EA Engineering, Science, and Technology, Inc.

405 S. Highway 121, Suite C-100
Lewisville, Texas 75067
Telephone: 972-315-3922
Fax: 972-315-5181
www.eaest.com

30 September 2014

Mr. Brian Mueller
Task Order Monitor
U.S. Environmental Protection Agency (EPA) Region 6
1445 Ross Avenue, Suite 1200
Dallas, Texas 75202-2733

Subject: **Field Sampling Plan Addendum 2**
Falcon Refinery Superfund Site
Remedial Investigation/Feasibility Study
EPA Region 6 Remedial Action Contract 2
Contract: EP-W-06-004
Task Order: 0088-RICO-06MC

Dear Mr. Mueller:

EA Engineering, Science, and Technology, Inc. (EA) is enclosing one hard copy and one electronic copy of the Final Field Sampling Plan Addendum 2 on compact disc for the above-referenced Task Order to EPA. This addendum updates the original Field Sampling Plan to incorporate samples collected during the October 2014 sampling event. Additional hard copies and electronic copies are being submitted to the recipients listed below.

If you have any questions regarding this submittal, please call me at (972) 315-3922.

Sincerely yours,
EA ENGINEERING, SCIENCE, AND TECHNOLOGY, INC.

Robert M. Owens
Project Manager

Enclosure

9598333

cc: Michael Pheeny, EPA Contracting Officer (letter only)
Rena McClurg, EPA Project Officer (letter only)
Anna Milburn, EPA Ecological Risk Assessor
Kenneth Shewmake, EPA Ecological Risk Assessor
Phillip Winsor, Texas Commission on Environmental Quality (TCEQ) RPM
Vickie Reat, TCEQ Ecological Risk Assessor
Jessica White, National Oceanic and Atmospheric Association, RRC Region 6
Clare Lee, U.S. Fish and Wildlife Service (USFWS) Contaminant Biologist
Barry Forsythe, USFWS
Ron Brinkley, USFWS Contaminant Biologist
Don Pitts, Texas Parks and Wildlife Department (TPWD) Program Director
Andy Tirpak, TPWD NRDA Trustee
Jane Sarosdy, Texas General Land Office (TGLO) Director, NRDA Trustee
Tommy Mobley, TGLO Tech. Program Manager
Tim Startz, EA Program Manager (letter only)
File

TRANSMITTAL OF DOCUMENTS FOR ACCEPTANCE BY EPA		DATE: 30 September 2014	TRANSMITTAL NO.: **0020**
TO: **Mr. Brian Mueller** **U.S. Environmental Protection Agency (EPA) Region 6**		FROM: **Mr. Robert Owens** **EA Engineering, Science, and Technology, Inc.**	
SUBTASK NO.	DELIVERABLE	NO. OF COPIES	
1.2.1	Field Sampling Plan Addendum 2 Falcon Refinery Superfund Site Remedial Investigation/Feasibility Study	EPA - 3 hard copies, 3 electronic copies on compact disc (CD) National Oceanic and Atmospheric Admnistration (NOAA) - 1 hard copy, 1 electronic copy on CD Texas Commission on Environmental Quality (TCEQ) - 2 hard copies, 2 electronic copies on CD Texas General Land Office (TGLO) - 2 hard copies, 2 electronic copies on CD Texas Parks and Wildlife Department (TPWD) - 2 hard copies, 2 electronic copies on CD U.S. Fish and Wildlife Service (USFWS) - 3 hard copies, 3 electronic copies on CD	
ACCEPTANCE ACTION			
DOCUMENTS FOUND ACCEPTABLE (LIST BY SUBTASK NO.)		NAME/TITLE/SIGNATURE OF REVIEWER DATE	

Field Sampling Plan Addendum No. 2

Remedial Investigation/Feasibility Study

Falcon Refinery Superfund Site
Ingleside, San Patricio County, Texas
EPA Identification No. TXD086278058

Remedial Action Contract 2 Full Service
Contract: EP-W-06-004
Task Order: 0088-RICO-06MC

Prepared for

U.S. Environmental Protection Agency
Region 6
1445 Ross Avenue
Dallas, Texas 75202-2733

Prepared by

EA Engineering, Science, and Technology, Inc.
405 S. Highway 121
Building C, Suite 100
Lewisville, Texas 75067
(972) 315-3922

September 2014
Revision: 00
EA Project No. 14342.88

Field Sampling Plan Addendum No. 2

Falcon Refinery Superfund Site
Ingleside, San Patricio County, Texas
EPA Identification No. TXD086278058

Remedial Action Contract 2 Full Service
Contract: EP-W-06-004
Task Order: 0088-RICO-06MC

30 September 2014

Tim Startz, PMP
EA Program Manager

Date

30 September 2014

David S. Santoro, P.E., L.S.
EA Quality Assurance Officer

Date

OCTOBER 2, 2014

Brian Mueller
U.S. Environmental Protection Agency Region 6 Task Order Monitor

Date

LIST OF FIGURES

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1	AOC-1N Sample Locations
2	AOC-1S Sample Locations
3	AOC-2 Sample Locations
4	AOC-3 Sample Locations
5	AOC-4 Sample Locations
6	AOC-5 Sample Locations

LIST OF ACRONYMS AND ABBREVIATIONS

AOC	Area of Concern
COPC	Contaminant of potential concern
CSM	Conceptual Site Model
EA	EA Engineering, Science, and Technology, Inc.
EPA	U.S. Environmental Protection Agency
ERA	Ecological risk assessment
FS	Feasibility Study
FSP	Field Sampling Plan
HHRA	Human health risk assessment
QC	Quality control
RI	Remedial Investigation
site	Falcon Refinery Superfund Site
SVOC	Semivolatile organic compound
TDS	Total dissolved solids
VOC	Volatile organic compound

DISTRIBUTION LIST

U.S. Environmental Protection Agency

Name: Michael Pheeny
Title: EPA Region 6 Contracting Officer (Letter Only)

Name: Rena McClurg
Title: EPA Region 6 Project Officer (Letter Only)

Name: Brian Mueller
Title: EPA Region 6 Task Order Monitor

Name: Anna Milburn
Title: EPA Region 6 Ecological Risk Assessor

Name: Kenneth Shewmake
Title: EPA Region 6 Ecological Risk Assessor

Texas Commission on Environmental Quality

Name: Phillip Winsor
Title: Project Manager

Name: Vickie Reat
Title: Ecological Risk Assessor

Other State/Federal Natural Resource Trustees

Name: Jessica White
Title: National Oceanic and Atmospheric Association, Regional Resource Coordinator, Region 6

Name: Clare Lee
Title: U.S. Fish and Wildlife Services (USFWS) Contaminant Biologist

Name: Barry Forsythe
Title: USFWS

Name: Ron Brinkley
Title: USFWS Contaminant Biologist

Name: Don Pitts
Title: Texas Parks and Wildlife Department (TPWD) Program Director

Name: Andy Tirpak
Title: TPWD Natural Resource Damage Assessment (NRDA) Trustee

Name: Jane Sarosdy
Title: Texas General Land Office (TGLO) Director, NRDA Trustee

Name: Tommy Mobley
Title: TGLO Technical Program Manager

EA Engineering, Science, and Technology, Inc.

Name: Tim Startz
Title: Program Manager (Letter Only Via E-mail)

Name: Robert Owens
Title: Project Manager

Name: File
Title: EA Document Control File

1. PROJECT DESCRIPTION AND OBJECTIVES

EA Engineering, Science, and Technology, Inc. (EA) has been authorized by the U.S. Environmental Protection Agency (EPA), under Remedial Action Contract Number EP-W-06-004, Task Order 0088-RICO-06MC, to conduct a Remedial Investigation/Feasibility Study (RI/FS) at the Falcon Refinery Superfund Site (site). EA has prepared this Field Sampling Plan (FSP) Addendum No. 2 to address additions to the original FSP submitted to the EPA on 4 February 2012. These additions have been made to reflect the October 2014 sampling event. Appendix A has been modified to add the Method 1669 sampling technique which will be used to collect surface water samples in Area of Concern (AOC) -5. The sampling design matrix for investigative samples in Appendix B of the FSP has been updated and is included in this FSP Addendum. The figures from the original FSP have been updated for AOCs 1 through 5 to reflect the additions and are included in this FSP Addendum. The sections of the original FSP that have changed are discussed below. The section numbers correspond to the section numbers in the original FSP.

