and flux meter wells. The integration of PFM segment mass fluxes allowed comparison to mass discharge calculated from multi-level sample (MLS) concentrations. Figure 4-52 characterizes molar discharge rates (mass/hr divided by chemical molecular weight) for the 4 deployments. In order to estimate MLS flux in deployment # 4, an average rate was calculated from the pump log data for the previous month. For further comparison, Table 4-21 shows differences between PFM and central extraction well flux: the central extraction well shown in Figure 4-16 was assumed to represent the flux averaged concentration over the control plane.

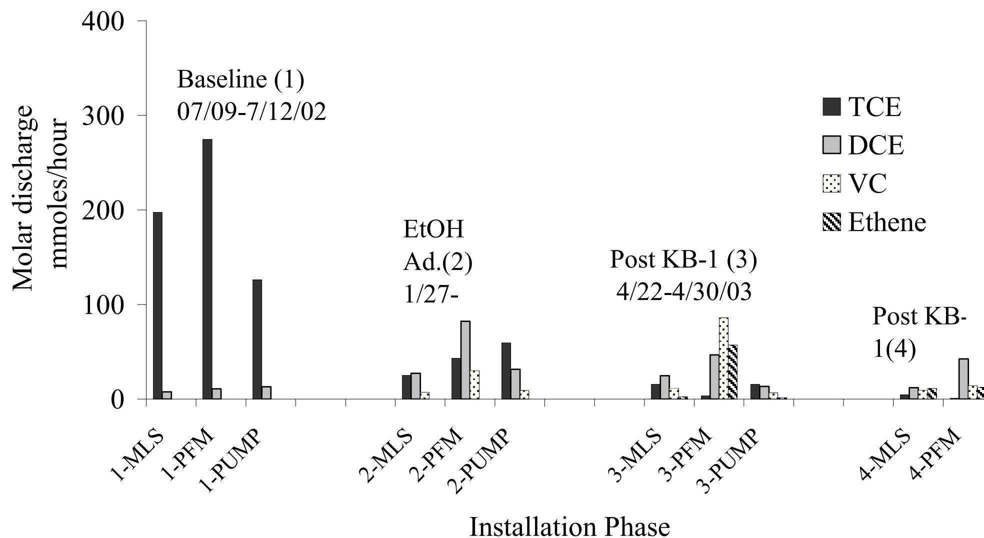


Figure 4-52. Molar discharge across flux plane at each PFM Phase.

Table 4-21. Comparison of central extraction well mass rate to PFM mass rate.

Trip 1	Ethene	%rel.ex.well	VC	%rel.ex.well	DCE	%rel.ex.well	TCE	%rel.ex.well
Central ex.well mass rate mghr			-	-	389.0		4200.0	-
mmoles/hr		-	-	-	4.0	-	31.9	-
PFM mass rate mghr		-	-	-	347.0	-11%	12039.0	97%
mmoles/hr		-	-		3.6	-	91.6	-
Trip 2	**Ethene**	**%rel.ex.well**	**VC**	**%rel.ex.well**	**DCE**	**%rel.ex.well**	**TCE**	**%rel.ex.well**
Central ex.well mass rate mghr			191.0	-	1018.0	-	2605.0	-
mmoles/hr			3.0	-	10.5	-	19.8	-
PFM mass rate mghr			632.0	107%	2658.0	89%	1892.0	-32%
mmoles/hr			-	-	27.4	-	14.4	-
Trip 3	**Ethene**	**%rel.ex.well**	**VC**	**%rel.ex.well**	**DCE**	**%rel.ex.well**	**TCE**	**%rel.ex.well**
Central mg/hr	14.0	-	135.0	-	431.0	-	689.0	-
mmoles/hr	0.5	-	2.2	-	4.4	-	5.2	-
PFMmass rate mghr	540.0	190%	1795.0	172%	1517.0	112%	143.0	-131%
mmoles/hr	19.1	-	28.6	-	15.6	-	1.1	-

*percent difference is calculated (a-b)/((a+b)/2) where a=central ext well, b=PFM

For lower molecular weight compounds, mass flux measured by the passive flux meters was significantly higher than the MLS and extraction well averaged fluxes. This may indicate problems with sampling of these highly volatile compounds and low water solubility in multilevel samples (Screening Information Data Set (SIDS) program operated under the auspices of the Organization for Economic Cooperation and Development (OECD) Chemical screening Reports, Vinyl Chloride, Ethylene, 2002). The activated carbon of the passive flux meters has a large capacity to sorb these compounds and may minimize gas production (Scamehorn, 1979).

However, there was significant variability in the TCE flux results when comparing PFM and water samples. This may be a reflection of another difficulty with water sampling in that the samples reflect instantaneous point concentrations and can be easily compromised by variability in local groundwater flux. Additionally, TCE was found in free phase form in some samples (which were discarded if phase was visible to the eye); contaminant phases present can dramatically alter measured flux values.

Spatial/vertical distribution of Contaminant Flux using Surfer 8.0

The fluxes for each approximate 20 cm segment of the flux meters, according to x, y position in the flux plane (Figure 4-53), were contoured using Surfer version 8.0 graphical software and Kriging geostatistical estimation from the grid of approximately 30 points in the plane (approximately 10 sampling intervals per flux meter). The mapping allowed visualization of the estimated distribution of contaminant flux within the plane. In addition to the PFM contaminant flux levels, multi level samples were taken at each of 5 multilevel sampler (MLS) wells in order to compare contaminant flux estimated from these point samples (5 per well: total 25). An average contaminant flux was derived using the point samples concentrations and assuming a groundwater velocity based on the applied pumping flow rate.

