PROTOCOL REPORT

Demonstration and Validation of a Water and Solute Flux Measuring Device

ESTCP Project ER-0114

DECEMBER 2006

Dr. Kirk Hatfield
Dr. Michael D. Annable
University of Florida

Dr. P. Suresh C. Rao
Purdue University

Environmental Security Technology Certification Program

PROTOCOL REPORT
ESTCP Project: ER-0114

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (continued)

Page

TABLE OF CONTENTS (continued)

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

ACRONYMS AND ABBREVIATIONS

μg/mL	microgram/milliliter
μL	microliter
μm	micrometer
%R	percent recoveries
AC	activated carbon
ACS	American Chemical Society
AR	analytical reagent
CAR	corrective action report
CFR	code of federal regulations
CLP	Contract Laboratory Program (EPA)
COD	chemical oxygen demand
CPVC	chlorinated polyvinyl chloride
CV	coefficient of variation
DCE	dichloroethane
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
ECD	electron capture detector
ED	electrochemical detector
FID	flame-ionization detector
GAC	granular activated carbon
GC	gas chromatography/gas chromatograph
GC/MS	gas chromatography-mass spectrometry
HPLC	high pressure liquid chromatography
IBA	isobutyl alcohol
IC	ion chromatography/ion chromatograph
ID	inner diameter
IDL	instrument detection limit
IPA	isopropyl alcohol
IR	infrared
KCI	kaolinite crystallinity indices
L	liter
LC	liquid chromatography
LCS	Laboratory Computer System (EPA)

MDL	method detection limit
mg/L	milligrams per liter
mL	milliliter
mM	unit of concentration
MS	matrix spike
MSD	matrix spike duplicate
MSDS	Materials Safety Data Sheets
NAPL	non-aqueous phase liquid
NBS	National Bureau of Standards
NITS	National Institute of Standards and Testing
OD	outer diameter
PCE	perchloroethylene
PFM	Passive Flux Meter
pH	hydrogenion concentration
PQL	practical quantitation limit
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
RPD	relative percent difference
RRF	relative response factors
RRT	relative retention times
SD	standard deviation
SOP	standard operating procedure
SRM	Standard Reference Materials
SS	stainless steel
TBA	tert-butyl alcohol
TCE	trichloroethylene
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
VC	vinyl chloride
VOA	volatile organic analysis
VOC	volatile organic compound
VWR	Van Waters and Rogers

This page left blank intentionally.

1.0 PASSIVE FLUX METER CONSTRUCTION, STORAGE, AND TRANSPORT

1.1 DESCRIPTION OF PASSIVE FLUX METER

The passive flux meter (PFM) is a self-contained permeable unit that is inserted into a well to measure cumulative water and contaminant fluxes (See Figure 1). The device operates by allowing groundwater to flow passively through it.

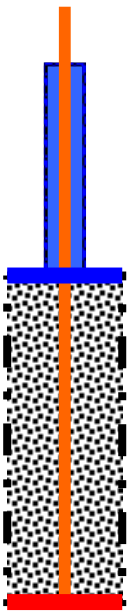

Figure 1. Schematic of a Flux Meter Composed of a Permeable Sock Filled with a Selected Sorbent.

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 contaminant masses are used to calculate cumulative and time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative or time-averaged 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 can range over orders of magnitude. This data is used to estimate local cumulative water and contaminant fluxes.

1.2 PREPARATION OF SORBENT (ACTIVATED CARBON) AND TRACERS

Table 1 lists equipment needed to prepare the PFM sorbent, and Table 2 lists all the parts required. A tracer mixture is prepared by combining appropriate ratios of all tracers used for the test. Tracer volumes are measured in graduated cylinders and transferred to a volumetric flask for mixing. The flask is manually mixed. The sample mixture includes 100 milliliters (mL) of methanol, 100 mL of ethanol, 200 mL of isopropyl alcohol (IPA), 200 mL of tert-butyl alcohol (TBA) and 66 mL of 2,4-dimethyl-3-pentanol. A volume of the tracer mixture is transferred to a 22-liter (L) plastic jar containing water (190 mL of tracer solution is added to 15 L of water). The jar cap is tightened with several layers of Teflon tape to provide a seal. This is mixed manually over a period of a few hours until all immiscible liquids have dissolved.

Table 1. Equipment Needed to Construct and Sample PFM (task-based)**.**

Preparing activated carbon (AC) and tracers
Prepare tracer solution in water:
Graduated cylinders (50, 100, 500 mL; 1, 2 L)
1-L volumetric flask
Glass funnel
Stir bars
Stir plate
Pipets (10, 25, 50, 100 mL)
Pipet bulb
22-L plastic jars (Cole-Parmer)
Adding AC to 22-L jars:
2L plastic jars
Balance (2 decimal place up to 4 kg)
Dust masks
Teflon tape (3/4 inch heavy duty)
Mixing AC:
55-gal drum roller
55-gal drum with removable top
Dense foam pieces to hold 22-L jars in place
Preparing wire lines for PFMs:
Wire cutters
Polyvinyl Chloride (PVC) pipe cutter
Pliers
Wire crimper (McMaster Carr 3582T5 multigroove hand tool for all $^{3}/_{64}$-in sleeves and amp; $^{3}/_{32}$-in aluminum oval sleeves)
200-ft tape measure
Drill with $^{1}/_{8}$-in bit
Dremel tool
Constructing PFMs:
Nut drivers ($^{5}/_{16}$-in)
400-mL beakers
Work table

Table 1. Equipment Needed to Construct and Sample PFM (task-based) (continued)**.**

Constructing PFM carrying tubes:
Hack saw
Sand paper
PVC glue
Teflon tape
Sampling PFMs:
Preparing sample vials:
Balance
Syringe dispenser (for isobutyl alcohol [IBA]) (Fisher item)
Sampling in the field:
Spatulas
Scissors
Mixing bowls
Buckets

Table 2. PFM Parts List, 10/3/05.

Part	Supplier	Part Number	Cost
Silver Impregnated Granular Activated Carbon	Eric R. Hasis Inside Sales Representative Site Services/Remediation Calgon Carbon Corporation Ph: 800-422-7266 x 4770 Fax 412-787-4523 website: www.calgoncarbon.com		50–200 lbs@$7.22/lb
IBA 2.5 L	Fisher Scientific	15828-0025	$95
40 mL volatile organic analysis (VOA) vials, max=300, 432 ordered direct to site, 222 left	Fisher Scientific	03-339-14A	
60+ 5.5-ft-long socks	Lili's Alterations		$4/sock
330 ft of red mesh (needed for stainless steel [SS] wells only)	Cole-Parmer	U-09405-30	$95/164 ft
1/2-in chlorinated PVC (CPVC) tube	Hardware store		
Rubber washers	Servalite 1-800-477-6760	RT258 RM258	$0.52 each
Hose clamps	McMaster-Carr www.mcmaster.com	54155K15 5415K32	$0.56 $0.39
Threaded rod for pushing wells in	GeoProbe		$500
Wire lines	McMaster-Carr www.mcmaster.com	3461T9 3883T39	Wire $0.08/ft
PFM Parts List (Need to have on site)			
1.8-in PVC pipe (to pack socks in)	Hardware store		
3/4-in PVC pipe for packing	Hardware store		
Funnels	Hardware store		
Vibrator			
Power cord	Hardware store		
Bucket for fluid leakage	Hardware store		
Large spoon for transferring			
Calibrated jar	Fisher Scientific		
Spatula for C_o sampling	Fisher Scientific	14-357	$6.06