1.3 PROJECT OBJECTIVES

The key components for the RI/FS have been changed as noted below:

- **Ground Water Sampling**
  - Up to 16 additional ground water samples will be collected from permanent monitoring wells to determine the nature and extent of ground water contaminants of potential concern (COPCs). The data will be used in the Human Health Risk Assessment (HHRA) and Ecological Risk Assessment (ERA). Data collected during the onsite ground water investigation will also be used to update the pathway and receptor analysis presented in the conceptual site model (CSM), if necessary.
  - The additional ground water samples will be analyzed for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), total dissolved solids (TDS), and total and dissolved metals.
- **Surface Water Sampling**
  - Up to 10 additional surface water samples will be collected from AOC-5 to define the nature and extent of COPCs, provide data to be used in the HHRA and ERA, and to update the pathway and receptor analysis presented in the CSMs, if necessary.
  - The additional surface water samples will be collected using sampling protocol EPA Method 1669 in order to provide reliable data of trace metals (Appendix A).
  - The additional surface water samples will be analyzed for VOCs, SVOCs, TDS, and trace metals including antimony, arsenic, cadmium, chromium (III), chromium (VI), copper, lead, mercury, nickel, selenium, silver, thallium, and zinc.

2. METHODOLOGY

2.1 SAMPLE COLLECTION

2.1.3 Surface Water Sampling

Surface water samples to be analyzed for total and dissolved metals will be collected and filtered using EPA Method 1669 (Appendix A). This sample collection method is accompanied by the 1600 series methods listed in Table 4. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.

2.3 SAMPLE CONTAINER, VOLUME, PRESERVATION, AND HOLDING TIME REQUIREMENTS

The ground water and surface water samples are being analyzed by EA subcontractor laboratories. Therefore, Table 4 of the original FSP has been modified as follows.

TABLE 4 REQUIRED VOLUME, CONTAINERS, PRESERVATIVES, AND HOLDING TIMES

Parameter	Method	Volume and Container	Preservatives	Holding Time [a]
Investigative Water Samples				
Total TAL Metals	EPA SW6020A	One 1-liter HDPE bottle	Nitric acid to pH<2; store at <6°C	180 days
Dissolved TAL Metals	EPA SW6020A	One 1-liter HDPE bottle	Nitric acid to pH<2; store at <6°C; Field filtered	180 days
Total Mercury	EPA SW7470A	One 1-liter HDPE bottle	Nitric acid to pH<2; store at <6°C	28 days
Dissolved Mercury	EPA SW7470A	One 1-liter HDPE bottle	Nitric acid to pH<2; store at <6°C Field filtered	28 days
Total Trace Metals (Surface Water)	EPA 1631E (Mercury) EPA 1638 (Antimony) EPA 1640 (Arsenic,	One 1-liter PETG bottle (EPA 1640) One 250-mL HDPE bottle	Nitric acid to pH<2; store at <6°C	180 days/ 28 days for mercury

Parameter	Method	Volume and Container	Preservatives	Holding Time [a]
	Cadmium, Chromium, Copper, Lead, Nickel, Selenium, Silver, Thallium, Zinc) SM3500 – Chromium VI (Chromium III by difference)	(EPA 1638) One 250-mL PETG bottle (EPA 1631) One 250-mL HDPE bottle with NaOH field preservative (SM3500)		
Dissolved Trace Metals (Surface Water)	EPA 1631E (Mercury) EPA 1638 (Antimony) EPA 1640 (Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Selenium, Silver, Thallium, Zinc) SM3500 – Chromium VI (Chromium III by difference)	One 1-liter PETG bottle (EPA 1640) One 250-mL HDPE bottle (EPA 1638) One 250-mL PETG bottle (EPA 1631) One 250-mL HDPE bottle with NaOH field preservative (SM3500)	Nitric acid to pH<2; store at <6°C Field filtered using a 0.45 micron capsule filter	180 days/ 28 days for mercury
VOCs	EPA 8260B	Three 40-mililiter amber glass VOA vials	HCl to pH <2; store at <6°C	14 days
SVOCs	EPA 8270D	One 1-liter amber glass bottle	Store at <6°C	7 days
TDS	SM 2540C	One 1-liter HDPE bottle	Store at <6°C	7 days

NOTE:

a Holding time is measured from the time of sample collection to the time of sample extraction and/or analysis.
HDPE = high-density polyethylene
NA = Not applicable
NaOH = Sodium Hydroxide
PETG = Polyethylene terephthalate
SM = Standard Methods for the Examination of Water and Wastewater
SVOC = Semivolatile organic compound
SW = USEPA SW-846 – Test Methods for Evaluating Solid Waste, Third Edition and Updates
TAL = Target Analyte List
TDS = Total dissolved solids
VOA = Volatile organic analyte
VOC = Volatile organic compound

3. FIELD IMPLEMENTATION

3.1 AOC-1

Figures 1 and 2 identify the updated ground water sample locations for AOC-1N and AOC-1S, respectively. The following samples will be collected at AOC-1N: MW-01, MW-02, MW-03, MW-04, and MW-05. The following samples will be collected at AOC-1S: MW-06, MW-07, MW-08, MW-09, MW-10, MW-11, and MW-12. The sample design matrix in Appendix B has been updated to identify the number of samples that will be collected during the October 2014

sampling event including field quality control (QC) samples, and the associated analyses to be performed by the subcontractor laboratory.

3.2 AOC-2

Figure 3 identifies the updated ground water sample locations for AOC-2. One sample will be collected at MW-13. The sample design matrix in Appendix B has been updated to identify the number of samples that will be collected during the October 2014 sampling event including field QC samples, and the associated analyses to be performed by the subcontractor laboratory.

3.3 AOC-3

Figure 4 identifies the updated ground water sample locations for AOC-3. The samples will be collected at MW-15 and MW-16. The sample design matrix in Appendix B has been updated to identify the number of samples that will be collected during the October 2014 sampling event including field QC samples, and the associated analyses to be performed by the subcontractor laboratory.

3.4 AOC-4

Figure 5 identifies the updated ground water sample locations for AOC-4. One sample will be collected at MW-17. The sample design matrix in Appendix B has been updated to identify the number of samples that will be collected during the October 2014 sampling event including field QC samples, and the associated analyses to be performed by the subcontractor laboratory.

3.5 AOC-5

Figure 6 identifies the updated surface water sample locations for AOC-5. Ten surface water samples will be collected at AOC-5 (SW5-01 through SW5-10). The sample design matrix in Appendix B has been updated to identify the number of samples that will be collected during the October 2014 sampling event including field QC samples, and the associated analyses to be performed by the subcontractor laboratory.

3.6 AOC-6

No samples will be collected from AOC-6.

3.7 AOC-7

No samples will be collected from AOC-7.

3.8 BACKGROUND LOCATIONS

No background samples will be collected during the October 2014 sampling event.

