Lower Passaic River Restoration Project

Oversight Quality Assurance Project Plan

Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing

August 2009

In partnership with

623546

Lower Passaic River Restoration Project

Oversight Quality Assurance Project Plan

Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing

PREPARED BY:

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FOR:

US Environmental Protection Agency
US Army Corps of Engineers

August 2009

August 2009

Oversight Quality Assurance Project Plan

for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing

Prepared by:

Malcolm Pirnie, Inc. and Battelle Duxbury Operation

August 2009

Version: 2009/08/06

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TABLE OF CONTENTS

Introduction iv
QAPP Worksheet #1. Title and Approval Page 1
QAPP Worksheet #2. QAPP Identifying Information 2
QAPP Worksheet #3. Distribution List 8
QAPP Worksheet #4. Project Personnel Sign-Off Sheet 9
QAPP Worksheet #5. Project Organizational Chart 10
QAPP Worksheet #6. Communication Pathways 11
QAPP Worksheet #7. Personnel Responsibilities and Qualification Table 13
QAPP Worksheet #8. Special Personnel Training Requirements Table 14
QAPP Worksheet #9. Project Scoping Session Participants Sheet 15
QAPP Worksheet #10. Problem Definition 19
QAPP Worksheet #11. Project Quality Objectives/Systematic Planning Process Statements 22
QAPP Worksheet #12. Measurement Performance Criteria Table 26
QAPP Worksheet #13. Secondary Data Criteria and Limitations Table 44
QAPP Worksheet #14. Summary of Project Tasks 45
QAPP Worksheet #15. Reference Limits and Evaluation Table 47
QAPP Worksheet #16. Project Schedule Timeline Table 82
QAPP Worksheet #17. Sampling Design and Rationale 85
QAPP Worksheet #18. Sampling Locations and Methods/SOP Requirements Table 87
QAPP Worksheet #19. Analytical SOP Requirements Table 90
QAPP Worksheet #20. Field Quality Control Sample Summary Table 95
QAPP Worksheet #21. Project Sampling SOP References Table 101
QAPP Worksheet #22. Field Equipment Calibration, Maintenance, Testing, and Inspection Table 102
QAPP Worksheet #23. Analytical SOP References Table 103
QAPP Worksheet #24. Analytical Instrument Calibration Table 107
QAPP Worksheet #25. Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table 108
QAPP Worksheet #26. Sample Handling System 110
QAPP Worksheet #27. Sample Custody Requirements 115
QAPP Worksheet #28. QC Samples Table 120
QAPP Worksheet #29. Project Documents and Records Table 162
QAPP Worksheet #30. Analytical Services Table 165
QAPP Worksheet #31. Planned Project Assessments Table 170
QAPP Worksheet #32. Assessment Findings and Corrective Action Responses 171
QAPP Worksheet #33. QA Management Reports Table 175
QAPP Worksheet #34. Verification (Step I) Process Table 176
QAPP Worksheet #35. Validation (Steps IIa and IIb) Process Table 177
QAPP Worksheet #36. Validation (Steps IIa and IIb) Summary Table 178
QAPP Worksheet #37. Usability Assessment 181
References 182

FIGURES

Figure 1: Project Organizational Chart

Figure 2: Study Area Location Map

ATTACHMENTS

Attachment 1: SOP No. 1: Procedure to Conduct Sample Management for Contract Laboratory Program and Non-Contract Laboratory Program Samples

Attachment 2: SOP No. 2: Procedure to Conduct a Technical Systems Audit

Attachment 3: Example of Chain of Custody Form for Transfer of Split Samples

Attachment 4: Example of Chain of Custody Form for Non-Contract Laboratory Program Samples

Attachment 5: Field Modification Form

Attachment 6: Oversight Forms

Attachment 7: Laboratory Standard Operating Procedures
(Battelle Marine Sciences Laboratory Standard Operating Procedures are available to the Partner Agencies upon request.)