Table 2. PFM Parts List, 10/3/05 (continued)**.**

Part	Supplier	Part Number	Cost
Electrical tape **(order more)**	Hardware store		
Wrenches	Hardware store		
Pipe cutter	Hardware store		
Hacksaw	Hardware store		
Tape measure	Hardware store		
Balance **(on site)**	Fisher Scientific		
Cooler			
Blue Ice			
Syringe dispenser	Fisher Scientific	13-689-135D	$274
Field notebook	University of Florida (UF) Bookstore		
Gloves	Fisher Scientific		
Rope	Hardware store		
Hard hats			
Copper caps			
Safety vests			
Steel toe boots			
Methanol	Fisher Scientific	A452-4	$174.41
Ethanol	Fisher Scientific		
IPA	Fisher Scientific		
TBA	Fisher Scientific		
2,4-dimethyl-3-pentanol	Fisher Scientific		

Dry AC is added to the aqueous tracer solution, and 5 L of AC is slowly added to the 22-L jar. Each jar is weighed before transfer. Significant gas is generated as a result of adding the AC to water, so the process of adding AC occurs with gentle agitation until the AC is completely wet. A dust mask is worn during this process. Once all the AC is added, the jar is again sealed using several layers of Teflon tape.

Jars containing AC, water, and tracers are mixed by rotating. These jars are placed in a 55-gal drum and secured using foam packing. The drum is rotated or rolled for 6 hours to homogenize the AC-tracer mixture. Following mixing, the 22-L jars are placed in a cooler for subsequent shipping or packing.

1.3 ASSEMBLY OF PFMS

Table 1 lists equipment needed to prepare for PFM assembly, and Table 2 lists all required parts. Figure 2 illustrates the construction process. Passive flux meters are constructed in a pipe having the same diameter as the well screen. The exception is for SS well screens, in which case a nylon mesh material is used to encase the PFM; therefore, the pipe used for construction is slightly (0.1 in) smaller in diameter than the well screen. Regardless of screen type, the pipe used for PFM constructions is 5 ft long. A table is used as a work area for constructing the flux meters. All materials needed for constructing the PFMs are listed in Section 3.0. Nitrile protective gloves and protective clothing are worn during construction.

Figure 1-2. The Step-By-Step PFM Construction Process as Visualized in Pictures.

1) Place empty PFM sock into PVC packing tube.



2) Take a C_0 sample of the sorbent for each PFM created.


3) Scoop sorbent mixture into a 400-mL beaker. Pour sorbent mixture from beaker into PFM sock using a funnel placed inside the packing tube.


Figure 1-2. The Step-By-Step PFM Construction Process as Visualized in Pictures (continued)**.**

4) Slide a neoprene washer onto center tube after each 1-ft segment of sorbent is poured into sock (for vertical separation of segments). Use pipe with a larger inner diameter (ID) than the outer diameter (OD) of the PFM center pipe to push the washer into the mesh sock.

5) Repeat steps 3 and 4 until all the sorbent has been loaded into the PFM.

6) Attach retrieval mechanism to top of PFM.

7) Push newly constructed PFM out of packing tube and into transport tube.

Figure 1-2. The Step-By-Step PFM Construction Process as Visualized in Pictures (continued)**.**

8) Screw on Teflon-lined end caps to both ends of transport tube.

9) PFM is ready for transport.

10) Cut retrieval cable for each PFM to correct length. Use SS compression sleeves to form loops at both ends. Label the wire with the appropriate PFM I.D. For a detailed description of wire construction, see Section 1.3.

During construction, a PFM is packed with AC. Just prior to packing, the sock is attached to the center tube of the PMF. The center tube for 2-in wells consists of 1/2-in chlorinated polyvinyl chloride (CPVC) pipe cut to 5-ft lengths. The bottom of the sock is clamped to the CPVC pipe using a SS worm drive clamp (pipe band clamp). The sock is protected from the clamp by wrapping the CPVC pipe with electrical tape (four wraps) prior to attaching the sock and again between the sock and the SS clamp. This is important to avoid sharp edges of the clamp tearing the sock material. The sock and tube are then placed in the packing pipe and the top of the sock is pulled back over the outside of the packing pipe (the ends of the packing pipe should be sanded to remove sharp edges capable of tearing the sock material). Prior to adding AC to the PFM, a thick (⅛-in) viton washer is inserted in the bottom of the sock. The viton washers used should have an OD of the packing pipe and a center hole the same as the center tube (for 2-in wells, 2-in OD with a ⅝-in hole). The viton washers are pushed to the bottom of the PFM using a 3/4-in CPVC pipe.

Prior to packing, the top of the center tube must be plugged to prevent AC from entering the center tube. Any method of plugging (cork, rubber stopper, cap, electrical tape) is appropriate. At this point the PFM is ready for packing with AC. A funnel is used to add AC and create AC lifts inside the packing pipe. The funnel should be cut to have an opening slightly smaller than the packing pipe. AC is transferred to a 400-mL beaker using a large spoon and then poured into the funnel attached to the top of the packing pipe. The funnel is tapped on the side to facilitate the flow of AC into the sock and packing pipe. A vibrator (or manual tapping) is applied to the packing pipe to help settle the AC to the bottom of the sock and between AC lifts. After adding the required amount of AC (this will depend on the desired sampling interval), a thin (1/16-in) viton washer is pushed down the sock to pack the AC in place. This washer defines the boundaries of AC lift and serves to minimize vertical flow through the PFM during deployment. This packing process is continued until the sock is filled. During this period, an initial AC sample is collected and placed in a 40-mL vial containing 20 mL of extraction solvent (isobutyl alcohol [IBA]). For 5-ft long socks, typically 4 to 6 AC lifts are packed. At the top of the PFM, a thick viton washer is added followed by a sponge cut to the same size as the viton washer. The sponge is used to minimize AC loss from the top of the PFM since the connection between the top of the sock and the center tube must be loose.

At this point, the top of the sock is attached to the retrieval wire and short section of polyvinyl chloride (PVC) pipe. The outside of the PVC pipe section should be wrapped with electrical tape to protect the sock from the wire rope. The PVC pipe section is then slid over the center tube down to the position of the sponge. The sock is pulled up over this section. Electrical tape is applied over the sock attaching it to the PVC pipe section (four or five wraps). This is critical to protect the sock from the SS clamp. An SS clamp is attached to the sock, ensuring that the clamp is securely over the PVC pipe section and electrical tape is protecting the sock. This step is very critical since failure of this attachment will make PFM retrieval extremely difficult. This clamp should be tight but should not strip the worm drive of the clamp. Electrical tape is then wrapped around the outside of the clamp to prevent the clamp from catching on joints in the well screen and casing.

A 1/16-in SS steal wire rope is used to retrieve the PFMs. These are constructed prior to PFM assembly. The wires are fastened to the PFM using wire crimps and a crimping tool. For each

PFM, a long wire (length equal to the depth deployment) is needed and constructed using crimps to form loops at each. The long wire is then coupled to a shorter wire connected to the sock at the top of the PFM using a short section of PVC pipe (approximately 1½-in inch section of ¾-in PVC). This shorter wire is looped through holes drilled into the short section of PVC pipe. Four holes (⅛-in) are used to thread the short length of wire though the short section of PVC pipe. Two crimps are used to couple the two loose ends of the short wire. This in turn creates a wire loop attached to the short piece of PVC pipe.