Figures

N

0 100 200

Feet

Legend:

Proposed Monitoring Well Location

Area of Concern 1 Boundary

Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 1
AOC-1 North Sample Locations
Field Sampling Plan Addendum 2

2014-09-24 R:\Federal\EPA\RAC II\0088-Falcon Refinery RIFS\GIS\MXDs\FSP_Addendum\20140908\AOC1_N_FieldMap.mxd EA-Dallas jschwertz

N

0 100 200

Feet

Legend:

Proposed Monitoring Well Location

Area of Concern 1 Boundary

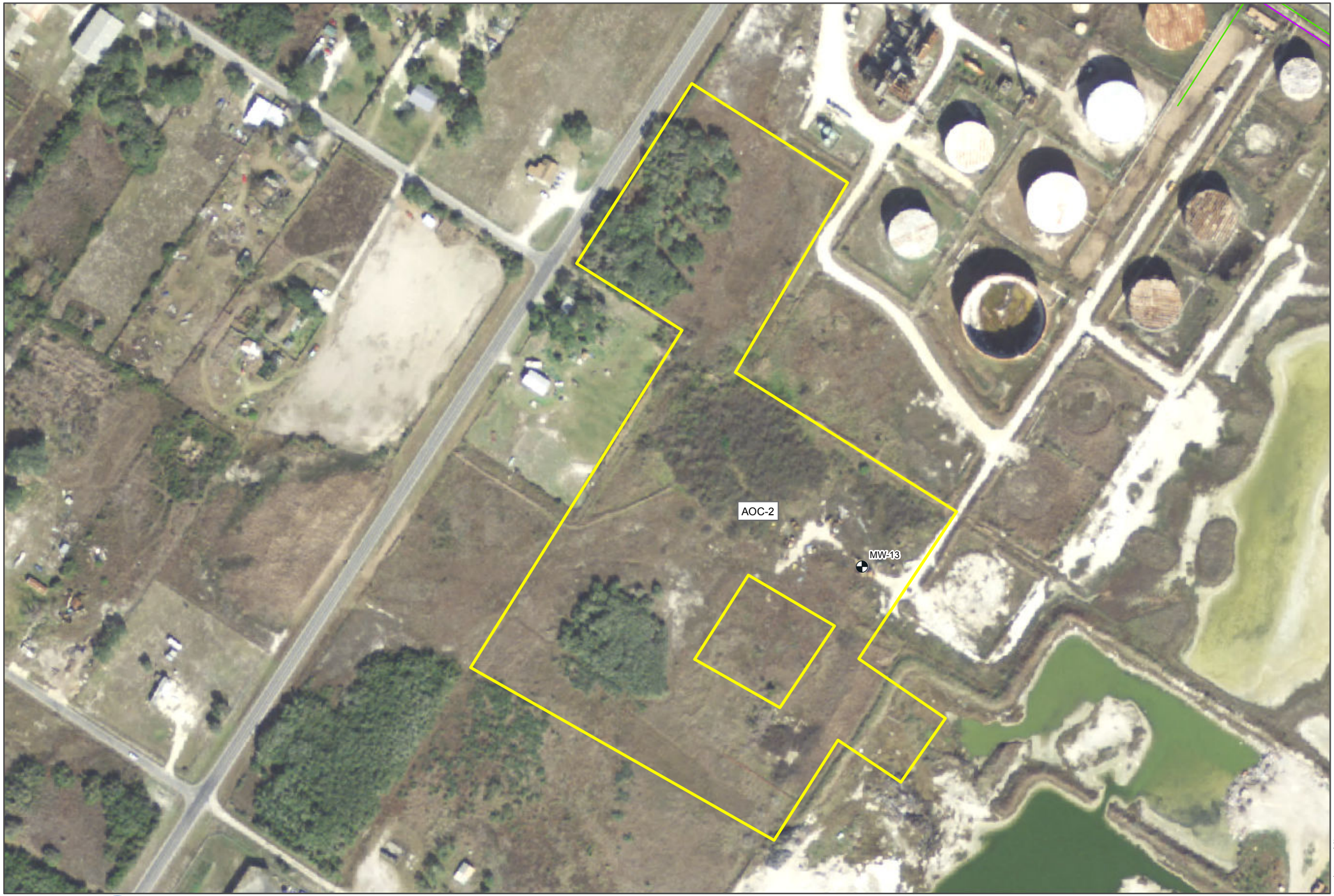
Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 2
AOC-1 South Sample Locations
Field Sampling Plan Addendum 2

2014-09-24 R:\Federal\EPA\RAC II\0088-Falcon Refinery RIFS\GIS\MXDs\FSP_Addendum\20140908AOC1_S_FieldMap.mxd EA-Dallas jschwertz



N

0 100 200

Feet

Legend:

Proposed Monitoring Well Location

Area of Concern 2 Boundary

Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 3
AOC-2 Sample Locations
Field Sampling Plan Addendum 2

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N

0 250 500

Feet

Legend:

Proposed Monitoring Well Location

Area of Concern 3 Boundary

Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 4
AOC-3 Sample Locations
Field Sampling Plan Addendum 2

2014-09-24 R:\Federal\EPA\RAC II\0088-Falcon Refinery RIFS\GIS\MXDs\FSP_Addendum2014\09\AOC3_FieldMap.mxd EA-Dallas jschwertz

N

0 50 100

Feet

Legend:

Proposed Monitoring Well Location

Area of Concern 4 Boundary

Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 5
AOC-4 Sample Locations
Field Sampling Plan Addendum 2

2014--09-24 R:\Federal\EPA\RAC II\0088-Falcon Refinery RI\FS\GIS\MXD\FSP_Addendum\201409\AOC4_FieldMap.mxd EA-Dallas jschwertz

N

0 150 300

Feet

Legend:

- Proposed Sediment/Surface Water Sample Location
- Area of Concern 5 Boundary

Source: AOC and pipeline locations from TRC, dated, March 10, 2011

Image Source: 2009 Texas Orthoimagery Program, Texas Strategic Mapping Program, TNRIS, 2009

Falcon Refinery Superfund Site
Ingleside, San Patricio County,Texas

Figure 6
AOC-5 Sample Locations
Field Sampling Plan Addendum 2

2014-09-24 R:\Federal\EPA\RAC II\0088-Falcon Refinery RI\FS\GIS\MXDs\FSP_Addendum\201409\AOC5.mxd EA-Dallas jschwertz

Appendix A

Standard Operating Procedures

Low Level Metals Surface Water Sampling Via Peristaltic Pump:

The USEPA 1600 series analytical methods for ultra-trace metals, and the accompanying sampling procedures, USEPA Method 1669− Sampling Ambient Water for Trace Metals at USEPA Water Quality Criteria Levels (USEPA 1996) will be used for surface water sampling. The sampling method establishes equipment requirements, procedures for cleaning equipment and containers before sampling, sampling procedures under various conditions, collecting blank samples, equipment blank and duplicate requirements, and storing samples to ensure that sample contamination does not occur during collection, transport, and analysis. Sample collection USEPA Method 1669 is commonly known as "Clean Hands / Dirty Hands."

All surface water samples will be collected from a boat using a laboratory certified trace metal clean peristaltic pump, laboratory certified trace metal clean pre-cleaned peristaltic pump tubing, and a laboratory certified trace metal clean pre-cleaned filter when necessary.

Grab samples will be collected using a peristaltic pump, and pre-cleaned peristaltic tubing. Once the sample has reached the end of the outlet tubing, it will be transferred into laboratory-supplied containers using the "Clean Hands / Dirty Hands" method (USEPA Method 1669-Sample collection) and shipped to the laboratory for analysis. Field measurements of pH, temperature, DO, turbidity, specific conductivity, and ORP will be made prior to the start of the grab sample process at each sample location. (Field measurements will not be utilized as stabilization parameters.) In addition, one set of equipment blanks (EB) (filtered and unfiltered) will be obtained prior to sample collection of a surface water sample by using two types of tubing: Teflon®-lined fluorinated ethylene propylene (FEP) tubing will be used for the inlet tubing placed into the sample water and which is connected to the inlet side of the peristaltic pump-head tubing. FEP tubing will also be used for the discharge tubing connected to the discharge side of the peristaltic pump-head tubing, which brings the sample water to the sample container; the peristaltic pump-head tubing made of silicon (flex tubing) will be placed into and clamped in place by the peristaltic pump-head. The flex tubing will connect both the FEP inlet tubing and the FEP discharge tubing; allowing for the peristaltic pump to create suction and push the sample water through the FEP tubing.

Clean Hands / Dirty Hands – Sample Set-up:

Upon arrival at the sampling location, one member of the sampling team will be designated Dirty Hands and another member will be designated Clean Hands. The individual designated as Clean Hands handles all operations involving contact with the sample collection tubing and sample container. Dirty Hands is responsible for preparation of the peristaltic pump and sampling equipment. The sampling technique will be as follows:

- If an EB is being collected at this location, see EB directions below and do not proceed. If an EB is not being collected, continue.

- Using a boat, sample location is approached from downstream or downwind. Avoid collecting surface water sample from water disturbed by boat traffic. Collect sample facing upstream or upwind.