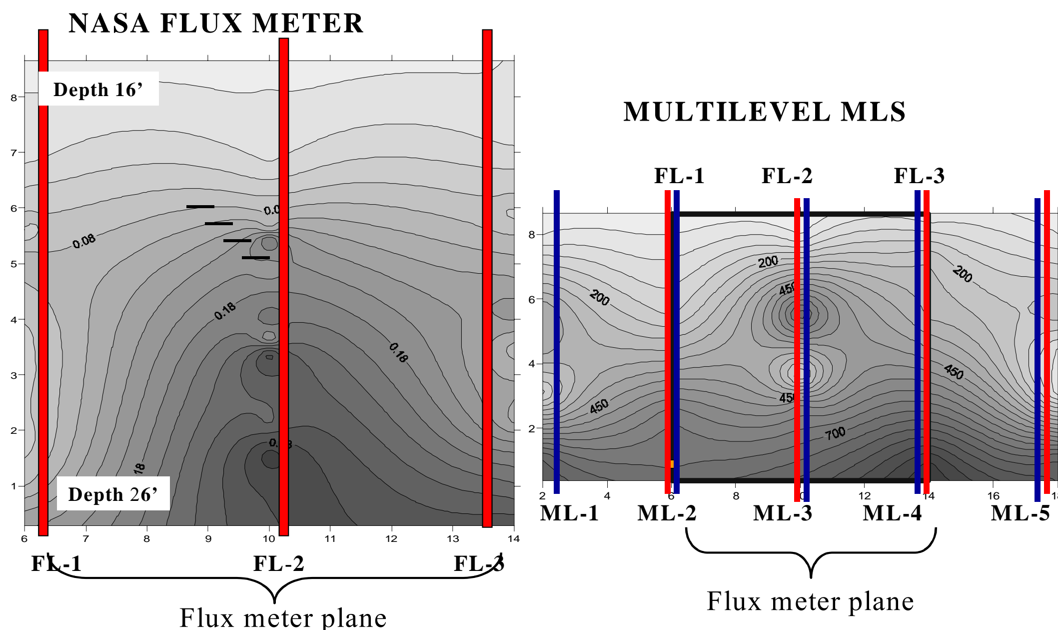
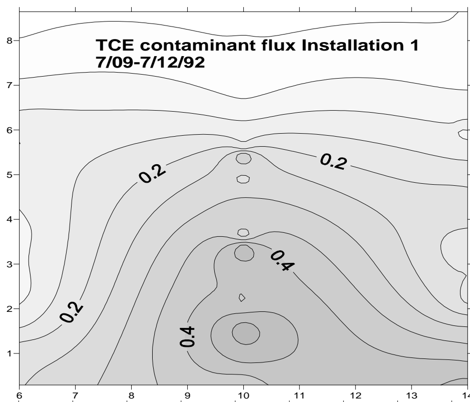
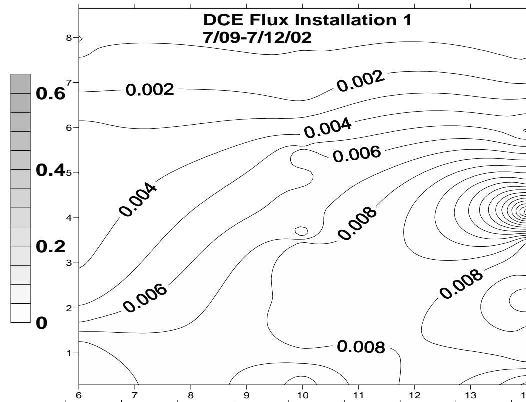


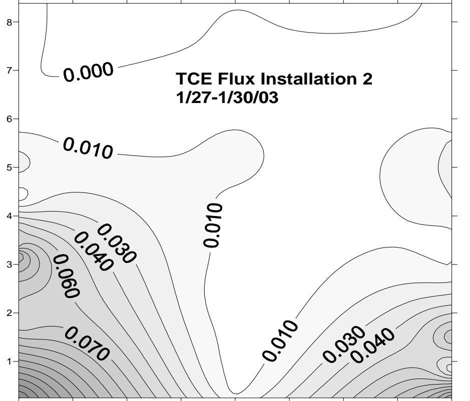
Figure 4-53. Contaminant distribution: the flux planes measured by the passive flux meters and the 5 multi-level sample wells. The flux wells are 4 feet apart, the multilevel wells, also 4 feet.

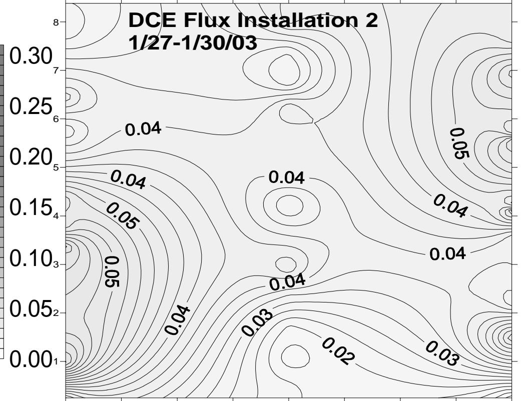
Figure 4-54 shows the compared TCE and DCE contaminant flux in all 4 deployments of the flux meters. The decrease in TCE flux distribution is visualized in each subsequent deployment. The TCE flux appeared concentrated at lower aquifer levels in deployments #1 and #2; in deployments #3 and #4, TCE flux was much lower throughout the flux plane. DCE flux distributes throughout the plane after ethanol treatment (deployment #2); after biogumentation there seemed to be an accelerated degradation of TCE from the lower levels with an increase in

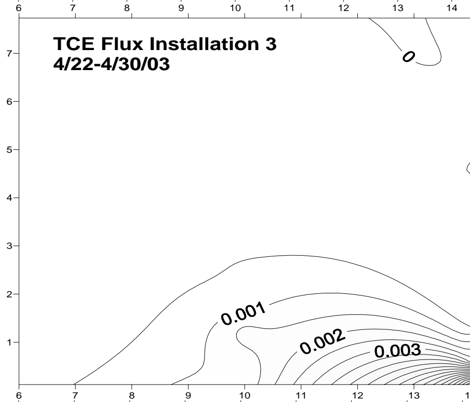
DCE flux emanating from this zone. It is interesting that after pumping had stopped and 11 months after bioaugmentation, the DCE distribution was more uniform throughout the aquifer again. This may be because microbial activity had lessened; evidence of this were the lower VC and ethene levels. Figure 4-55 compares VC and ethene contaminant flux in phases 2-4. Vinyl chloride was detected in installations 2, 3, 4 while ethene appeared only during the final two phases.

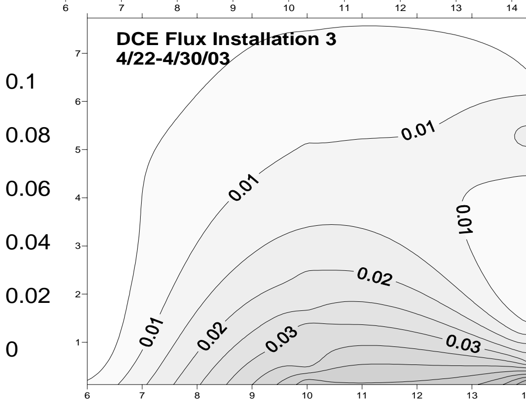

TCE contaminant flux Installation 1
7/09-7/12/92
0.2
0.2
0.4
0.2
0.4
0.6
0.4
0.2
0

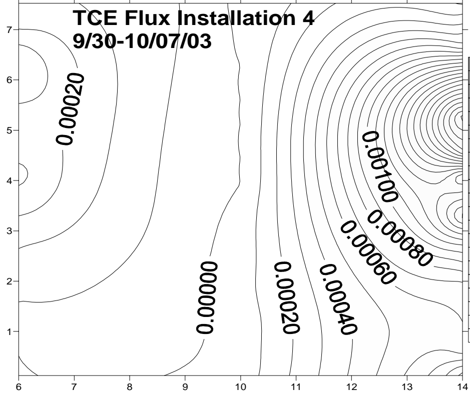

DCE Flux Installation 1
7/09-7/12/02
0.002
0.002
0.004
0.006
0.004
0.008
0.006
0.008
0.008