1.4 PFM STORAGE

Table 1-1 provides a complete list of equipment needed to prepare PFMs for storage, and Table 1-2 lists all required parts. If PFMs are constructed for transport to the field site, these PFMs will be stored in tubes and cooled. PFM storage tubes are constructed using PVC pipe the same diameter as the packing tube. The ends have threaded caps that are sealed using Teflon tape. A spacer is placed in the bottom of the storage tube to stop the PFM from sliding past the end of the PVC pipe (usually a gap exists between the pipe and end cap in which the PFM can expand during transport). A rubber stopper (#10) works well. The PFM is then extruded from the packing tube into the storage tube. A section of threaded rod or PVC pipe is used to push the PFM out of the packing tube and into the storage tube. The top of the storage tube is then sealed. The constructed PFM is then placed in cold storage (5 degrees Celsius [°C]) until transport.

1.5 PFM TRANSPORT

Table 1-1 lists equipment needed to prepare for PFM transport, and Table 1-2 lists all required parts. PFMs are transported in insulated containers to the site. Cardboard boxes (5 ft x 8 in x 8 in) with foam insulation (1 in) forming the walls, have been used for FedEx shipment. Blue ice is added to the box for cooling. For vehicle transport, the appropriate insulation used in box construction depends on the anticipated travel time.

This page left blank intentionally.

2.0 PFM DEPLOYMENT

2.1 PFM INSERTION

Table 1 lists equipment needed for PFM deployment, and Table 1-2 lists all required parts. Figure 3 illustrates the step-by-step PFM deployment process. At the field site the PFM in the packing tube or storage tube is prepared for PFM insertion into the well casing. A wire rope is attached to the top of the PFM using a safety carabineer (or, if packing on site, the required wire has been attached to the PFM). The tube is lined up with the top of the well casing and a section of push rod is used to push the PFM from the tube into the top section of well casing. Additional push rods are attached to continue pushing the PFM to the screen interval. If multiple PFMs are deployed in a single well, the wires from PFMs currently in place are held taut to avoid wires from catching on the PFM being inserted. When inserting the PFM, some back pressure may build since the water in the well casing must flow through the center tube as the PFM is inserted. Installation should proceed slowly as pressure builds. The wire cable attached to the PFM is then secured to an exterior 2-in segment of PVC pipe to ensure that it will not fall into the well and be lost to the well head.

Figure 2-1. The Step-By-Step PFM Deployment Process as Visualized in Pictures.

1) Transport PFMs to site using PVC transport tubes (either by vehicle or FedEx Overnight). Once on site, organize the flux meters for deployment.

2) Set up a workstation at the first deployment location by laying the PFMs for the first well across two portable sawhorses.

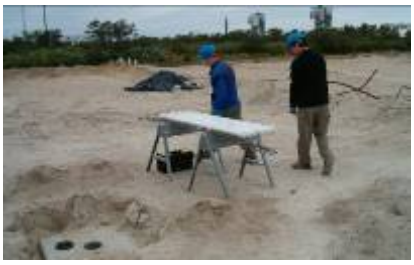

Figure 2-1. The Step-By-Step PFM Deployment Process as Visualized in Pictures (continued)**.**

3) Remove end caps from PVC transport tubes.

4) Remove well lid and cap.

5) Attach retrieval cable to the top of each PFM.

Figure 2-1. The Step-By-Step PFM Deployment Process as Visualized in Pictures (continued)**.**

6) Install PFM by setting the transport tube on top of the monitoring well casing and using Geoprobe rods to push the PFM out of the transport tube and into the well.

7) Push PFM into position in the well using Geoprobe rods while maintaining tension on the retrieval cable.

8) Repeat steps 5 through 7 for each PFM that is to be installed in the well.

9) Replace well lid and cap (wire cables are cut to a length that allows 2 ft of each retrieval cable to remain outside the well).

10) Repeat steps 2 through 9 for each well.

2.2 PFM RETRIEVAL AND SAMPLING

Table 1-1 lists equipment items needed to retrieve and sample PFM, and Table 1-2 lists all required parts. Figure 2-2 illustrates the step-by-step PFM retrieval process. At the field site the PFM in the packing tube or storage tube is prepared for PFM insertion into the well casing. PFMs are retrieved using the wire rope. The top PFM in the well is extracted first by gently pulling up on the wire (heavy work gloves should be worn when pulling on $^{1}/_{16}$-in cable). The PFM should be pulled to the top of the well casing. The PFM will occasionally catch on joints in the well screen. Simply apply more pressure to overcome. If the PFM will not move, look at troubleshooting options below. When the PFM is at the top of the well casing, untangle anywires that are twisted at the well head. Thread the retrieval cable through a 5-in x 2-in ID PVC pipe, and place the pipe over the well to guide and contain the extruded PFM. Move the PFM to the sampling work station.

Figure 2-2. The Step-By-Step PFM Retrieval and Sampling Procedure as Visualized in Pictures.

1) Retrieve PFM from well by pulling up on the attached wire cable. The PFM is pulled from the well pipe directly into a PVC tube of the same diameter.

2) Place tube on table and expose the first segment by pulling on the bottom end of the PFM.

3) Using scissors, cut open the nylon mesh covering the first segment and pour the exposed sorbent into a bowl.

Figure 2-2. The Step-By-Step PFM Retrieval and Sampling Procedure as Visualized in Pictures (continued)**.**

4) Stir the sorbent to homogenize.

5) Subsample the mixture and place into 40-mL vial containing IBA.

6) Measure the interval length of the PFM segment.

7) Repeat steps 3-6 for remaining segments of PFM.

8) After all PFMs are sampled, place 40-mL vials into cooler(s) and ship back for analysis.

9) Excess sorbent is collected in a plastic-lined container for proper hazardous waste disposal.

A tarpaulin acts as a "protective flooring" for the work zone. A portable table is used as a work zone for sampling the PFMs. All material listed in Table 2-1 will be contained in this area during the retrieval stage. Nitrile protective gloves and other necessary protective clothing will be worn by all samplers. A lined bucket is placed under the work area to capture unsampled residual AC from a retrieved PFM. The sock is extruded from the PVC pipe to the sampling interval extent. The flexible mesh and cotton packing materials are cut and the sorbent captured in plastic bowls for homogenization using a SS spatula. A subsample is then transferred into 40-mL volatile organic analysis (VOA) vials, each containing the extraction solvent. 10 grams of

sample or 1.5 cm sample depth is added to the vials. The vials are stored in a cooler containing blue ice prior to transport back to the laboratory for analysis. The center tube and viton washers are measured to obtain the sample interval lengths in the PFM. Sampling materials, spatula, scissors, and mixing bowls are wiped cleaned of AC grains prior to retrieval of the next PFM.

For AC sampling, 40-mL VOA vials are used. The vials are weighed empty (nearest 0.01 grams) and recorded. The vials are then filled with IBA (extraction solvent) using a fixed volume dispenser (20-mL syringe dispenser) and sealed. The vials with IBA are again weighed and the weights recorded. Following addition of AC (approximately 2-cm depth) the vials are weighed and the weights recorded.

All equipment and materials need for deployment and retrieval of PFM in the field are listed in Table 2-1.

Table 2-1. Field Equipment and Materials.