- Upon arriving to the sample location collect field measurements of pH, temperature, DO, turbidity, specific conductivity, and ORP at sample location.

- Clean Hands and Dirty Hands put on gloves. Clean Hands and Dirty Hands will replace gloves

prior to starting a new task.

- Clean Hands and Dirty Hands cover bow casting area and starboard areas of the boat with clear polyethylene. Dirty Hands places peristaltic pump at bow of boat (leaving pump in polyethylene bag). Peristaltic pump external batteries will be placed to the stern of the boat.

- Clean Hands and Dirty Hands don Tyvek® coverall suits, dust masks, and sampling gloves (in that order).

- Clean Hands opens a clear polyethylene bag.

- Dirty Hands places PVC boom into the clear polyethylene bag opened by Clean Hands. Clean Hands wraps and secures bag to boom with zip-ties. Clean Hands places boom into a second clear polyethylene bag (cover bag) and lays boom at bow of boat. A new polyethylene bag will be added prior to sampling at each location.

- Dirty Hands removes peristaltic pump from bag.

- Dirty Hands opens the outside bag of the double-bagged peristaltic tubing kit (48 inch (in.) inlet tubing, 12 in. flex tubing, 36 in. discharge tubing). Clean Hands opens inside bag, removes the tubing kit and feeds flex tubing through the peristaltic pump-head, being careful not to touch any pump components. Dirty Hands locks the flex tubing in place by flipping the tubing lock lever.

- Clean Hands attaches the inlet tubing to the boom and extends it from the bow of the boat over the surface water. The inlet tubing should extend 12" from the end of the boom and should be the only equipment in the water. To keep the boom from moving, use a 2.5 gallon jug of distilled water wrapped in a clear polyethylene bag and place on the end of the boom in the boat.

- Once the inlet tubing is just below the surface of the surface water, see below for purging directions of **unfiltered surface water samples** and **filtered surface water samples**.

For collection of **unfiltered surface water samples**

- Dirty Hands turns on the peristaltic pump and purges tubing kit. Collect purge water into appropriate waste container. Ensure tubing kit is purged with a minimum of 500 mL of surface water prior to the collection of the unfiltered surface water samples. Peristaltic pump will be in the off position when purging is not taking place. Sample collection of the unfiltered surface water samples can take place once the tubing kit is purged.

- See Clean Hands / Dirty Hands – Sample Collection directions below if ready to collect surface water sample.

For collection of **filtered surface water samples**

- Dirty Hands turns on the peristaltic pump and purges tubing kit and filter. Collect purge water into appropriate waste container. Ensure tubing kit and filter are purged with a minimum of 500 mL of surface water prior to the collection of the filtered surface water samples. Peristaltic pump will be in the off position when purging is not taking place. Sample collection of the filtered surface water samples can take place once the tubing kit and filter is purged.

- See Clean Hands / Dirty Hands – Sample Collection directions below if ready to collect surface water sample.

Clean Hands / Dirty Hands – Sample Set-up when collecting Equipment Blank:

- Clean Hands and Dirty Hands put on gloves.

- Clean Hands and Dirty Hands cover bow casting area of the boat with clear polyethylene. Dirty Hands places peristaltic pump at bow of boat (leaving pump in polyethylene bag).

- Clean Hands and Dirty Hands don Tyvek® coverall suits, dust masks, and sampling gloves (in that order).

- Dirty Hands removes peristaltic pump from bag.

- Dirty Hands opens the outside bag of the double-bagged peristaltic tubing kit (48 inch (in.) inlet tubing, 12 in. flex tubing, 36 in. discharge tubing). Clean Hands opens inside bag, removes the tubing kit and feeds flex tubing through the peristaltic pump-head, being careful not to touch any pump components. Dirty Hands locks the tubing in place by flipping the tubing lock lever.

- Dirty Hands opens the outside bag of the double bagged container of reagent grade blank water. Clean Hands accesses the, opens it, and places the inlet tubing into the reagent grade blank water. Once the inlet tubing has been placed into the reagent grade blank water container, see below for purging directions of **unfiltered equipment blank samples** and **filtered equipment blank samples**.

For collection of **unfiltered equipment blank samples**

- Dirty Hands turns on the peristaltic pump and purges tubing kit, collect purge water into appropriate waste container. Ensure tubing kit is purged with a minimum of 500 mL of reagent grade water prior to the collection of unfiltered equipment blank samples. Peristaltic pump will be in the off position when purging is not taking place. Sample collection of the unfiltered equipment blank samples can take place once the tubing kit is purged.

- See Clean Hands / Dirty Hands – Sample Collection directions below if ready to collect unfiltered equipment blank sample.

For collection of **filtered equipment blank samples**

- Collect filtered equipment blank samples after the unfiltered equipment blank samples are collected. Use the same tubing kit from which the unfiltered equipment blank samples were collected.

- Dirty Hands opens the outside bag of the double bagged filter. Clean Hands opens the inside bag and places the 0.45-micron filter onto the discharge end of the discharge tubing.

- Dirty Hands turns on the peristaltic pump and purges tubing kit and filter, collect purge water into appropriate waste container. Ensure tubing kit and filter are purged with a minimum of 500 mL of reagent grade water prior to the collection of the filtered equipment blank samples. Peristaltic pump will be in the off position when purging is not taking place. Sample collection of the filtered equipment blank samples can take place once the tubing kit and filter are purged.

- Note: At the end of the collection of the filtered equipment blank samples, the filter is re-bagged for use when the filtered surface water sample is collected at that same location. Dirty Hands retrieves the double-bagged filter bag, opens the outside bag containing the inside bag for the filter. Clean Hands opens the inside bag for the filter, places filter into inside bag and reseals the inside bag. Dirty Hands places the double bagged filter in appropriate storage container.

- See Clean Hands / Dirty Hands – Sample Collection directions below if ready to collect filtered equipment blank sample.

Clean Hands / Dirty Hands – Sample Collection:

As with the sample set-up discussed above, one member of the sampling team will be designated Dirty Hands and another member will be designated Clean Hands. The individual designated as Clean Hands handles all operations involving contact with the sample container, sample tubing and transfer of the sample from the discharge tubing to the sample container. Dirty Hands is responsible for preparation of the peristaltic pump and equipment. The sampling technique will be as follows:

- Dirty Hands turns off the pump following purging of sample tubing.

- Dirty Hands opens the outside bag of the double-bagged sample containers. Clean Hands opens inside bag, and removes the sample container.

- Dirty Hands reseals outside bag of the sample container, returns it to the appropriate storage container, and closes container lid.

- Clean Hands removes sample container lid, ensures discharge tubing end is over sample container opening, and instructs Dirty Hands to turn pump on. While filling the sample container, Clean Hands holds the container lid upside down. Peristaltic pump will be in the off position when sampling is not taking place.

- Once sample container is filled, Clean Hands instructs Dirty Hands to turn pump off. Clean Hands replaces the container lid.

- Dirty Hands retrieves double-bagged sample container bag from storage container. Dirty Hands opens the outside bag containing the inside bag for the sample container.

- Clean Hands opens the inside bag for the sample container, places sample container into inside bag and reseals the inside bag.

- Dirty Hands reseals outside bag of the sample container and places the double bagged sample container into a clean, ice-filled sample cooler.

Surface Water QA/QC Samples

Field Duplicates—For grab samples, field duplicates will be collected using rapid succession (once the native sample container is filled the duplicate sample container will be filled). All sample setup and collection procedures will be the same for surface water samples and for field duplicates. Field duplicates will be taken at a rate of 1 per 10 samples.

Matrix Spike/Matrix Spike Duplicate—MS/MSD samples will be collected using the same procedures used to collect the original sample. MS/MSD samples for dissolved metals will be extracted from the native sample bottle and do not require additional volume to be collected with the exception of EPA 1640, which will require one (1) extra 1- liter sample container. MS/MSD samples will be collected at a rate of 1 per 20 samples.

Equipment Blanks—EBs will be collected by passing reagent grade blank water through all certified clean tubing (tubing kit) and clean tubing/filter. EBs will be collected once during the sampling event, due to the laboratory providing certified clean trace metal data for the tubing kits and filters. Both unfiltered and filtered samples will be collected for the EB.