TCE Flux Installation 2
1/27-1/30/03
0.000
0.010
0.010
0.030
0.040
0.060
0.070
0.010
0.030
0.040
0.30
0.25
0.20
0.15
0.10
0.05
0.00


DCE Flux Installation 2
1/27-1/30/03
0.04
0.05
0.04
0.04
0.05
0.04
0.04
0.05
0.04
0.04
0.03
0.02
0.03


TCE Flux Installation 3
4/22-4/30/03
0
0.001
0.002
0.003
0.1
0.08
0.06
0.04
0.02
0


DCE Flux Installation 3
4/22-4/30/03
0.01
0.01
0.01
0.02
0.01
0.02
0.03
0.03


TCE Flux Installation 4
9/30-10/07/03
0.00020
0.00100
0.00080
0.00060
0.00000
0.00020
0.00040
0.10
0.08
0.06
0.04
0.02
0.00

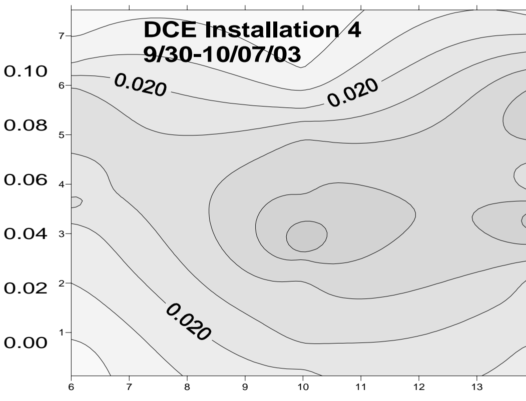

DCE Installation 4
9/30-10/07/03
0.020
0.020
0.020

Figure 4-54. Comparison of TCE, DCE flux Phase 1,2,3,4. Flux mg/cm^2/hr.

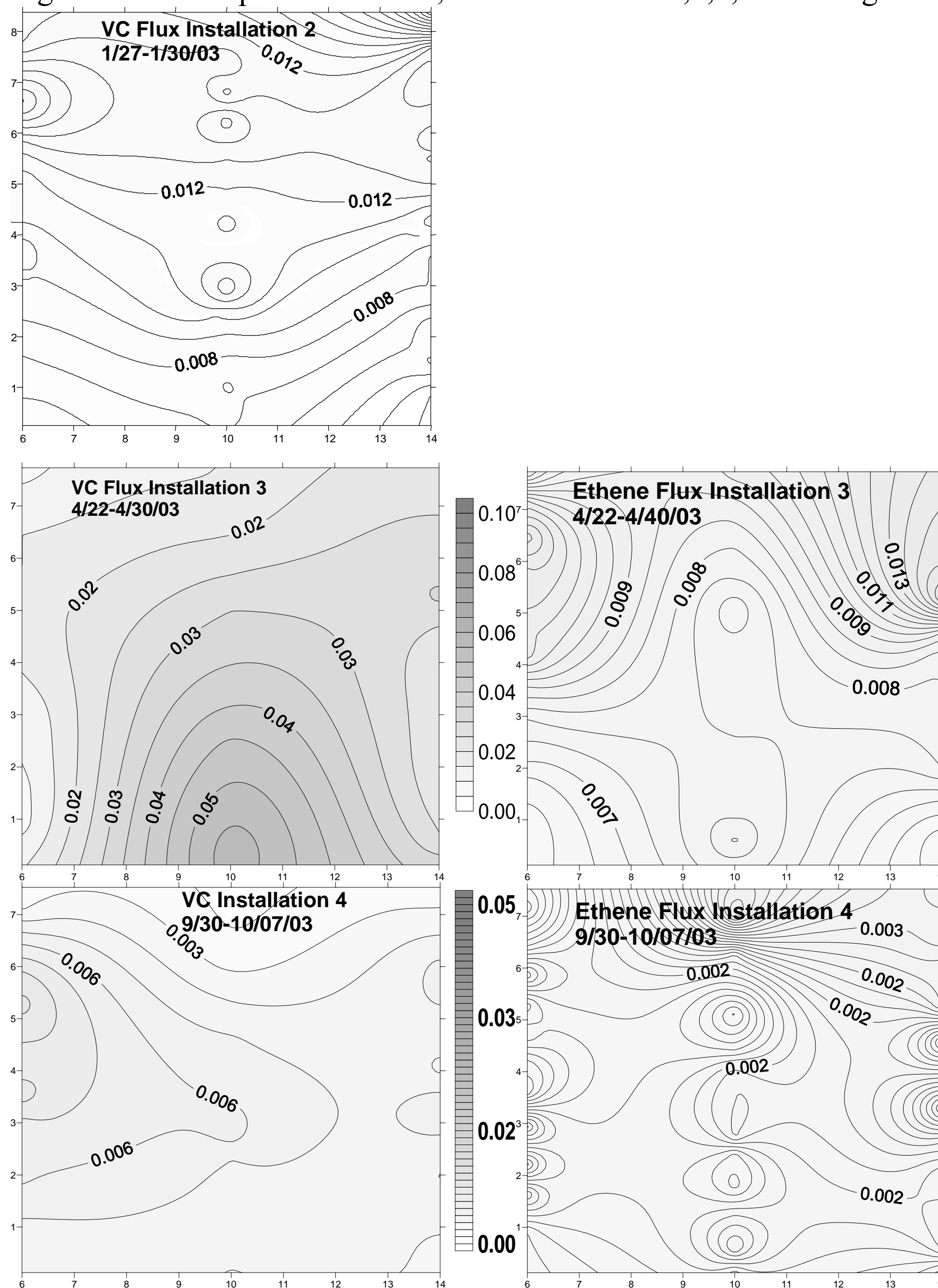


Figure 4-55. Comparison of VC and Ethene contaminant flux for Phase 2,3,4,no vinyl chloride at phase 1, ethene appears at phase 3,4 only. Flux mg/cm^2/hr.

Further discussion of chemical properties of contaminants and results.

The graphical plots of contaminant distribution for all 4 deployments revealed chemical characteristics as well as the distribution throughout the plane. The denser TCE, as expected, was at larger concentrations at the screened well bottom. However, as TCE converted to DCE, the resultant DCE appeared to be distributing vertically in the plane and emanating from the lower areas of TCE. As VC and ethene appeared, they distributed easily and appeared to move higher in the plane; this would be consistent with properties of low solubility, high vapor pressure, and low density. For example, research reports that ethene has a solubility limit of 100-200 mg/l in water (OECD SIDS 2004). Also, ethene has a specific gravity 0.34 relative to water, and exists as a gas at temperatures above -104º C. Ethene is lighter than air; vapor density reported value is 0.975 relative to air at 0ºC. Vinyl chloride vapor density is 2.2 relative to air at 20ºC and the EPA reports its water solubility at 1.1 g/l. Its density relative to water is 0.92. Table 4-22 lists several physical properties for TCE, DCE, VC and ethene that may affect aquifer distribution.