Item	Used During Deployment	Used During Retrieval
Field notebook	X	X
Cotton flux socks	X	
SS rods	X	
Flexible plastic mesh	X	
Plastic funnel	X	
Tracer loaded AC	X	
Rubber washers	X	
Steel-wire retrieval cable	X	
Medium threaded SS clamps	X	
Small SS threaded clamps	X	
Electrical tape	X	X
Spoon/scoop	X	
Paper towels	X	X
Clean cloth	X	X
Garbage bags	X	X
20-L Carboy containing deionized water	X	X
Portable workbench	X	X
Tarpaulin	X	X
Latex gloves	X	X
Protective work gloves	X	X
Wire crimper	X	
40-mL VOA vials containing 20 mL solvent	X	X
1-in ID PVC packing rod	X	
1.8-in ID PVC packing pipe	X	
2-in ID PVC Transporting pipe	X	X
4-ft plastic attachable insertion rods	X	
Tape measure		X
SS spatulas		X
Tool box	X	X
Plastic homogenizing bowls		X
Scissors	X	X
Bucket	X	X
Alconox solution	X	X
20-L Carboy for liquid waste	X	X
Nitrile protective gloves	X	X

2.3 TROUBLESHOOTING PFM EXTRACTION

In the event that the PFM is difficult to remove from the well, the following steps might be considered. Take the rods used to insert the PFM, push down to move the PFM below the obstruction. In this case it is useful to attach a viton 2-in washer at the end of the push rod to center the rod in the well. Holding both the retrieval wire and the push rod, surge the PFM up and down to attempt to overcome the obstacle.

In the event that the wire breaks or becomes detached from the PFM, a corkscrew attachment can be added to the rod to attempt to "grab" the top of the PFM and advance it upwards. If this fails, the corkscrew can be used to dig into the AC and viton washers again in an attempt to "grab" the PFM. Finally, a pump with tubing lowered to the top of the PFM can be used to extract the AC. This slow process obviously destroys the PFM, but it can be successful in clearing the well.

This page left blank intentionally.

3.0 ANALYTICAL METHODS SUPPORTING THE EXPERIMENTAL DESIGN AND SAMPLING PLAN

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

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

3.1.1 Scope and Application

1. This standard operating procedure (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, Florida.

3. The selected constituents are organic contaminants (vinyl chloride [VC], dichloroethane [DCE], trichloroethylene [TCE], and perchloroethylene [PCE]) and alcohol tracers (methanol, ethanol, IPA, TBA, n-propanol, n-pentanol, n-hexanol, and 2,4-dimethyl-3-pentanol).

4. The selected sorbents are AC and surfactant modified zeolytes.

5. The method involves liquid extraction in 40-mL VOA vials using organic solvents.

3.1.2 Purpose

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

3.1.3 Procedures

3.1.3.1 Sample Containers, Collection, Transportation, and Storage

3.1.3.1.1 Sample Containers

Field samples will be collected in 40-mL glass sample vials (Fisher Catalog # 03-339-14A) with Teflon-faced rubber-backed caps. All vials and caps are nonreusable.

3.1.3.1.2 Sample Collection

Each field sample vial will be partially filled with the extraction solvent (IPA, IBA, etc. or methylene chloride) using a pipet or repeating volume dispenser. Typically, 20 mL of solvent will be used. Sorbent aliquots collected over 1-ft increments from a flux meter will be transferred

to a mixing bowl and homogenized with a metal spatula. Approximately 10 grams of mixed sorbent will be placed into the 40-mL VOA vials containing extracting solvent.

3.1.3.1.3 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 University of Florida 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 4°C until gas chromatograph (GC) analysis is performed. After subsampling, the samples are returned to cold storage.

3.1.3.2 Sample Extraction and Preparation

3.1.3.2.1 Alcohol Tracer Extraction

About 10 grams of sample will be collected into 40-mL volatile organic compound (VOC) vials containing 20 mL of IBA. Vials should be rotated on a Glas-Col Rotator (Glas-Col model RD 4512), set at 20 (%) rotation speed, for 24 hr, and then refrigerated for up to 48 hr to allow suspended particulate matter to settle out. When the suspended particle is completely settled out, the supernatant will be taken into a 2-mL gas chromatography vial for alcohol tracer analysis and into a 5-mL vial for back-up samples. The supernatant should be decanted, and remaining liquid in vials is removed out using a disposable pipet for sequential extraction with acetone/hexane.

3.1.3.2.2 Organic Contaminant Extraction

The supernatant should be decanted for sequential extraction with acetone/hexane and 32 mL of an acetone:hexane (25 mL:7 mL) solvent mixture will be added to the decanted 40-mL VOC vials. The vials will be then rotated on a Glas-Col Rotator, set at 20% rotation speed, for 24 hr, and refrigerated for up to 48 hr to allow suspended particulate matter to settle out. The supernatant will be taken into a 2-mL vial for gas chromatography (GC-flame-ionization detector [FID] or electron capture detector [ECD]). Pipets will be used to transfer samples from 20-mL sample vials to the 2-mL GC vials.

3.1.3.3 Apparatus and Materials

3.1.3.3.1 Glassware

Glass pipets are required for subsampling.

3.1.3.3.2 Rotator

A rotator is required for sample extraction.

3.1.3.4 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.

3.2 STANDARD OPERATING PROCEDURE FOR THE SAMPLING, COLLECTION, EXTRACTION, AND ANALYSIS OF ALCOHOL TRACERS

3.2.1 Scope and Application

1. The following SOPs are currently utilized by the Department of Environmental Engineering Sciences at the University of Florida, Gainesville, Florida, and the Environmental Engineering area of the School of Civil Engineering at Purdue University, West Lafayette, Indiana.

2. This SOP was updated March 3, 2004, by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida and I.C. Poyer School of Civil Engineering, Purdue University. 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. This SOP describes the extraction and analytical procedures of alcohol tracers from a sorbent (silver-impregnated AC) packed into borehole flux meters. Some of the alcohols have been used as partitioning tracers in both laboratory and field studies to quantify the amount and distribution of dense non-aqueous phase liquids (DNAPL) in source zones. Here, these alcohols are used as "resident" tracers that are preloaded on to the sorbent packed into the flux meter sock; loss of tracers via desorption and advective/diffusive/dispersive transport resulting from groundwater flow under natural hydraulic gradients is measured to estimate cumulative groundwater and contaminant fluxes.

4. The alcohol tracers used in the lab and field studies are methanol, ethanol, IPA, 2-methyl-2-propanol, and 2,4-dimethyl-3-pentanol.

5. The established analytical method involves GC analysis for alcohol concentrations in extracted samples. An FID is used to determine and quantify the analyte concentrations in the samples. The method has been found to provide reliable and reproducible quantitation of alcohols for concentrations greater than 1 μg/mL. This value may be considered the reportable minimum detection level. The linear standard calibration range for the FID response is up to a concentration of approximately 3,000 μg/mL per analyte of interest.

6. 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.

3.2.2 Purpose

The purpose of this SOP is to insure reliable and reproducible analytical results for alcohols in samples extracted from a sorbent for laboratory-based GC-FID analyses and to permit tracking sources of error in analytical results.

3.2.3 Procedures

3.2.3.1 Sample Containers, Collection, Transportation, and Storage

3.2.3.1.1 Sample Containers

Sorbent samples will be collected in 40-mL VOA vials (Fisher Scientific Catalog # 03-339-14A) sealed with Teflon-lined septa caps. Vials should contain 20 mL of extraction solvent (IBA), prepared previously in the laboratory. All vials and caps are nonreusable.

3.2.3.1.2 Sample Collection

Sorbent aliquots collected over 1-ft increments from an exfiltrated flux meter will be transferred to a mixing bowl and homogenized with a metal spatula. Approximately 10 grams of mixed sorbent will be placed into the 40-mL VOA vials containing extracting solvent. The vials will not be opened until the time for analysis.