Container Blanks—CBs will not be collected, due to the laboratory providing certified clean trace metal data for the sample containers provided.

Method 1669

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

July 1996

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

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Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Further Information

For further information, contact:

W.A. Telliard
Engineering and Analysis Division (4303)
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460
Phone: 202/260–7134
Fax: 202/260–7185

Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489–8190

Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.

1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr^{+3}	16065-83-1
Chromium (VI)	Cr^{+6}	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.

1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.

1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

1.6 Clean and Ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques (Reference 10).

1.7 This sampling method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 11).

1.8 Method 1669 is "performance-based"; i.e., an alternate sampling procedure or technique may be used, so long as neither samples nor blanks are contaminated when following the alternate procedures. Because the only way to measure the performance of the alternate procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 9.2 provides additional details on the tests and documentation required to support equivalent performance.

1.9 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.

1.10 The procedures in this method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 Summary of Method

2.1 Before samples are collected, all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory or cleaning facility is responsible for generating an acceptable equipment blank to demonstrate that the sampling equipment and containers are free from trace metals contamination before they are shipped to the field sampling team. An acceptable blank is one that is free from contamination below the minimum level (ML) specified in the referenced analytical method (Section 9.3).

2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

NOTE: *EPA has found that, in some cases, it may be possible to empty the weak acid solution from the bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).*

2.3 The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water (Section 7.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least

one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots are processed as described in Section 9.6.

2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.

2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.

2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.

2.8 Sampling

2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.

2.8.2 Samples may be collected while working from a boat or while on land.

2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.

2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.

2.9 Samples for dissolved metals are filtered through a 0.45 µm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.

2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.

2.11 Sampling activities must be documented through paper or computerized sample tracking systems.

3.0 Definitions

3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

3.2 Definitions of other terms are given in the Glossary (Section 15.0) at the end of this method.

4.0 Contamination and Interferences

4.1 Contamination Problems in Trace Metals Analysis

4.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 12). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.2 Contamination Control

4.2.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.

4.2.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.

4.2.1.2 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements. Requirements and suggestions for protecting the

Apparatus are given in this sampling method and in the methods referenced in Table 1.

4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse

in or out of other materials, resulting either in contamination or low-biased results (Reference 3). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

4.2.2.3.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 13).

4.2.2.3.3 Serialization—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.

4.2.2.3.4 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.2.2.3.5 Details for recleaning the Apparatus between collection of individual samples are provided in Section 10.0.

4.2.2.4 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.2.2.4.1 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the

highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).

4.2.2.4.2 Contamination by samples—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.

4.2.2.4.3 Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health

hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling. It is also suggested that the organization responsible perform personal hygiene monitoring of each sampling team member who uses this method and that the results of this monitoring be made available to the member.

5.2 Operating in and around waterbodies carries the inherent risk of drowning. Life jackets must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.

5.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

6.0 Apparatus and Materials

NOTE: *Brand names, suppliers, and part numbers are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.*

6.1 All sampling equipment and sample containers must be precleaned in a laboratory or cleaning facility, as described in the methods referenced in Table 1, before they are shipped to the field site. Performance criteria for equipment cleaning is described in the referenced methods. To minimize difficulties in sampling, the equipment should be packaged and arranged to minimize field preparation.

6.2 Materials such as gloves (Section 6.7), storage bags (Section 6.8), and plastic wrap (Section 6.9), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.

6.3 Sample Bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. If mercury is a target analyte, fluoropolymer or glass bottles should be used. Refer to the methods referenced in Table 1 for bottle cleaning procedures.

6.3.1 Cleaned sample bottles should be filled with 0.1% HCl (v/v). In some cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

6.3.2 Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. Preparation of the devices in the field should be done within the glove bag (Section 6.6). Regardless of design, sampling devices must be constructed of nonmetallic material (Section 4.2.2.3.1) and free from material that contains metals. Fluoropolymer or other material shown not to

adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.

6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.

6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.

6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).

6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.

6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick

fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.

6.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, Section 6.15) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 14). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.

6.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.

6.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (Reference 14).

6.5.2 Continuous-flow sampler (References 16-17)—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

6.5.2.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

6.5.2.2 The sampling team assembles the system in the field as described in Section 8.2.8. System components include an optional polyethylene pole to remove sampling personnel from the immediate vicinity of the sampling point and the pump, tubing, filter, and filter holder listed in Sections 6.14 and 6.15.

6.6 Field-Portable Glove Bag—I2R, Model R-37-37H (nontalc), or equivalent. Alternately, a portable glove box may be constructed with a nonmetallic (PVC pipe or other suitable material) frame and a frame cover made of an inexpensive, disposable, nonmetallic material (e.g., a thin-walled polyethylene bag) (Reference 7).

6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.

6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.

6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.

6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).

6.9 Plastic Wrap—Clean, colorless polyethylene.

6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.

6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.

6.12 Wind Suit—Pamida, or equivalent.

NOTE: *This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.*

6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.

6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.

6.13 Boat

6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.

6.13.1.2 Samples should be collected upstream of boat movement.

6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:

6.13.2.1 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement.

6.13.2.2 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution.

6.13.2.3 The boat should be frequently visually inspected for possible contamination.

6.13.2.4 After sampling, the boat should be returned to the laboratory or cleaning facility, cleaned as necessary, and stored away from any sources of contamination until next use.

6.14 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.

6.14.1 Filter—0.45 µm, 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175, or equivalent.

6.14.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps.

NOTE: *A filter holder may not be required if one or a few samples are to be collected. For these cases, it may only be necessary to attach the filter to the outlet of the tubing connected to the pump.*

6.15 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

NOTE: *Equivalent pumps may include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.*

6.15.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.

6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.

6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).

6.17.2 Filters—0.4 µm, 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).

6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.

6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 µL)

6.17.5 Wrist-action shaker—Burrel or equivalent.

6.17.6 Fluoropolymer wash bottles—One filled with reagent water (Section 7.1) and one filled with high- purity 10% HCl (Section 7.4.4), for use in rinsing forceps and pipet tips.

7.0 Reagents and Standards

7.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.

7.2 Nitric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.

7.3 Sodium Hydroxide—Concentrated, 50% solution for use when field-preserving samples for hexavalent chromium determinations (Section 8.4.5).

7.4 Reagents—For field-processing aliquots for trivalent chromium determinations

7.4.1 Nitric Acid, Ultrapure—For use when field-preserving samples for trivalent chromium determinations (Sections 6.17 and 8.4.4).

7.4.2 Ammonium Iron (II) Sulfate Solution (0.01M)—Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.

7.4.3 Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.

7.4.4 Hydrochloric acid—High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.

7.4.5 Chromium stock standard solution (1000 µg/mL)—Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.

7.4.6 Standard chromium spike solution (1000 µg/L)—Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the

chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.

7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).

8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).

8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume

should be collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.

8.2.1 Four sampling procedures are described:

8.2.1.1 Section 8.2.5 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.

8.2.1.2 Section 8.2.6 describes a procedure for using a grab sampling device to collect samples.

8.2.1.3 Section 8.2.7 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.

8.2.1.4 Section 8.2.8 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.

8.2.2 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the bow.

If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.

8.2.3 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.

8.2.5 Manual collection of surface samples directly into the sample bottle.

8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).

8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.

8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

8.2.5.7 "Dirty hands" zips the outer bag.

8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.5.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 8.3.

8.2.6 Sample collection with grab sampling device—The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 6.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 6.4.2.

8.2.6.1 The sampling team puts on gloves (and wind suits, if applicable). Ideally, a sample bottle will have been preattached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation, described in Section 6.4.2, inside the field-portable glove bag (Section 6.6).

8.2.6.2 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

8.2.6.3 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

8.2.6.4 "Clean hands" changes gloves.

8.2.6.5 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.

8.2.6.6 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.

8.2.6.7 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 8.2.5.6 through 8.2.5.7.

8.2.6.8 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 7.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

8.2.6.9 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.

8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)

8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).

8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.

8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).

8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.

8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.