Table 4-22. Physical properties pertinent to contaminant distribution

Chemical	Molecular Weight	Vapor pressure 20’C atm	Density kg/l	Solubility in Water mg/l
trichloroethylene	165.83	8x10-2	1.46	1100
cis-1,2-dichloroethene	96.94	0.26	1.28	3500
Vinyl chloride	62.5	3.4	0.92	90-2800
ethene	28.05	41	0.34	100-200. Note gas above -104º C

Bias in contaminant flux estimates

Since the true values remain unknown in groundwater flux estimation, the indirect methods used with the MLS and PFM measurements are compared. As neither can be described as a more correct method, an alternative approach to assess the degree of agreement is evaluated.

Method comparisons. Comparisons of tests without a measure of truth have several limitations. Since the true value (the quantity being measured) is unknown, comparison of the methods can only establish the degree of equivalence, not superiority of one method over another. Additionally, agreement is not a measure of correctness because both methods could agree on an incorrect value. For quantitative measurement, level of agreement often depends on the magnitude of the measurement. When agreement is heterogeneous over a variable, its statistical analysis should be stratified by that variable. This is of course one of the advantages of the flux meter method in that cumulative flux is measured over a small vertical interval whereas the MLS

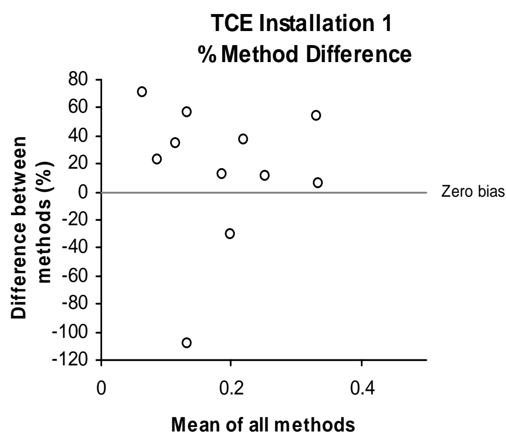
derived flux is based on a single point instantaneous measurement integrated over a larger vertical level.

For quantitative method comparison data without a truth standard, Bland Altman plots are very useful for decomposing the error of agreement into systematic and random error. Random error is assessed by the spread of the scatter, i.e., the variability between the methods. A Bland-Altman scatter plot of the difference between paired measurements from the two methods versus their average is useful for detecting trends in systematic and random errors over the measurement range (Bland, J.M. and D.G. Altman. 2003, 1995. 1986, 1983; Kuznetsov, 2001). In this approach, without the true value, the mean of the two measurements is considered the best estimate available and plotting the difference between the two methods against the mean provides a visual tool for comparison. It is a mistake to plot the difference against either value separately because the difference will be related to each other.

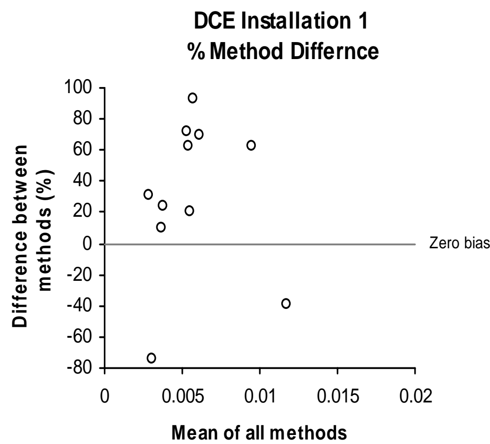
Figures 4-56 and 4- 57 show Bland Altman plots with percent difference compared to the average of the two methods. In these plots, the mean is the average of the PFM and MLS flux measurements plotted on the x axis and the percent method difference is plotted against that average.

The percent method difference is $\% \frac{PFMflux - MLSflux}{(average : PFMflux, MLSflux)}$

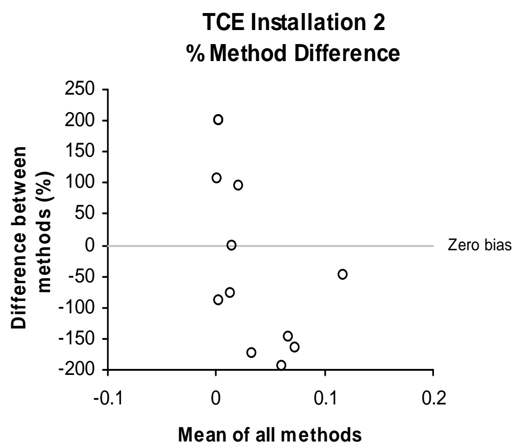
The scatter of the data for TCE and DCE for the first two deployments reveals no significant method bias. However, on the third deployment, the error shows bias in both TCE and DCE measurements; PFM TCE mass flux is significantly lower than that based on water MLS while in the DCE samples, the PFM method biases higher. This may suggest that there is conversion from TCE to DCE, VC and ethene after TCE is sorbed to the activated carbon. For deployments #2, #3 and #4, where both VC and ethene appear, the PFM shows a consistently higher flux measurement as compared to the MLS and reflects that in the bias. However, since this could suggest a conversion of the DCE to VC and ethene after sorption to the activated carbon, more research is needed to evaluate the accuracy of the data. The kinetics of these reactions are critical; however, it appears likely that the positive bias for the PFM lower MW compounds is due to the inherent ability of the carbon to sorb the lower MW weight compounds with resultant limited volatilization as compared to water sampling methods. Also, some ML water samples presented with free phase TCE (samples were discarded), and presented concerns for overall sampling accuracy due to chemical phase kinetics.