3.2.3.1.3 Transportation and Storage

Field samples will be stored in coolers containing blue ice and later stored in refrigerators in a facility located on the site. The samples will be packed in coolers containing blue ice and shipped via overnight air express (e.g., FedEx) to the University of Florida/Purdue University laboratory. The samples will be stored in the cold storage room or refrigerator at 4°C, until extraction and GC analysis. After subsampling, the samples are returned to cold storage.

3.2.3.2 Apparatus and Materials

3.2.3.2.1 Glassware

Volumetric class 'A' pipets and volumetric class 'A' flasks are required for preparation of calibration standards and sample dilutions. Disposable Pasteur glass pipets (Fisher Catalog # 13-678-20B) are required for subsampling. GC vials (2 mL) with Teflon-faced caps (Fisher Catalog # 03-375-16A) are required for GC analysis.

3.2.3.2.2 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 (or A Shimadzu GC17A GC) with an FID and an integrated autosampler are suitable for analysis of field and laboratory samples. The Perkin Elmer auto system (or A Shimadzu GC17A GC) is linked to a PC-based data acquisition/analysis software system

A J&W Scientific DB-624 capillary column (50 m or 75 m x 0.53 mm, 3 μm [micrometer] film thickness) is required. Zero-grade air and ultra-high purity hydrogen are required for the FID. Ultra-high purity nitrogen or helium is required for the carrier gas.

3.2.3.3 Reagents

Deionized water is prepared by refiltration of deionized water through a Barnstead Ultrapure Deionization Unit. This water should be referred to as "reagent water."

Certified American Chemical Society (ACS)-grade alcohols are required for analysis. The alcohols are purchased from one or more of the following vendors—Fisher Scientific, Van Waters and Rogers (VWR), or Sigma-Aldrich—and used as received.

3.2.3.4 Standard Solutions

3.2.3.4.1 Stock Standard Solution

Individual alcohol stock standard solutions should be prepared in reagent water using volumetric glassware and stored in 20-mL glass vials with Teflon-lined caps. Stock solutions should be kept in a refrigerator at 4°C. Fresh stock standards should be prepared every 6 months and follow protocols outlined in the Federal Register, Rules and Regulations, Thursday, November 29, 1979, Part III, Appendix C, Section 5.10, "Standard Stock Solutions." The single modification from the cited procedure is the use of reagent water instead of methanol as the solvent.

3.2.3.4.2 Calibration standards

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

3.2.3.5 Quality Control Blank Spike/Matrix Spike

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

3.2.3.6 Quality Control

GC injector septa should be changed every 100 to 150 injections, or sooner if any related problems occur.

Injector glass liners should be cleaned or changed after 100 to 150 injections or sooner if any related problems occur.

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

A complete set of calibration standards (a minimum of five) should be run at the beginning of each day with a continuing calibration standard run after every 25 samples.

A matrix spike and a blank spike and a duplicate should be analyzed in every 25 samples.

3.2.3.7 Instrumental Procedures

A Perkin Elmer Autosystem GC (by University of Florida)

Column dimensions	J&W DB-624 Column, 50 m x 0.53 μm x 3μm
Injection port temperature	200°C
FID detector temperature	220°C
Column Temperature Program	Isothermal at 45°C for 6 min; ramp to 75°C at 3°C/min, hold 3 min; ramp at 10°C/min to 200°C, hold 1 min
Carrier gas	Helium, 99.995% purity
Flame gases	Air, 99.995% purity; hydrogen, 99.995% purity

A Shimadzu GC17A GC (by Purdue University)

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

3.2.3.8 Sample Preparation

The collected sorbent samples should be rotated for a period not to exceed 24 hr, set at 20% rotation speed on a Glas-Col Rotator. The samples then should be refrigerated for up to 48 hr to allow suspended particulate matter to settle out. When the suspended particle completely settled out, the supernatant is taken into a 2-mL GC vial with Teflon-lined septa caps for GC analysis and into a 5-mL vial for back-up samples. If the suspended particulate matter does not settle out, a syringe filter (Teflon, 0.22 micron) or a centrifuge (for 5 min at 2,000 rpm) can be used to remove the suspended granular activated carbon (GAC) particles from the samples. Extraction vials will be stored at 4°C.

3.2.3.9 Sample Analysis

The samples should be allowed to reach ambient temperature prior to GC analysis. Sample vials (2 mL) are loaded onto the GC auto-injector. A 1-μL (microliter) injection volume should be used for both samples and standards.

Analyte identification should be based on absolute retention times compared to calibration standards. The analytes of interest should elute at their characteristic retention times within 0.1 min for the automated GC system.

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

Sample analysis should be selected from the analytical methods having the minimum facility specific method detection limit (MDL)/practical quantitation limit (PQL) defined in Section 4.3

of this manual. The MDL and PQL studies should be conducted according to the procedures specified in Section 4.3. The MDL and PQL documentation should include date of measurements, analytical method, and compounds measured.

3.2.3.10 Interferences

Contamination by carryover may occur when high-level and low-level samples are sequentially analyzed. To reduce carryover, the injector syringe should be rinsed with reagent water between samples.

Potential carryover should 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 carryover has been minimized.

3.2.3.11 Safety

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.

Reference to the MSDS should be made for information on toxicity, flammability, and other hazard data.

3.3 STANDARD OPERATING PROCEDURE FOR THE SAMPLING, COLLECTION, EXTRACTION, AND ANALYSIS OF TARGET CONTAMINANTS

3.3.1 Scope and Application

1. The following SOPs are currently utilized by the Department of Environmental Engineering Sciences at University of Florida.

2. This SOP was written by M.D. Annable, Department of Environmental Engineering Sciences, University of Florida. 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 cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene.

4. This SOP describes the extraction and analytical procedures of target contaminants from a sorbent (silver-impregnated AC).

5. The method involves GC analysis or high pressure liquid chromatography (HPLC) for target analyte concentrations in samples extracted from a sorbent

(AC). HPLC with an ultraviolet (UV) detector or GC-ECD is used to quantify the analyte concentrations in the samples.

6. Samples selected for HPLC or GC-ECD analysis may be chosen on the basis of preliminary screening, which will provide approximate concentration ranges.

An ECD is used to quantify the analyte for concentrations in the samples. This method has been found to provide reliable and reproducible quantitation of analytes for concentrations greater than 0.1 μg/mL (microgram/milliliter). The linear standard calibration range for the ECD response is up to a concentration of approximately 1 µg/mL per analyte of interest.

HPLC is used to quantify the analyte in the samples with some interference compounds or the analytes for high concentrations. This method has been found to provide reliable and reproducible quantitation of analytes for concentrations greater than 0.5 μg/mL. The linear standard calibration range for the HPLC UV response is up to a concentration of approximately 300 µg/mL per analyte of interest.

3.3.2 Purpose

The purpose of this SOP is to insure reliable and reproducible analytical results for target contaminants in samples extracted from a sorbent for laboratory-based HPLC or GC-ECD analyses, and to permit tracking sources of error in analytical results.

3.3.3 Procedures

3.3.3.1 Sample Containers, Collection, Extraction, Transportation, and Storage

3.3.3.1.1 Sample Containers

Sorbent samples will be collected in 40 mL VOA vials (Fisher Scientific Catalog # 03-339-14A) sealed with Teflon-lined septa caps. All vials and caps are nonreusable.

3.3.3.1.2 Sample Collection

Each field sample vial will be partially filled with the extraction solvent (IBA) using a pipet or repeating volume dispenser. Typically 20 mL of solvent will be used. Sorbent aliquots collected over 1-ft increments from a flux meter will be transferred to a mixing bowl and homogenized with a metal spatula. Approximately 10 grams of mixed sorbent will be placed into the 40-mL VOA vials containing extracting solvent.