8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.

8.2.7.8 Both "clean hands" and "dirty hands" change gloves.

8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.

8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.

8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."

8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.

8.2.7.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.8 Continuous-flow sampling (Figure 4 and Section 6.5.2)—The continuous-flow sampling system uses peristaltic pump (Section 6.15) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.

8.2.8.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump (Section 6.15), SEBS-resin tubing (Section 6.15.2), batteries (Section 6.15.4), gloves (Section 6.7), plastic wrap (Section 6.9), wind suits (Section 6.12), and, if samples are to be filtered, the filtration apparatus (Section 6.14) from the coolers or storage containers in which they are packed.

8.2.8.2 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 6.7.2).

8.2.8.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.

8.2.8.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.

8.2.8.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 6.7.1).

8.2.8.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.

8.2.8.7 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

NOTE: *The filtration apparatus is not attached until immediately before sampling to prevent buildup of particulates from clogging the filter.*

8.2.8.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.

8.2.8.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.3 Sample Filtration—The filtration procedure described below is used for samples collected using the manual (Section 8.2.5), grab (Section 8.2.6), or jar (Section 8.2.7) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 8.2.8.7. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.

8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.

8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.

8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).

8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."

8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.

8.4.2 If field preservation is required, preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus (Section 6.17.3), and an area should be available for setting up the wrist-action shaker (Section 6.17.5). It is also advisable to set up a work area that contains a "clean" cooler for storage of clean equipment, a "dirty" cooler for storage of "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.

8.4.3 Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.

8.4.4 Preservation of aliquots for trivalent chromium (References 8-9).

8.4.4.1 Decant 100 mL of the sample into a clean polyethylene bottle.

8.4.4.2 Clean an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section (7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution (Section 7.4.3) to each sample and blank.

8.4.4.3 Cap each bottle tightly, place in a clean polyethylene bag, and shake on a wrist action shaker (Section 6.17.5) for one hour.

8.4.4.4 Vacuum-filter the precipitate through a 0.4 µm pretreated filter membrane (Section 6.17.2), using fluoropolymer forceps (Section 6.17.1) to handle the membrane, and a 47 mm vacuum filtration apparatus with a precleaned filter holder (Section 6.17.3). After all sample has filtered, rinse the inside of the filter holder with approximately 15 mL of reagent water.

8.4.4.5 Using the fluoropolymer forceps, fold the membrane in half and then in quarters, taking care to avoid touching the side containing the filtrate to any surface. (Folding is done while the membrane is sitting on the filter holder and allows easy placement of the membrane into the sample vial). Transfer the filter to a 30 mL fluoropolymer vial. If the fluoropolymer vial was not pre-equipped with the ultrapure nitric acid (Section 7.4.1), rinse the pipet by drawing and discharging 1 mL of 10% HCl followed by 1 mL of reagent water into a waste container, and add 1 mL of ultrapure nitric acid to the sample vial.

8.4.4.6 Cap the vial and double-bag it for shipment to the laboratory.

8.4.4.7 Repeat Steps 8.4.4.4-8.4.4.6 for each sample, rinsing the fluoropolymer forceps and the pipet with 10% high-purity HCl followed by reagent water between samples.

8.4.5 Preservation of aliquots for hexavalent chromium (Reference 20).

8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.

8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.

8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require must require sampling personnel to collect a clean equipment blank before performing on-site field activities.

9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.

9.3.5 The equipment blank must be analyzed using the procedures detailed in the

referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

9.4 Field Blank

9.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for every 10 samples that are collected at a given site. Field blanks are collected before sample collection.

9.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.

9.4.3 Filter the field blanks using the procedures described in Section 8.3.

9.4.4 If it is necessary to acid clean the sampling equipment between samples (Section 10.0), a field blank should be collected after the cleaning procedures but before the next sample is collected.

9.4.5 If trivalent chromium aliquots are processed, a separate field blank must be collected and processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.5 Field Duplicate

9.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.

9.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.

9.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 8.3. Field duplicates for trivalent chromium must be processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.6 Additional QC for Collection of Trivalent Chromium Aliquots

9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.

9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 µg/L.

9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples in unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.

10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.

10.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:

10.3.1 In the glove bag, and using the "clean hands/dirty hands" procedure in Section 8.2.5, process the dilute nitric acid solution (Section 7.2) through the Apparatus.

10.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.

10.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.

10.3.4 Collect a field blank as described in Section 9.4.

10.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.

10.4 Procedures for recleaning trivalent chromium preservation equipment between samples are described in Section 8.4.4.

11.0 Method Performance

Samples were collected in the Great Lakes during September–October 1994 using the procedures in this sampling method.

12.0 Pollution Prevention

12.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.

12.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

12.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

13.0 Waste Management

13.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

13.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

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15.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

15.1 Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

15.2 Apparatus—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.

15.3 Equipment Blank—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.

15.4 Field Blank—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine whether the field or sample transporting procedures and environments have contaminated the sample.

15.5 Field Duplicates (FD1 and FD2)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel

inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

15.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

15.7 May—This action, activity, or procedural step is optional.

15.8 May Not—This action, activity, or procedural step is prohibited.

15.9 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).

15.10 Must—This action, activity, or procedural step is required.

15.11 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.

15.12 Should—This action, activity, or procedural step is suggested but not required.

15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS APPLICABLE TO METHOD 1669

Method	Technique	Metal	MDL (µg/L) [1]	ML (µg/L) [2]
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Trivalent Chromium	0.10	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS	Cadmium	0.0024	0.01
		Copper	0.024	0.1
		Lead	0.0081	0.02
		Nickel	0.029	0.1

[1] Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.
[2] Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% $HN0_3$ to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 µm membrane, add 1 mL 10% $HN0_3$; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