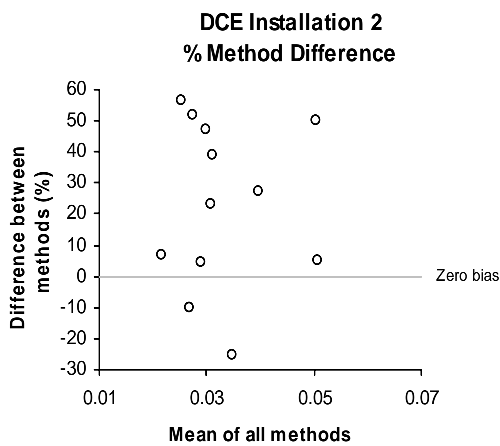
A



B



C



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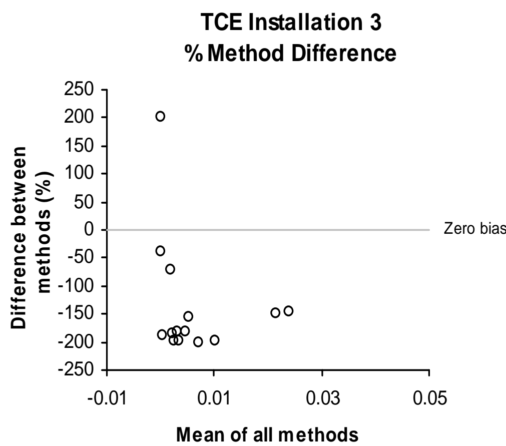
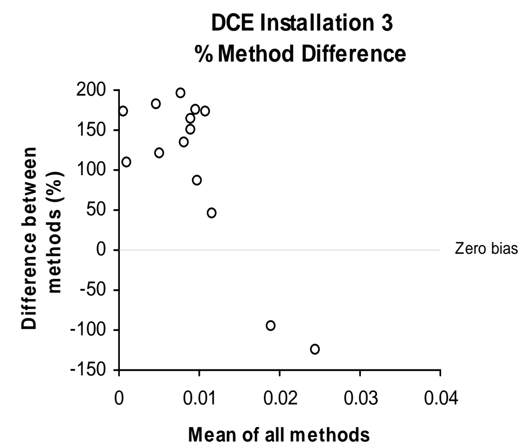
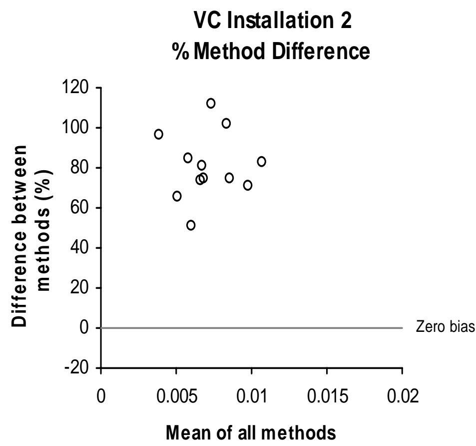


E

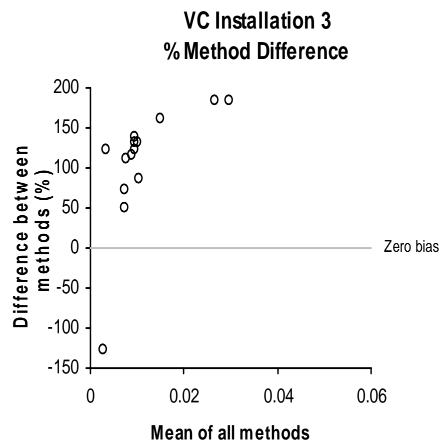


F

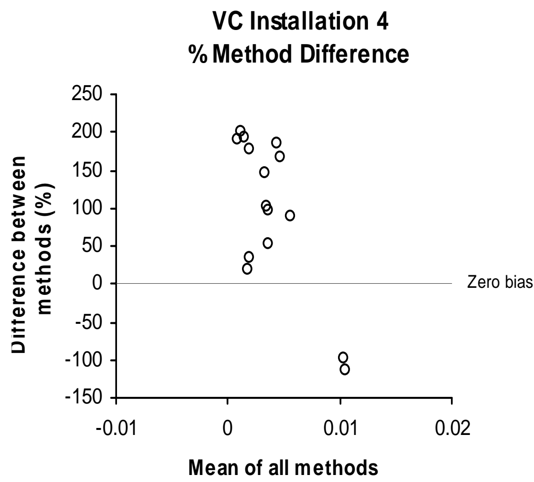
Figure 4-56. Bland Altman TCE, DCE Bias plots using MLS as reference. A) TCE installation 1. B) DCE installation 1. C) TCE installation 2. D) DCE installation 2. E) TCE installation 3. F) DCE installation 3.



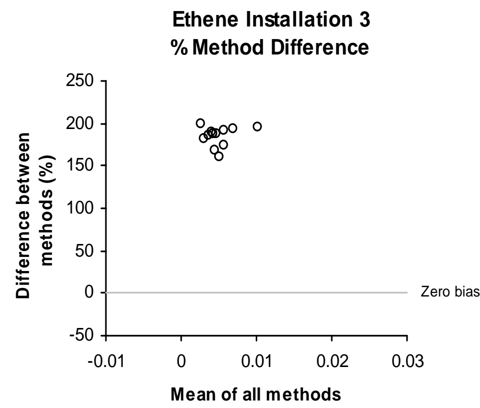
A



B



C



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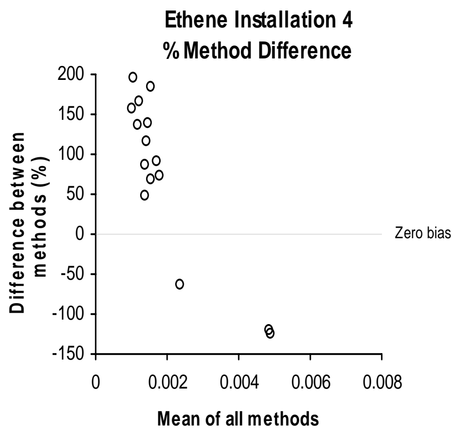

E

Figure 4-57. Bland Altman VC ethene bias plots using MLS as reference A) VC installation 2. B) VC installation 3. C) VC installation 4. D) Ethene installation 3. E) Ethene installation 4.

Conclusions

The vertical variations in the contaminant flux distribution were visualized using the PFM method at NASA LC34. The compared mass discharges at the distinct phases of the project demonstrated predicted dechlorination and mass reduction after biostimulation and then KB-1 augmentation. The graphical plots of flux distribution showed the ability of the PFM to vertically and more clearly characterize contaminant distribution. The integrated PFM measurements provided contaminant mass load at each of the treatment phases of the bioaugmentation.

Comparing water flux estimates (Table 4-17) measured with the PFM (during background flood) to modeled water flux, the estimates were within 20% when using ethanol as the tracer to measure water flux. Estimates using isopropanol as the tracer during biostimulation with ethanol (since ethanol was not included in the tracer suite) were within 30%. After KB-1 bioaugmentation estimates were within 67%. The site bioactivity appeared to compromise the integrity of the tracer alcohols; the tracer mass loss then overestimated water flux. The use of the less degradable alcohols, more highly sorbed alcohols resulted in higher residual mass and less error in the water flux estimates (mass fraction Ω_R equals approximately 0.6 to 0.9).

Comparing contaminant flux estimates during the background flood (Table 4-18), estimates varied between 20 to 61% (average absolute difference). Comparing contaminant flux estimates during the biostimulation phase (Table 4-19), the PFM and MLS derived estimates showed an absolute relative error for each measured contaminant between 26 to 150%. After bioaugmentation (Table 4-20), the average error between the MLS and PFM methods ranged from 95 to 189%.

The PFM measurements for vinyl chloride and ethene were significantly higher than the extraction well and multilevel water measurements and reflected a possible advantage of the activated carbon sorbent to trap these highly volatile and gaseous compounds (Baumann, 1989; Scamehorn, 1979). It is also hypothesized that the TCE and/or DCE sorbed was converted while on the activated carbon (Browne, 1990). Method comparison bias analysis showed these trends in random and systematic error.