3.3.3.1.3 Transportation and Storage

Field samples will be stored in coolers containing blue ice and later stored in refrigerators in a facility located on the site. The samples will be packed in coolers containing blue ice and shipped via overnight air express (e.g., FedEx) to the University of Florida laboratory. The samples will be stored in the cold storage room or refrigerator at 4°C, until extraction and GC analysis. After subsampling, the samples are returned to cold storage.

3.3.3.2 Apparatus and Materials

3.3.3.2.1 Glassware

Volumetric class 'A' pipets and volumetric class 'A' flasks are required for preparation of calibration standards and sample dilutions. Disposable Pasteur glass pipets (Fisher Catalog # 13-678-20B) are required for subsampling. GC vials (2 mL) with Teflon-faced caps (Fisher Catalog # 03-375-16A) are required for GC or HPLC analysis.

3.3.3.2.2 Rotator

A rotator is required for sample extraction.

3.3.3.2.3 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-ECD operation.

A Shimadzu GC17A GC with an ECD and an integrated autosampler are suitable for analysis of field and laboratory samples. The Shimadzu GC17A GC is linked to a PC-based data acquisition/analysis software system.

3.3.3.2.4 Liquid Chromatograph System

An analytical liquid chromatography (LC) system with 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 mobile phase required for HPLC operation.

A Perkin Elmer 200 Series with a UV detector and an integrated autosampler are suitable for analysis of field and laboratory samples. The Perkin Elmer Liquid Chromatograph is linked to a PC-based data acquisition/analysis software system.

3.3.3.3 Reagents

Deionized water is prepared by refiltration of deionized water through a Barnstead Ultrapure Deionization Unit. This water should be referred to as "reagent water."

Certified ACS-grade methanol and analytes are required for analysis. The methanol and analytes are purchased from; Fisher Scientific and Sigma-Aldrich or used as received.

3.3.3.4 Standard Solutions

3.3.3.4.1 Stock Standard Solution

Mixed target analyte stock standard solutions should be prepared in methanol using volumetric glassware and stored in 40-mL glass vials with Teflon-lined caps. Stock solutions should be kept in a refrigerator at 4°C. Fresh stock standards should be prepared every 6 months.

3.3.3.4.2 Calibration Standards

Mixed calibration standards are prepared by diluting stock standards in methanol using volumetric glassware. A minimum of five standards should be prepared and should cover the expected concentration range in the samples.

3.3.3.5 Quality Control Blank Spike/Matrix Spike

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

3.3.3.6 Quality Control

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

A complete set of calibration standards (minimum of five) should be run at the beginning of each day with a continuing calibration standard run after every 25 samples.

A matrix spike and a blank spike and a duplicate should be analyzed in every 25 samples.

3.3.3.7 Instrumental Procedures

A Perkin Elmer 200 Series HPLC	
Column dimensions	SUPELCO LC-PAH HPLC Column, 25 cm x 4.6 mm, 5 μm
Detector wave length	230 nm
Eluent concentration	70% methanol
Column flow rate	1 mL/min
A Shimadzu GC17A GC	
Column dimensions	J&W DB-624 Column, 30 m x 0.53 μm x 3 μm
Injection port temperature	200°C
ECD detector temperature	350°C
Carrier gas	Nitrogen, 99.995% purity
Column temperature program	Isothermal at 60°C; ramp to 120°C at 5°C/min, hold 2 min; ramp at 20°C/min to 200°C, hold 1 min

3.3.3.8 Sample Preparation

After extraction of alcohol tracers, described in Section 3.2.3, the supernatant in sample vials will be decanted for sequential extraction with acetone/hexane and 32 mL of an acetone:hexane (25 mL:7 mL) solvent mixture will be added to the decanted 40 mL-VOA vials. The vials will then be rotated on a Glas-Col Rotator, set at 20% rotation speed for 24 hr and refrigerated for up to 48 hr to allow suspended particulate matter to settle out. The supernatant will be taken into a 2-mL vial with Teflon-lined septa caps for GC-ECD or HPLC. If the suspended particulate matter does not settle out, a syringe filter (Teflon, 0.22 micron) or a centrifuge (for 5 min at 2,000 rpm) can be used to remove the suspended AC particles from the samples. Extraction vials will be stored at 4°C.

3.3.3.9 Sample Analysis

Sample analysis should be selected from the analytical methods having the minimum facility specific MDL/PQL defined in Section 4.3. The MDL and PQL studies should be conducted according to the procedures specified in Section 4.3.

The samples should be allowed to reach ambient temperature prior to GC/LC analysis. Sample vials (2 mL) are loaded onto the GC/LC auto-injector.

Analyte identification should be based on absolute retention times compared to calibration standards. The analytes of interest should elute at their characteristic retention times within 0.1 min for the automated GC/LC system.

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

3.3.3.10 Interferences

Contamination by carryover may occur when high-level and low-level samples are sequentially analyzed. To reduce carryover, the injector syringe should be rinsed with reagent water between samples.

Potential carryover should 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 carryover has been minimized.

3.3.3.11 Safety

Reference to the MSDS should be made for information on toxicity, flammability, and other hazard data.

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

3.4.1 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. 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 vinyl chloride, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, tetrachloroethene, benzene, toluene, o-xylene, 1,1,1-trichloroethane, 1,3,5,-trimethylbenzene, 1,2-dichlorobenzene, decane, and naphthalene.

4. The method involves GC analysis for target analyte concentrations in aqueous samples. Headspace analysis with a 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 μg/L. This value may be considered the minimum detection level.

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

3.4.2 Purpose

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

3.4.3 Procedures

3.4.3.1 Sample Containers, Collection, Transportation, and Storage

3.4.3.1.1 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.

3.4.3.1.2 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.

3.4.3.1.3 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 the University of Florida 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 4°C, until GC analysis. After subsampling, 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.

3.4.3.2 Subsampling and Dilution

Field samples will be subsampled placing 10 mL into 20-mL headspace vials containing 2 grams 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.

3.4.3.3 Apparatus and Materials

3.4.3.3.1 Glassware

Glass pipets are required for subsampling.

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 preparation of the calibration standards.

3.4.3.3.2 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 Auto system will be linked to an IBM-compatible PC loaded with Turbochrom (version 4.01) software.

A J&W Scientific DB-624 capillary column 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.

3.4.3.4 Reagents

3.4.3.4.1 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.

3.4.3.5 Standard Solutions

3.4.3.5.1 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 6 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."

3.4.3.5.2 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 3,000 μg/L.

3.4.3.6 Quality Control 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.

3.4.3.7 Quality Control

A method blank will be included in every 50 samples.

A complete set of calibration standards (five) will be run at the beginning of each day and after every 50 samples.

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.

3.4.3.8 Instrumental Procedures

3.4.3.8.1 Gas Chromatography with Headspace

A Perkin Elmer Autosystem GC

Column dimensions	J&W DB-624 Column, 30 m x 0.53 μm x 3 μm
Headspace sample temperature	90°C

Injection needle temperature	100°C
Transfer line Temperature	110°C
FID detector temperature	220°C
Carrier gas pressure	8 psi
Temperature program	Isothermal at 50°C for 0 min; ramp to 200°C at 5°C/min, hold 10 min
Carrier gas	Helium 99.995% purity
Flame gases	Air, 99.995% purity; hydrogen, 99.995% purity

3.4.3.9 Sample Preparation

3.4.3.9.1 SubSampling

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.