Attachment 8: Axys Analytical Services PCB Congener Co-Elution List

INTRODUCTION

On May 8, 2007, the United States Environmental Protection Agency (USEPA) announced that it had reached agreement with 73 companies considered potentially responsible for contamination in the Lower Passaic River (New Jersey) to undertake a Remedial Investigation/Feasibility Study (RI/FS) pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendment and Reauthorization Act (SARA). These parties, referred to as the Cooperating Parties Group (CPG), have retained the consultants de maximis, inc., AECOM, and Windward Environmental LLC to support them in the RI/FS effort for the lower 17.4 miles of the Passaic River. The CPG's work is closely monitored by USEPA, in consultation with its partner agencies, the United States Army Corps of Engineers (USACE), New Jersey Department of Transportation (NJDOT), New Jersey Department of Environmental Protection (NJDEP), National Oceanic and Atmospheric Administration (NOAA), and United States Fish and Wildlife Services (USFWS). Further detail on the project background and objectives can be found at http://www.ourPassaic.org.

During calendar year 2009, the CPG committed to conducting an initial round of fish and benthic tissue and community sampling in late summer (subsequent biological sampling is anticipated in winter 2009 and spring 2010). The objective of this data collection is to support the human health and ecological risk assessments for the Lower Passaic River Restoration Project, as presented in the "Problem Formulation Document" (Windward Environmental, LLC, 2009a). The scope of the proposed CPG field sampling plan was based on a planning framework prepared by USEPA and the partner agencies in 2006 and referred to as "Field Sampling Plan (FSP) Volume 2" (Malcolm Pirnie, Inc., 2006). After assuming responsibility for the RI/FS, the CPG reviewed the plans prepared for FSP Volume 2 and developed and submitted their own Quality Assurance Project Plan (QAPP) documents, titled "Quality Assurance Project Plan Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" (Windward Environmental LLC, 2009b) and "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing" (Windward Environmental LLC, 2009c).

On behalf of the USACE and USEPA, Malcolm Pirnie, Inc. will provide oversight and will collect and analyze government split samples from the CPG field sampling program (fish and benthic organisms). The oversight program is designed to provide technical review and evaluation of the CPG-implemented field sampling plan. This Oversight QAPP is intended to integrate the technical and quality control aspects of the oversight program and to provide guidance on biological sampling, community surveys, and toxicity and bioaccumulation testing that will occur during the summer 2009 sampling event. (As necessary, the Oversight QAPP will be modified to account for the subsequent winter 2009 and spring 2010 oversight programs.) The Oversight QAPP details the planning processes for conducting field oversight and collecting split sampling data, and describes the implementation of the quality assurance (QA) and quality control (QC) activities developed for this oversight program. The purpose of this Oversight QAPP is to generate project data that are technically valid and legally defensible. The Oversight QAPP consists of four main components:

- Project Management.
- Measurement and Data Acquisition.
- Assessment and Oversight.
- Data Validation and Usability.

The above components will incorporate QA/QC requirements cited within the following documents:

- USEPA "Requirements for Quality Assurance Project Plans." QA/R-5, March 2001.
- USEPA "Guidance on Systematic Planning using the Data Quality Objectives Process." QA/G-4, February 2006.
- USEPA "Uniform Federal Policy (UFP) for Quality Assurance Project Plans." 505-B-04-900A, March 2005.

At the request of USEPA, the Oversight QAPP follows the action levels, criteria, and analytical methods in the two RI/FS QAPP documents prepared by the CPG.[1,2] Where appropriate, footnotes have been added to this Oversight QAPP to indicate when action levels and criteria were obtained from the RI/FS QAPP documents prepared by the CPG.

A summary of the oversight program for 2009 is provided below and fully described in the attached worksheets:

- Benthic community survey: Oversight will include field observation of the benthic community survey and review of CPG-selected sampling locations (as necessary, oversight staff will communicate with USEPA on sampling locations).
- Fish community survey and fish health evaluation: Oversight will include field observation of the fish community survey and review of CPG-selected sampling locations (and as necessary communication with USEPA on sampling locations). As part of the fish community survey, oversight staff will also observe fish health evaluations that are documented by the CPG field laboratory. No oversight is anticipated at this time for the histopathology component of the fish health evaluation.
- Fish egg count: No oversight is anticipated at this time for the fish egg count of gravid mummichogs, which is anticipated to occur during the 2010 sampling event.
- Fish tissue samples: Oversight will include field observations, review of CPG-selected sampling locations, review of species "catches" and CPG-selected receptor species, and review of individual species selected by CPG field crew for compositing (as necessary, oversight staff will communicate with USEPA on selected sampling locations, selected receptor species, and selected compositing schemes). Oversight will also include coordination with the CPG-designated laboratory to collect government split samples of fish tissue.
- Fish stomach content taxonomy samples: Oversight will include field observations of fish stomach content taxonomy at the CPG field laboratory.