5.0. Cost Assessment

5.1 Cost Reporting

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

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

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

By varying the principal cost drivers of tables 5.1 and 5.2 which include 1) mobilization - demobilization, 2) labor and 3) analytical costs, the cost impacts can be determined. A 50% percent increase or decrease in each of these estimated drivers would alter the PFM total costs by ~33%. Similarly, a 50% increase or decrease in each of these estimated drivers for the MLS/BDH costs would alter the total cost by ~20%. Therefore, the unit cost per linear foot for the PFM method could range from $325 to $650; the unit cost per linear foot for the MLS/BDH method could range from $372 to $560.

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

COST CATEGORY	**Sub Category (3 wells - 30 linear feet)**	**Costs ($)**
	FIXED COSTS	
1. CAPITAL COSTS	Operator Training For passive flux meter installation and sampling. Cost of $2500 per person. Amortize over 10 deployments.	$500
	Planning/Preperation (assume 8 hours, $80/hr) Organizing supplies, site access, deployment duration, sorbent/tracers selection and approval	$640
	Equipment: Sorbent preparation mixing equipment and PFM packing equipment ($10,000 capitol) amortize over 10 major deployments	$1,000
	Environmental Safety Training ($1000/yr/person). Amortize over 10 deployments for two people	$200
		Sub-Total $2340
		VARIABLE COSTS
2. OPERATING COSTS	Operator Labor - 2 people are require to construct and install passive flux meters and to collect, prepare, and ship samples. One day for deployment and a second day for retrieval. (8hr/day * 2 people *2 days *$80/hr)	$2560*
	Mobilization/demobilization Assumes 2 trips to and from the site, each requires 0.5 days of travel plus travel costs for two people. $80/hour labor, air fare, travel costs up to ~$800 per person.(4 trips * 4hrs/trip * 2 people * $80/hr +2 *~$800)	$4200*
	Raw Materials Sorbent and resident tracers	$500
	Consumables, Supplies Sorbent, Socks, ancillary components of the Passive flux meter, and sample vials	$550
	Residual Waste Handling Consumed sorbent and socks	$1000
	Sampling and Analysis for contaminants and resident tracers retained on passive flux meter sorbent $100/sample	$3000*
		Sub-Total $11,810
3. OTHER TECHNOLOGY-SPECIFIC COSTS	Data analysis. Six hours required.	$480
		Sub-Total $14,630
TOTAL TECHNOLOGY COST	$14,630	
Unit Cost per linear foot (ft)	$488/ft	

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

5.2. Cost Analysis

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

5.3 Cost Comparison

The cost estimates for the PFM deployments and the MLS/BDH measurements indicate that the PFM method results in a lower unit cost per foot depending on cost variability. The cost of each approach is fairly scalable to larger and smaller deployments. Both approaches do have similar costs in terms of mobilization, materials, and analytical costs. However, contaminant flux values derived from MLS/BDH methods represent short-term evaluations that reflect current conditions and not long-term trends. Therefore, in the absence of continuous monitoring, it may be more cost effective and in the best interests of stakeholders to deploy systems designed to gather cumulative measures of water flow and contaminant mass flow. Cumulative monitoring devices generate the same information derived from integrating continuous data. These systems should produce robust flux estimates that reflect long-term transport conditions and are less sensitive to day-to-day fluctuation in flow and contaminant concentration. Another major advantage over the MLS/BHD method results from the lengthy time required to collect samples from MLS and to conduct borehole dilutions on site. Some cost savings may be realized by automating the borehole dilution method such that one operator can conduct multiple tests simultaneously. Also, the estimation of 2 hours per BDH test may be appropriate for sites with average or high groundwater velocities, but may be too small for lower velocity sites. In this case, BDH tests may be impractical to conduct. Obviously, site specific conditions can lead to changes in the cost estimates. In general, it is likely that for most conditions, costs for the two approaches would be comparable with future PFM method costs perhaps significantly lower depending on method refinements and cost driver variations.

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

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

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

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

6.0. Implementation Issues

6.1. Environmental Checklist

Permission to introduce small quantities of tracers was obtained through NASA from both the Florida DEP and US EPA. The 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 at the NASA site. 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 have 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.

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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 application (i.e. performance) of the technology.

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

SCOPE AND APPLICATION

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

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

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

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

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

PURPOSE

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

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

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

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

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

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

2. Sub-sampling and Dilution

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

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

3. Apparatus and Materials

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

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

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

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

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

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

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

4. Reagents

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

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

5. Standard Solutions

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

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

6. QC blank Spike/Matrix Spike

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

7. Quality Control

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

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

A method blank will be included in every 50 samples

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

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

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

8. Instrumental Procedures

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

Injection port temperature 200C
FID detector temperature 225C

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

9. Sample Preparation

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

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

10. Sample Analysis

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

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

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

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

11. Interferences

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

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

12. Safety

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

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

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

The main operating drawback to locating the gas cylinders externally is that it is not easy to monitor the cylinder contents from inside. The gas which could be used up most quickly is air

for the FID, particularly if two instruments are hooked up to the same supply and they are running continuously. A reserve cylinder of air should be available at all times to prevent down time.

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

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

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

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

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

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

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

SCOPE AND APPLICATION

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

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

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

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

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

PURPOSE

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

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

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

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

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

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

2. Sub-sampling and Dilution

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

3. Apparatus and Materials

Glassware: Glass pipets are required for sub-sampling.

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

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

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

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

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

4. Reagents

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

5. Standard Solutions

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

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

6. QC blank Spike/Matrix Spike

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

7. Quality Control

A method blank will be included in every 50 samples

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

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

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

8. Instrumental Procedures

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

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

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

9. Sample Preparation

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

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

10. Sample Analysis

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

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

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

11. Interferences

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

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

12. Safety

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

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

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

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

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

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

SCOPE AND APPLICATION

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

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

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

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

Potential Sorbents include:

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

Solid

Activated Carbon
Surfactant modified zeolytes

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

PURPOSE

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

PROCEDURES

1. Sample Containers, Collection, Transportation and Storage

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

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

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

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

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

3. Sub-sampling and Dilution

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

3. Apparatus and Materials

Glassware: Glass pipets are required for sub-sampling.

Safety

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

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

Appendix C: Quality Assurance Project Plan (QAPP)

C.1 Purpose and Scope of the Plan

This Quality Assurance plan is written to cover activities associated with testing the Flux Meter at the NASA LC-34 site. The plan focuses on field installation, sampling and processing of data from the Flux Meters.