Figure 1 - Grab Sampling Device

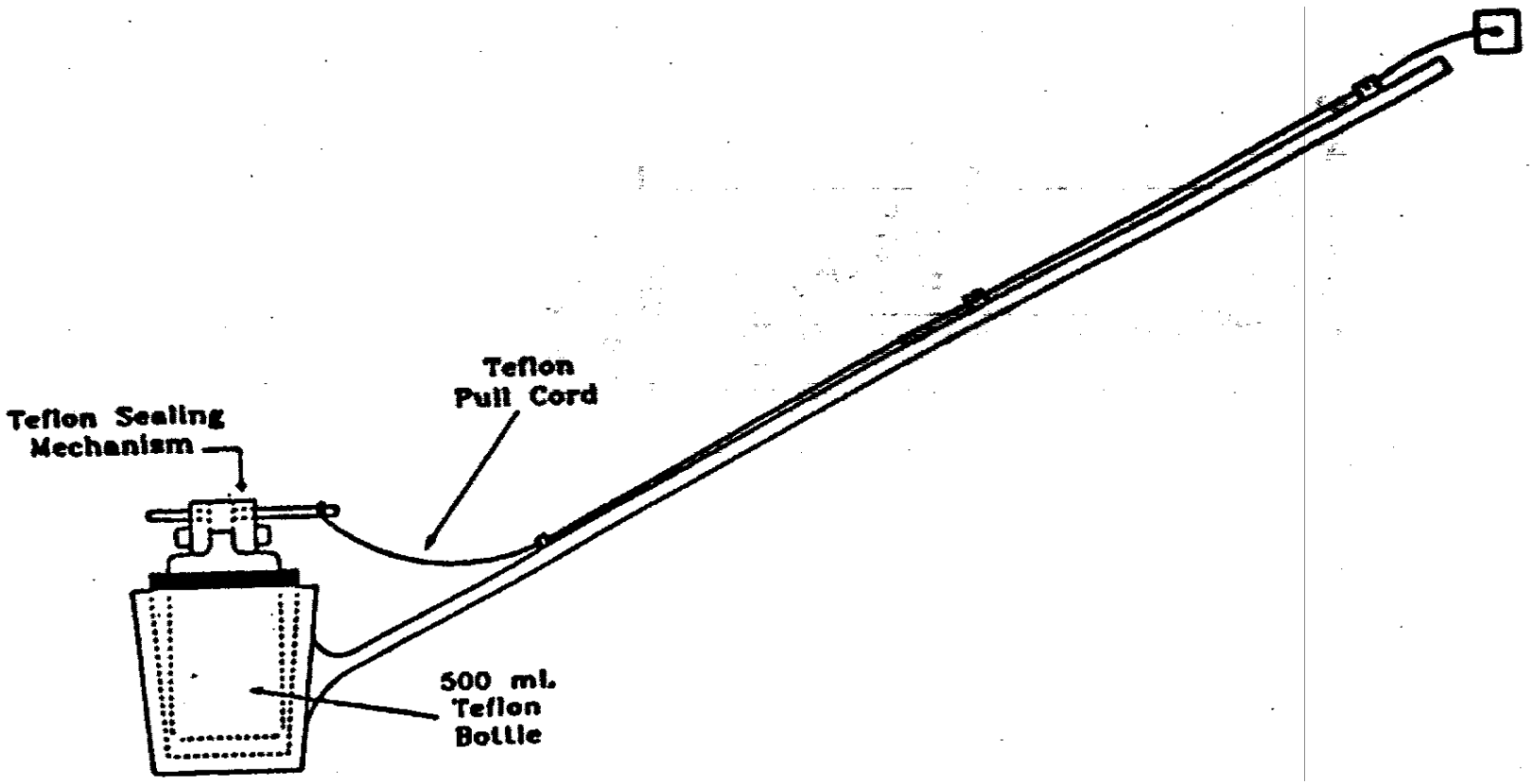


Figure 2 - Grab Sampling Device

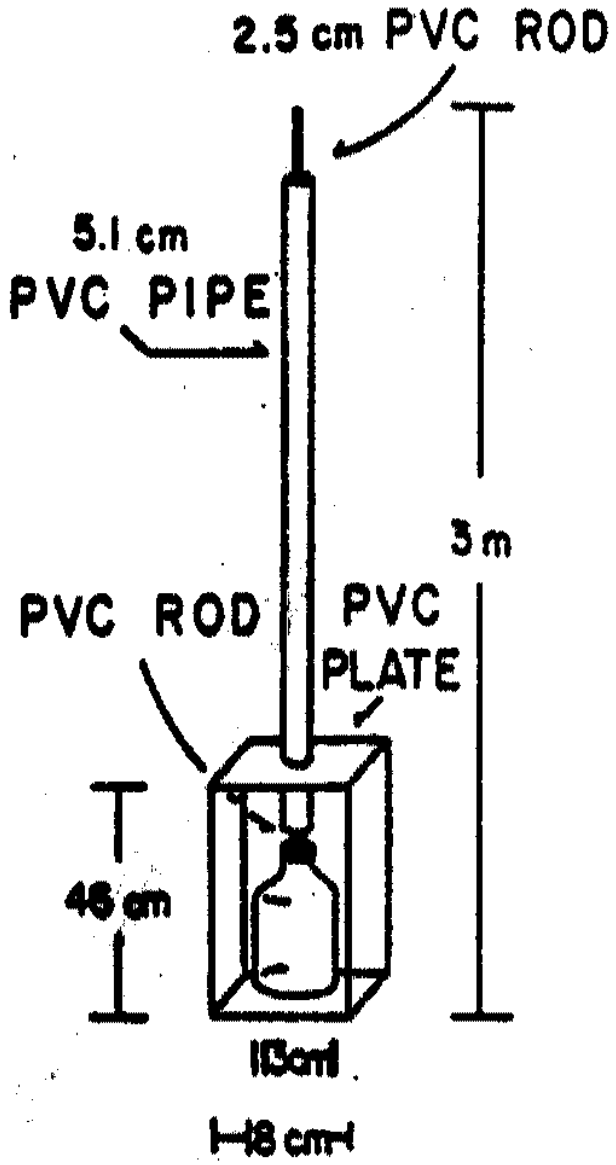


Figure 3 - Jar Sampling Device

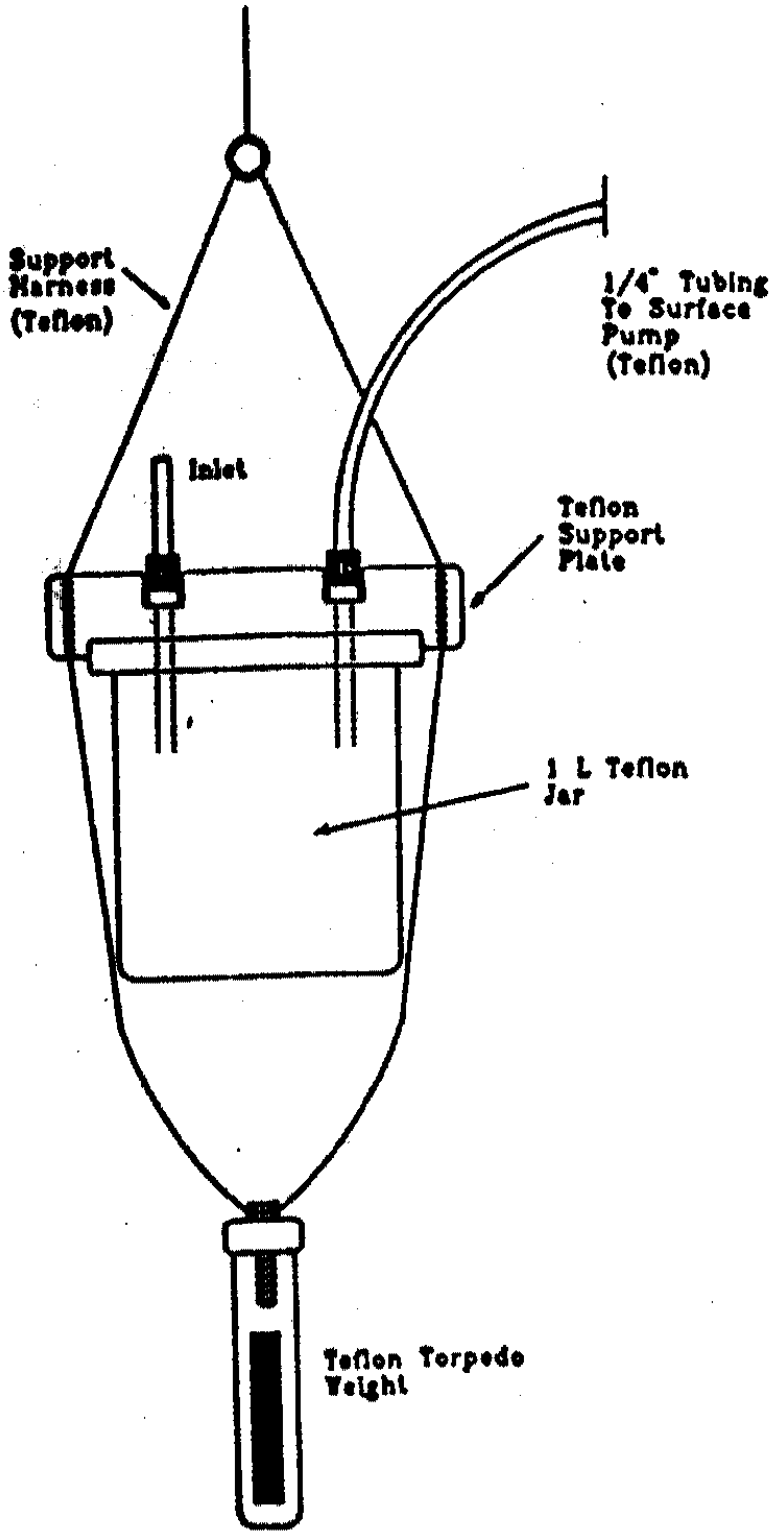
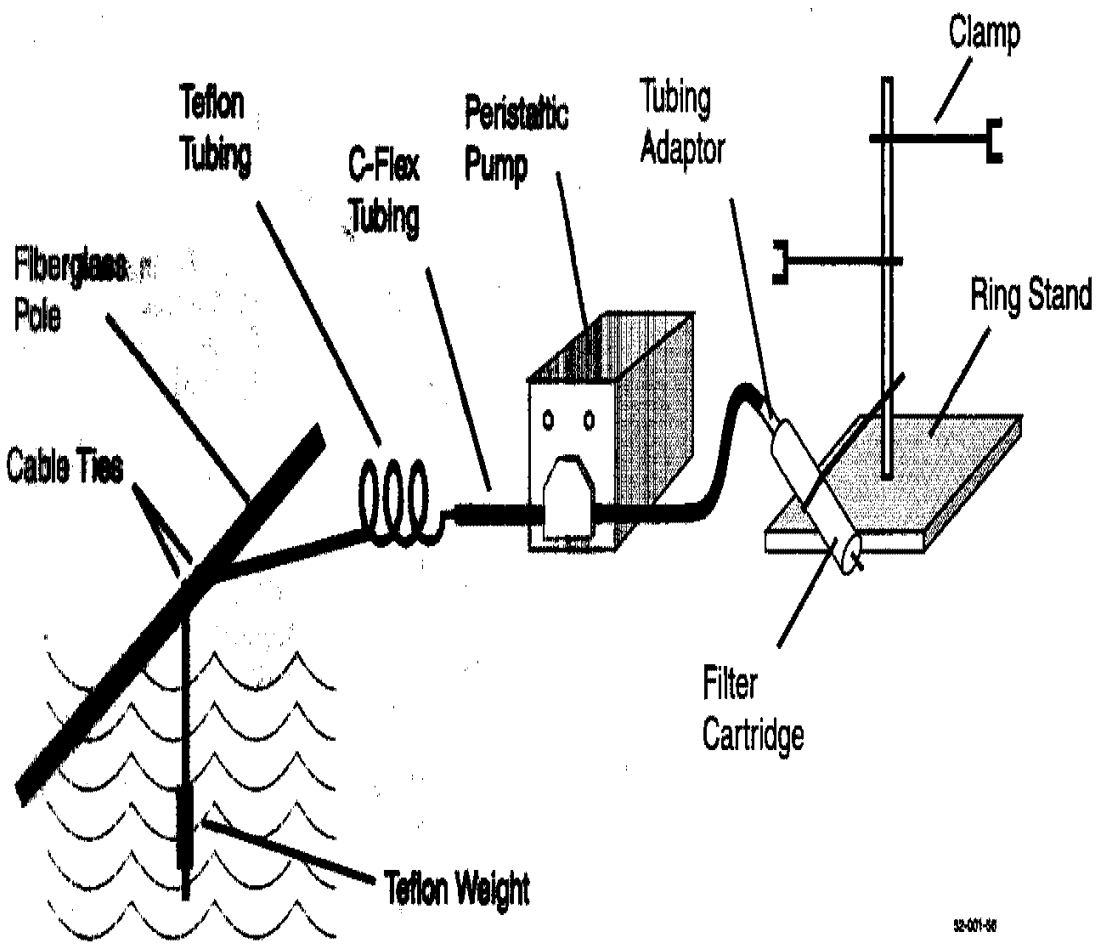