3.4.3.9.2 Dilution

Samples will be diluted if chromatographic peak areas for any of the analytes exceed those of the highest calibration standard. 1 mL of sample will be added to an appropriate amount of reagent water to make the dilution.

3.4.3.10 Sample Analysis

Sample analysis should be selected from the analytical methods having the minimum facility-specific MDL/PQL defined in Section 4.3. The MDL and PQL studies should be conducted according to the procedures specified in Section 4.3. The MDL and PQL documentation should include date of measurements, analytical method, and compounds measured.

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

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

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.

3.4.3.11 Interferences

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

Potential carryover 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 carryover has been minimized.

3.4.3.12 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 MSDS will be made for information on toxicity, flammability, and other hazard data.

3.5 STANDARD OPERATING PROCEDURE FOR THE SAMPLING, COLLECTION, EXTRACTION AND ANALYSIS OF PERCHLORATE FROM SORBENTS PACKED IN BOREHOLE FLUX METERS

3.5.1 Scope and Application

1. This SOP describes the extraction and analytical procedures of perchlorate from sorbent (silver-impregnated AC) packed into the borehole flux meters. The mass of perchlorate accumulated by sorption on the sorbent from the groundwater passing through the flux meter is used to estimate the cumulative contaminant flux.

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

3.5.2 Purpose

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

3.5.3 Procedures

3.5.3.1 Sample Containers, Collection, Transportation, and Storage

3.5.3.1.1 Sample Containers

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

3.5.3.1.2 Sample Collection

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

3.5.3.1.3 Transportation and Storage

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

3.5.3.2 Laboratory Supplies and Materials

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

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

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

3.5.3.3 Reagents

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

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

3.5.3.4 Calibration and Stock Standard Solutions

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

3.5.3.5 Quality Control Blank Spike/Matrix Spike

A blank spike will be prepared by the addition of 1 mL of calibration standard to 1mL of reagent water. A matrix spike will be prepared by the addition of 1mL of calibration standard to 1 mL of

sample. Spike recoveries will be calculated using the difference between the two measured concentrations and the known spike concentration.

3.5.3.6 Analytical Instrumentation

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

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

3.5.3.7 IC Parameters and Analytical Conditions

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

3.5.3.8 Quality Control of IC System

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

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

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

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

3.5.3.9 Extraction of Perchlorate from Sorbent Matrix

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

3.5.3.10 Sample Analysis

Sample analysis should be selected from the analytical methods having the lowest facility specific MDL/PQL defined in Section 4.3. The MDL and PQL studies should be conducted

according to the procedures specified in Section 4.3. The MDL and PQL documentation should include date of measurements, analytical method, and compounds measured.

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

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

3.5.3.11 Interferences

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

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

3.5.3.12 Safety

Reference to the MSDS will be made for information on toxicity, flammability, and other hazard data.

This page left blank intentionally.

4.0 QUALITY ASSURANCE PROJECT PLAN

4.1 PURPOSE AND SCOPE OF THE PLAN

This Quality Assurance (QA) Plan focuses on field installation, sampling, and processing of data from the flux meters.

4.2 QUALITY ASSURANCE RESPONSIBILITIES

The responsibilities for QA were shared by Kirk Hatfield and Mike Annable at the University of Florida. During field activities one of the principal investigators 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.

4.3 DATA QUALITY PARAMETERS

This section discusses measures to be taken to ensure the representativeness, completeness, comparability, accuracy, and precision of the data.

4.3.1 Accuracy

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

The percent recoveries (%R) of surrogates, quality control (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:

$$X = \frac{SSR}{SA} x\,100 \qquad (1)$$

For matrix spikes:

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

where:

SSR = piked sample result
SS = sample result
SA = spike added from spiking mix

The mean percent recovery (X) is defined by:

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N} \qquad (2)$$

where:

X_i = percent recovery value of a spike replicate
N = number of spikes

4.3.2 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. RPD is defined in the following equation:

$$\%RPD = \frac{2(X1 - X2)}{\bar{x}} \, x \, 100 \qquad (3)$$

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:

$$S = \sum_{i=1}^{N} \left[\frac{(X_i - \overline{X})^2}{N - 1} \right]^{\%o} \qquad (4)$$

where:

X_i = the recovery value of a spike replicate
X = arithmetic average of the replicate values
N = number of spikes

4.3.3 Representativeness

Representativeness is defined as how well the samples represent the environmental condition.

It is controlled primarily by how we choose a sampling location and timing. In the discussion of representativeness of a samples site, the rationale for the sampling design is provided. Demonstration of sample representativeness will involve a description of the steps by which the sample is collected and how the sample is collected in the field site.

4.3.4 Comparability

Comparability is defined as how well data collected can be compared with other data.

Demonstration of the comparability involves a description of the methods used to collect and analyze the sample. The SOPs will outline methods used by laboratory. To maintain comparability, the methods used for collecting and analyzing samples will remain consistent. If the methods are modified, these changes will be documented.

4.3.5 Completeness

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

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

4.4 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.

4.4.1 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.

4.4.2 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.

4.4.3 Quality Control Reference Materials

All QC Reference Materials are acquired only from authorized vendors or sources commonly used by U.S. Environmental Protection Agency (USEPA) Regional Laboratories.

4.4.4 Standards Traceability

When standard reference materials (SRM) 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	=	Standards 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

4.4.5 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.

4.4.6 Gas Chromatography Section

4.4.6.1 Initial Calibration

The linear calibration range of the instrument must be determined before the analysis of any samples. GC 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 five-level calibration is run. The concentrations of the standards must bracket the linear range of the instrument. Calibration using fewer than five levels is done only when specifically allowed by the method.

4.4.6.2 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:

$$RRT = \frac{RT^{target}}{RT^{is}} \tag{5}$$

The RRF may be calculated as follows:

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

Note: **"**Amount" in this equation refers to the mass (e.g., μg) 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:

$$RRF = \frac{A_s \, x \, C_{is}}{A_{is} \, x \, C_s} \tag{6}$$

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

$$S = \sum_{i=1}^{N} \left[\frac{(RRF_i - RRF_m)^2}{N - 1} \right]^{\text{‰}} \tag{7}$$

where:

RRF_i = individual RRF
RRF_m = mean RRF
N = number of RRF

and

$$\%CV = \frac{S \, x \, 100}{RRF_m} \tag{8}$$

4.4.6.3 Coefficient of Variation

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

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

4.4.6.4 Initial Calibration Verification

The calibration curve must be validated further by analyzing a QC check sample. The QC check sample must be obtained from USEPA, 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%. 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.

4.4.6.5 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 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:

$$\%D = \frac{(RRF_m - RRF) \times 100}{RRF_m} \qquad (9)$$

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.

4.4.6.6 Other Calibrations

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

4.4.6.7 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 4.

Table 4. Criteria for Balance Calibration Checks.

Class S Weight (grams)	Class S Weight (grams)	Control Level (grams)
Analytical Balances		
0.0100	0.0100	0.0097-0.0103
0.1000	0.098-0.102	0.097-0.103
1.000	0.995-1.005	0.097-0.103
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

4.4.6.8 Incubators, Ovens, and Waterbaths

Temperatures are checked daily with a National Bureau of Standards (NBS) grade thermometer and necessary adjustments made as required. All temperature readings are recorded and posted on the appropriate equipment.

4.4.6.9 DO Meters

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

4.4.6.10 Conductivity Bridges

Conductivity meter is standardized daily against a solution of kaolinite crystallinity indices (KCI) to obtain a new cell constant.