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:

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

where:

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

The mean percent recovery (X) is defined by:

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

where:

X_i = The percent recovery value of a spike replicate

N = Number of spikes

Precision

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

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

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

X1 = First duplicate value

X2 = Second duplicate value

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

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

where:

X_i = The recovery value of a spike replicate

X = Arithmetic average of the replicate values

N = Number of spikes

Completeness

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

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

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

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

Supplies and Quality Control Materials

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

Reagents

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

Quality Control Reference Materials

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

Standards Traceability

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

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

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

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

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

Instrument Calibration

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

GC Section

Initial Calibration

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

The calibration is performed in accordance with the SOP derived from the methods used. For most GC analyses, a 5-level calibration is run. The concentrations of the standards must bracket

the linear range of the instrument. Calibration using fewer than 5-levels is done only when specifically allowed by the method.

Relative Retention Times and Relative Response Factors

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

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

The RRF may be calculated as follows:

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

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
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

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 C.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 flux meter 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 flux meters 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 LC-34 site will be sent to the University of Florida for analysis. In the laboratory, instrument maintenance will include the following.

Maintenance Schedule

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

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

Instrument maintenance logbooks are maintained in the laboratory at all times. The logbook contains a complete history of past maintenance, both routine and 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. 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 Rinsate--**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 meanṇ 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.

C.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:

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

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

C.10 Data Storage and Archiving Procedures

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

Appendix D: Health and Safety Plan

Field Evaluation of the Florida Flux Meter at NASA LC-34 site, Cape Canaveral Florida

Health and Safety Plan

May 30, 2006

University of Florida, Gainesville, FL

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INTRODUCTION

This Health and Safety Plan (HASP) has been developed for conducting field tests of the Florida Flux Meter at the NASA LC-34 Cape Canaveral Florida. 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

LC-34 is a former Apollo launch facility that is contaminated with TCE for past component cleaning activities. The site has an extensive DNAPL source zone that is the focus of this study. The bioremediation cell is located inside of an engineering support building at the LC-34 site.

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
- Flux meter installation, extraction and sampling

1.3. Site Hazard Evaluation

1.3.1. DNAPL Source Zone. The DNAPL source zone extend under the engineering support build present at the site. The DANPL is TCE and present from about 10 to 40 feet below ground surface.
1.3.2. Groundwater. The shallow ground water downgradient within and down gradient of the DNAPL source zone is contaminated with high levels of TCE and some degradation by-products. TCE concentrations range up the solubility limit of about 1500 mg/L.

1.3.3. Exposure Potential. The chemical contaminants present at LC-34 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 flux meter sorbents. Skin absorption is possible if skin is in direct contact with contaminated soil, water, or DNAPL, particularly when collecting ground-water samples.
1.3.4. The potential toxic exposure hazard to site personnel associated with chemical contaminants possibly present at the site can be expressed in Permissible Exposure Limit (PEL) values established by the Occupational Safety and Health Administration (OSHA), the Threshold Limit Values-Time Weighted Averages (TLV-TWA) as established by the American Conference of Governmental Industrial Hygienists (ACGIH) and by Immediately Dangerous to Life or Health (IDLH) values established by the National Institute for Occupational Safety and Health (NIOSH).

TLV-TWA: The time-weighted average airborne concentration of a substance, for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. Certain substances will have a skin notation in the exposure route column. This indicates that the overall exposure to that substance is enhanced by skin, mucous membrane, or eye contact.

PEL: PELs are similar in concept to TLV-TWAs, except that PELs are promulgated by OSHA and are legally enforceable. The numerical values for the PEL and TLV-TWA for a given compound may be different. In the absence of a PEL for a given substance, OSHA will enforce the lowest published "safe" exposure level.

IDLH (NIOSH): The maximum airborne concentration of a substance which one could escape within 30 minutes without escape-impairing symptoms or any irreversible health effects.

1.3.5. Table 1 identifies the PEL, TLV-TWA and IDLH values for the contaminants of concern while conducting the field work associated with the Flux Meter assessment. Ionization potentials (IP) are listed to determine which compounds can be detected by a photoionization detector with a 10.2 electron volt (eV) probe. Additionally, routes of exposure, symptoms of acute exposure and carcinogenicity are summarized.

1.3.6. All site activities will comply with the exposure standards mandated by OSHA; personnel will adhere to TLV-TWA recommendations when these are more protective of employee health.

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

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

TABLE 1
SITE CHEMICAL HAZARD SUMMARY

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

1.4. Activity Hazard Analysis

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

1.4.2. Ground-Water Sampling. The major potential hazard associated with this activity is exposure to contaminants (principally VOCs) present in the ground water through inhalation or skin contact. Waterproof, chemical resistant gloves shall be worn by site personnel when collecting ground-water samples.

1.4.3 Flux Meter Tests. Hazard associated with this activity is exposure to contaminants (CM,TCE, PCE) present in the sorbent material used in the flux meters through inhalation or skin contact. Waterproof, chemical resistant gloves shall be worn by site personnel when sub-sampling the flux meters 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 NASA. Should a health and safety issue develop in the performance of the contract requiring consultation, the PM will immediately contact the NASA 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.

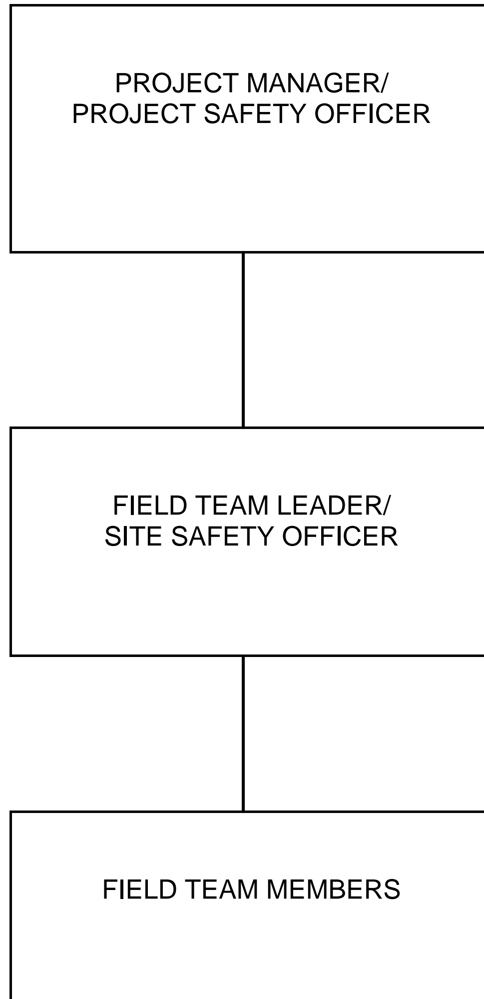


FIGURE 1. SITE SAFETY RESPONSIBILITY CHART

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 Cosolvent Enhanced Remediation field activities at Hill AFB Operable Unit 1 site in Layton, Utah, you are required to read and understand the HASP. When you have fulfilled this requirement, please sign and date this personal acknowledgment.