Figure 4 - Sample Pumping System



Appendix B

Sample Design Matrix

Appendix B
Sampling Design Matrix - Additional Samples

SAMPLING AREA	SAMPLE METHOD	Judgmental or Random	SAMPLE INTERVAL (feet bgs)	FIELD SCREENING	SAMPLE COLLECTION DESCRIPTION/ FREQUENCY	ANALYSES															
						TCL VOC	TCL SVOC	TAL METALS	Dissolved Metals	Trace Metals Total	Trace Metals Dissolved	AVS/SEM	TDS	TOC	TSS	Tributyltin	Permeability Sampling*	Lipids	PCBs	PCBs Congeners	Herbicides and Pesticides
SURFACE WATER SAMPLES																					
AOC-3	Peristaltic Pump	Random	Not Applicable	pH, specific conductance, temperature, TDS, ORP, and turbidity	Grab Samples	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		Judgmental	Not Applicable			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AOC-5		Judgmental	Not Applicable			10	10	0	0	10	10	0	10	0	0	0	0	0	0	0	0
Background		Judgmental	Not Applicable		Grab Samples - 10 samples collected from marine/coastal and 10 from the wetlands	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL SURFACE WATER SAMPLES						**10**	**10**	**0**	**0**	**10**	**10**	**0**	**10**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
QC FOR SURFACE WATER SAMPLES																					
QC MS/MSD* {1/20 organics}		Various	Various	Not Applicable	As stated above for each designated sample location	1	1	N/A	N/A	N/A	N/A	0	N/A	0	N/A	0	N/A	N/A	0	0	0
QC MS/MD* {1/20 inorganics}		Various	Various			N/A	N/A	0	0	1	1	0	N/A	0	N/A	N/A	N/A	N/A	0	0	0
QC field duplicate {1/10}		Various	Various			1	1	0	0	1	1	0	1	0	0	0	N/A	N/A	0	0	0
QC field blank		Various	Various		1 per day as determined by site conditions	3	3	N/A	N/A	N/A	N/A	N/A	N/A	0	N/A	N/A	N/A	N/A	0	0	0
QC trip blank		N/A	N/A		1 per VOC cooler	3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0	N/A	N/A	N/A	N/A	0	0	0
QC equipment rinsate		N/A	N/A		1 per day per nondedicated equipment	N/A	N/A	N/A	N/A	2	2	0	N/A	0	N/A	N/A	N/A	N/A	0	0	0
TOTAL QC						**8**	**5**	**0**	**0**	**4**	**4**	**0**	**1**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
TOTAL SURFACE WATER SAMPLES INCLUDING QC						**18**	**15**	**0**	**0**	**14**	**14**	**0**	**11**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
GROUND WATER SAMPLES																					
AOC-1N	Low Flow Sampling (Peristaltic Pump)	Judgmental	Not Applicable	Not Applicable	Grab Sample	5	5	5	5	0	0	0	5	0	0	0	0	0	0	0	0
AOC-1S						7	7	7	7	0	0	0	7	0	0	0	0	0	0	0	0
AOC-2						1	1	1	1	0	0	0	1	0	0	0	0	0	0	0	0
AOC-3						2	2	2	2	0	0	0	2	0	0	0	0	0	0	0	0
AOC-4						1	1	1	1	0	0	0	1	0	0	0	0	0	0	0	0
Background						0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL GROUND WATER SAMPLES						**16**	**16**	**16**	**16**	**0**	**0**	**0**	**16**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
QC FOR GROUND WATER SAMPLES																					
QC MS/MSD* {1/20 organics}		Various	Various	Not Applicable	As stated above for each designated sample location	1	1	N/A	N/A	N/A	N/A	N/A	N/A	0	N/A	N/A	N/A	N/A	0	0	0
QC MS/MD* {1/20 inorganics}		Various	Various			N/A	N/A	1	1	0	0	0	1	N/A	0	0	N/A	N/A	N/A	N/A	N/A
QC field duplicate {1/10}		Various	Various			2	2	2	2	0	0	0	2	0	0	0	N/A	N/A	0	0	0
QC field blank		Various	Various		1 per day as determined by site conditions	2	2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
QC trip blank		N/A	N/A		1 per VOC cooler	2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
QC equipment rinsate		N/A	N/A		1 per day per nondedicated equipment	4	4	4	N/A	0	0	0	0	0	0	N/A	N/A	N/A	0	0	0
TOTAL QC						**11**	**9**	**7**	**3**	**0**	**0**	**0**	**3**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
TOTAL GROUND WATER SAMPLES INCLUDING QC						**27**	**25**	**23**	**19**	**0**	**0**	**0**	**19**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

NOTES:
* Permeability sampling includes analysis for particle size, fraction organic carbon, moisture content, specific gravity, wet sieve, and or Atterberg limits.

AOC	Area of Concern
AVS/SEM	acid volatile sulfides/simultaneously extracted metals
bgs	below ground surface
MD	Matrix Duplicate
MS	Matrix Spike
MSD	Matrix Spike Duplicate
N/A	Not Applicable
PCB	Polychlorinated Biphenyls
QC	Quality Control
SVOC	Semi-volatile Organic Compound
TAL	Target Analyte List
TCL	Target Compound List
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solid
VOC	Volatile Organic Compound