4.4.6.11 Hydrogenion Concentration Meters

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

4.4.6.12 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.

4.4.6.13 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.

4.4.6.14 Calibration Standards

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

4.4.6.15 Traceability

All standards are traceable to the National Institute of Standards and Testing (NITS) SRM or to the U.S. USEPA Reference Standards.

4.4.6.16 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.

4.4.6.17 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.

4.4.7 CORRECTIVE ACTIONS

4.4.7.1 Laboratory Imposed

Corrective actions will be initiated if the QC 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 that 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 the project manager, and by the laboratory manager. CARs will be filed in appropriate department files and in the lab manager's files.

4.4.7.2 Agency Imposed

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

4.4.7.3 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.

4.4.7.4 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, QC criteria being exceeded, statistically out-of-control events, deviations from normally expected results, suspect data, deviations from the SOP, 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 USEPA.

4.4.7.5 Corrective Action Procedures

The procedure requires documenting the condition requiring corrective action on a CAR and implementing corrective action based on the results of the investigation performed to determine the cause of the condition (Tables 5 and 6).

Table 5. 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	CV >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 continuing calibration standard 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 Contract Laboratory Program (CLP) criteria	Re-extract and/or reanalyze
Surrogate recovery (GC/MS volatiles)	0 outside criteria	Reanalyze

*GC/MS = gas chromatography-mass spectrometry

Table 6. Corrective Action Report Criteria for Control Charts.

Criteria	Corrective Action
A point outside ±3 SD	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 a CAR and submit it to the project manager and the field site manager for approval.
Three consecutive points accuracy outside ± SD	Conduct investigation. Check accuracy of data input, calculations, instrument, standards, etc., to locate the source of the problem. Document results in a CAR. Have the report approved by the supervisor. No results can be reported until the CAR has been approved. Send a copy of the CAR and a copy of the QC chart to the field site manager.

Table 6. Corrective Action Report Criteria for Control Charts (continued)**.**

Criteria	Corrective Action
Obvious outlier	Conduct investigation. Check accuracy of data input, calculations, dilutions, instrument, standard, etc. Present initial findings to the field site manager, who will jointly decide what actions need to be taken. Document the results in a CAR and have it approved by the field site manager. No results can be reported until the CAR is approved. Send a copy of the CAR 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 CAR. Have the CAR approved by the field site manager. No results can be reported until the report is approved. Send a copy of the CAR and a copy of the QC chart to the field site manager.

When a condition requiring corrective action arises, the CAR 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 CAR is reviewed by the project manager and the fied site manager, who either approves the recommended corrective action or indicates 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 CAR being signed and dated by the person who implemented the corrective action.

4.5 DEMONSTRATION PROCEDURES

Initiating the flux meter experiments will involve limited field effort. All 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 subsampling also require fairly minimal time and personnel. Only the controlled flow flume experiments required establishing steady flow from one end of the flume using peristaltic pumps. These pumps were calibrated in the field using simple time and volume measurements. Periodic flow measurements were made to determine total average flow.

Samples collected at the Borden site were sent to the University of Florida for analysis. In the laboratory, instrument maintenance included the following.

4.5.1 Maintenance Schedule

Preventive maintenance, including 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 QC criteria. Table 7 lists routine equipment maintenance procedures and frequency.

Table 7. Preventive Maintenance.

Instrument	Activity	Frequency
GC	Change septum	As needed
	Check carrier gas	Daily
	Change carrier gas	As needed
	Change in-line filters	As needed
	Perform ECD wipe test	As license requires
	Clean ECD	Return to vendor as needed
	Check system for leaks	As needed
	Clean/replace injection point liner	As needed
	Clean/replace jet tip	As needed
	Service flame photomeric detector	As needed
Infrared (IR)	Change desiccant	Every 6 months
	Electronics maintenance	Every 6 months
UV	Clean and align optics	Annually
	Replace lamp	As needed
	Calibrate	Weekly
pH meter	Calibrate	Daily
	Check fluid in probe	Daily
DO meter	Clean and replace membrane and HCl solution	Daily
	Calibrate	Daily
Balance	Calibrate	Daily
	Maintenance	Annually
Ovens	Temperature checks	Daily
Refrigerators and freezers	Temperature checks	Daily
Chemical oxygen demand (COD) heating block	Check temperature with NBS thermometer	As needed
Conductivity meter	Standardize with KCl	Daily
	Check probe visually	Daily

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.

4.6 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.

4.6.1 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 USEPA CLP acceptance criteria as a minimum. Often, in-house criteria are more stringent than those 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.

4.6.2 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.

4.6.3 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 %R 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, not 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.

4.6.4 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 MS and the matrix spike duplicate (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 RPD between the MS and the MSD is also calculated.

The observed %R and RPD between the MS and the MSD is used to determine the accuracy and the precision of the analytical method for the sample matrix. If the %R 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.

4.6.5 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.

4.6.6 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.

4.6.7 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.

4.6.8 Other QC Samples

Under some sampling analysis, additional QC 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 %R is calculated with no likelihood of matrix effect. For many contracts, an externally provided Laboratory Computer System (LCS) sample (USEPA) serves as a blank/spike sample.

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

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

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

4.6.9 Control Charts

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

4.6.10 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% 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 CAR. The CAR prompts the analyst to initiate investigation and corrective action.

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

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

4.6.11 Instrument Detection Limits, Method Detection Limits, and Reporting Limits

4.6.11.1 Instrument Detection Limits

Instrument Detection Limits (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 SD is calculated for each set of seven replicates and the average of the SDs is obtained. This average is multiplied by 3 to give the IDL.

4.6.11.2 Method Detection Limits

MDL is the minimum concentration of a substance that can be measured and reported with 99% 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 code of federal regulation (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 MDL. 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.

$$MDL = t \times SD \tag{10}$$

where:

t = the student t value for a 99% confidence interval
SD = standard deviation of the replicate analyses

4.6.11.3 Practical Quantitation Limit

PQL is the minimum concentration of a substance of interest that can be measured and reported with a specific degree of confidence. The PQL is determined as 12 times the SD that is derived from the procedures used to determine MDL.

$$PQL = 12 \times SD$$

4.6.11.4 Reporting Limits

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

4.7 PERFORMANCE AND SYSTEM AUDITS

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

4.7.1 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.

4.7.2 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 that covers all sections of the laboratory. An audit report is issued within 2 weeks of completion. The field site manager is responsible for coordinating all responses to the audit finding and for following up on the required corrective action. A follow-up audit is made

when deemed necessary by the by the field site manager or the laboratory manager. A QA 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 follow-up 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.

4.8 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.

QA 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.

4.9 DATA FORMAT

4.9.1 Introduction

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

4.9.2 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.

4.9.3 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.

4.9.4 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.

4.9.5 Data Reduction Formulas

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

$$Y' = a + bx \tag{11}$$

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:

$$\frac{Area_{Target} \ x \ Amount_{IS}}{Area_{IS} \ x \ Response \ Factor} \tag{12}$$

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

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}}\right)\left(\frac{A_{IS}^{standard}}{A_{IS}^{sample}}\right)\left(amt_x^{standard}\right)\left(\frac{P}{T}\right)\left(\frac{amt_{IS}^{Sample}}{Amt_{IS}^{standard}}\right) \tag{13}$$

where:

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

For calculations using an external standard:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}} \right) \left(C_x^{standard} \right) \left(\frac{V}{T} \right) \quad (14)$$

where:

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

4.10 DATA STORAGE AND ARCHIVING PROCEDURES

Data from GCs 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.