Signature Date Name (Printed)

______________________________ ____________ ______________________________

FIGURE 2. PERSONAL ACKNOWLEDGMENT

Date: ____________ Time:
Client: University of Waterloo
Site Location: CFB LC-34, Ontario, Canada
Scope of Work:

SAFETY TOPICS PRESENTED

Protective Clothing/Equipment:
Chemical Hazards:
Physical Hazards:
Special Equipment:
Other:
Emergency Procedures:
Hospital: ________________ Phone: _______________ Ambulance Phone:
Hospital Address and Route:

ATTENDEES

NAME PRINTEDSIGNATURE

Meeting Conducted By:

Project Manager/Project Safety Officer:

______________________________	______________________________
______________________________	______________________________
______________________________	______________________________
______________________________	______________________________
______________________________	______________________________

FIGURE 3. SITE SAFETY MEETING FORM

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

4.0 PERSONAL PROTECTIVE EQUIPMENT

4.0.1. Personal protective equipment (PPE) will be required during the course of the field work at LC-34. PPE selection will be based primarily on hazard assessment data and work task requirements.
4.0.2. Based on the known contaminant release, the level of protection for all field activities is Level D. The personal protective equipment associated with Level D is described below.

4.1. Level D Personal Protective Equipment

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

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

5.0 HAZARD ASSESSMENT

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

5.1. Site Area Survey

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

5.2. Cold Stress Monitoring

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

- Educate workers to recognize the symptoms of frostbite and hypothermia.

- Ensure that workers wear clothing that will keep them warm and dry.
- Take breaks in a heated area as necessary to allow workers to warm up. Hot liquids should be available in this area.

6.0 SITE CONTROL

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

6.1. Regulated Area(s)

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

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

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

6.2. Work Zones

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

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

6.2.2. Zone 1: Exclusion Zone (work zone). The exclusion zone, the innermost of the three designated areas, will be the area where activities require personnel protective equipment (PPE). All personnel entering the exclusion zone must wear the prescribed PPE. An entry and exit check point must be established at the periphery of the exclusion zone to regulate the flow of personnel and equipment into and out of the zone. The outer boundary of the exclusion zone, the "hotline", will be established by visually surveying the site and determining the area where significant amounts of organic vapors and/or a potential for explosive vapor conditions might exist. Physical hazards associated with the work task will be identified in the exclusion zones. Once the "hotline" has been determined, it will be defined by the use of stakes, cones, or surveyor tape. During subsequent site operations, the boundary may be modified and adjusted by the FTL/SSO as more information becomes available. Potential exclusion zones at the LC-34 site have been identified as the ground water sampling sites.

6.2.3. Personnel will be decontaminated as they move through the contamination reduction corridor. Detailed decontamination procedures are provided in Section 7.
6.2.4. Zone 3: Support Zone. The support zone, the outermost part of the site, will be considered a noncontaminated or clean area. Support equipment (command post/trailer, safety vehicle, etc.) is located in this area.
6.2.6. The location of the command post and other support facilities in the support zone at each site depends on a number of factors, including:

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

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

7.0 DECONTAMINATION PROCEDURES

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

7.1. Decontamination of Personnel

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

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

7.1.2. Personnel shall be instructed in the proper decontamination technique, which entails removal of protective clothing in an "inside-out" manner. Removal of contaminants from clothing or equipment by blowing, shaking or any other means that may disperse material into the air is prohibited.
7.1.3. All disposable personal protective clothing that has been removed will be containerized at the decontamination station pending disposal. At the conclusion of work in a site exclusion zone, all protective equipment must be placed in plastic bags prior to disposal or transfer off-site. Non-disposable equipment will be decontaminated and properly stored outside the exclusion zone when not in use.
7.1.4. All employees will wash their hands and face with soap and water or disinfectant moist towelettes before eating, drinking, smoking, or applying cosmetics. These activities will be restricted to the designated rest area(s) in the support zone. This restriction also applies to work activities that do not require an exclusion zone, such as ground-water sampling.

7.2. Equipment Decontamination and Disposal of Contaminated Materials

7.2.1. Equipment that may require decontamination includes water sampling devices and certain protective equipment.
7.2.2. All materials and equipment used for decontamination must be disposed of properly. Disposable clothing, tools, buckets, brushes, and all other equipment that is contaminated will be secured in appropriate Department of Transportation (DOT) specification 55-gallon drums or other containers and marked. Clothing that will be reused, but which is not completely decontaminated on site, will be secured in plastic bags before being removed from the site. Contaminated wash water solutions shall be transferred to the effluent storage tank, pending transfer to a specified location for subsequent treatment.

8.0 GENERAL SITE SAFETY REQUIREMENTS

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

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

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

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

9.0 EMERGENCY PROCEDURES

9.1. Accident Prevention and Hazard Analysis

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

TABLE 2. SAFETY AND EMERGENCY EQUIPMENT

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

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

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

9.2. Emergency Medical Assistance and First Aid Equipment

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

9.3. Emergency Protocol

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

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

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

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

Thumbs down: No, negative

9.4. Decontamination During Medical Emergencies

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

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

9.4.4. For inhalation exposure cases, treatment can only be performed by a qualified physician. If the contaminant is on the skin or the eyes, immediate measures can be taken on site to counteract the substance's effect. First aid treatment consists of flooding the affected area with copious amounts of water. The FTL/SSO must assure that an adequate supply of running water or a potable emergency eyewash is available on site.
9.4.5. When protective clothing is grossly contaminated, contaminants can possibly be transferred to treatment personnel and cause an exposure. Unless severe medical problems have occurred simultaneously with personnel contamination, the protective clothing should be carefully removed.

TABLE 3. EMERGENCY ASSISTANCE INFORMATION

Kirk Hatfield/Mike Annable (Project Manager/ Project Safety Officer)	Phone numbers to be established when site work begins
LC-34 Emergency Service	
Police/Sheriff	911
Fire	911
Ambulance	911

Hospital Facilities (Off-Base)

On-base...dial 911
From cell phones dial 321.867.7911

Recommended Route: (See map, Figure 4)

10.0 CHEMICAL HAZARDS AND CONTROLS

10.1. Tracers. Small quantities of alcohol and inorganic tracers will be used in the Flux meters. 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.

HOSPITAL: NEXT FIGURE

Emergency numbers

On-base...dial 911
From cell phones dial 321.867.7911

LC34

wind direction

Test Rd

Samuel C Phillips Pkwy Freedom Rd

Icbm Rd

Titan Iii Rd

Heavy Launch Rd

Industry Rd

Industrial By Pass Rd

Azusa Rd

Seb Rd

W Skid Strip Rd

Central Control Rd

Mercury Gemini Rd

Hangar Rd

E Skid Strip Rd

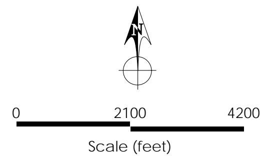
Armory Rd

Timing Rd

Lighthouse Rd

Flight Control Rd

Source: 2001 MapQuest.com, Inc.; 2001 Navigation Technologies



Route to Nearest Medical Clinic

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