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[1] Windward Environmental LLC. 2009b. "Quality Assurance Project Plan Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Revised Draft version July 2009.

[2] Windward Environmental LLC. 2009c. "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Draft version May 2009.

- Laboratory toxicity testing: Oversight will include collection of sediment split samples to conduct split-sample toxicity tests at a government laboratory.
- Laboratory bioaccumulation testing: Oversight will include coordination with the CPG-designated laboratory to collect split samples of benthic tissue from laboratory bioaccumulation tests for analysis at a government laboratory.
- *In-situ* bioaccumulation testing: Oversight will include field observation of deployment of *in-situ* bioaccumulation tests and coordination with the CPG-designated laboratory to collect government tissue split samples of benthic *tissue f*rom *in-situ* bioaccumulation testing.
- Surface sediment samples: Oversight will includ*e field* observation and collection of sediment split samples as part of the triad approach to benthic organism evaluation.

As part of the oversight *progra*m, tissue samples (fish and benthic tissue) and sediment samples will be analyzed for select contaminants, including: polychlorinated biphenyl (PCB) congeners, polychlorodibenzodioxin/furan (PCDD/F) congeners, polycyclic aromatic hydrocarbon (PAH) compounds, pesticides, semivolatile organic compounds (SVOC), metals (including mercury and methylmercury), and physical parameters [percent moisture, percent lipid, and total organic carbon (TOC)]. Target fish tissue species may consist of the following types: mummichog (whole body), white perch (skinless fillet and carcass), brown bullhead (skinless fillet and carcass), American eel (skinless fillet and carcass), largemouth bass (skinless fillet and carcass), blue crab (muscle), and crayfish (whole body). However, the fish tissue samples will depend on the "catch," as necessary alternative fish species may be analyzed. Target benthic species for the *in-situ* and laboratory bioaccumulation tests include: *Lumbriculus variegatus, Corbicula fluminea, Neanthes virens*, and *Macoma nasula*. Toxicity testing will include: 28-day survival and growth of *Hyalella azteca*, 10-day survival and growth of *Chironomus dilutus*, and 10-day survival of *Ampelisca abdita*.

QAPP Worksheet #1 (UFP-QAPP Section 2.1)
Title and Approval Page

Site Name/Project Name: Lower Passaic River Restoration Project (NJD980528996)
Site Location: New Jersey
Operable Unit: 02

Document Title: Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing

Lead Organization: USEPA Region 2

Preparer's Name and Organizational Affiliation: AmyMarie Accardi-Dey and James M. McCann (Malcolm Pirnie, Inc.) and Rosanna Buhl (Battelle Duxbury Operation)

Preparer's Address, Telephone Number, and E-mail Address:
104 Corporate Park Drive, White Plains, New York 10604; (914) 641-2699; aaccardi-dey@pirnie.com
17-17 Route 208 North, Fair Lawn, New Jersey 07410; (201) 398-4310; jmccann@pirnie.com
397 Washington Street, Duxbury, MA 02332; (781) 952-5309; buhl@battelle.org

Preparation Date (Day/Month/Year): August 6, 2009

Investigative Organization's
Project Manager/Date:

Len Warner, Malcolm Pirnie, Inc.

Investigative Organization's
Site Quality Control Officer/Date:

James McCann, Malcolm Pirnie, Inc.

Lead Agency's Project Manager/Date:

Stephanie Vaughn, USEPA

QAPP Worksheet #2 (UFP-QAPP Section 2.2.4)
QAPP Identifying Information

Site Name/Project Name: Lower Passaic River Restoration Project

Site Location: New Jersey
Site Number/Code: NJD980528996
Operable Unit: OU-02
Contractor Name: Malcolm Pirnie, Inc.
Contract Number: W912DQ-08-D-0017
Contract Title: Indefinite Delivery/Indefinite Quantity Type Contract for Miscellaneous Military and Civil Hazardous Waste Cleanup Projects and Related Work
Work Assignment Number: Task Order 0010

Title: Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing
Revision Number: 01
Revision Date: August 6, 2009

1. Identify regulatory program:
   Comprehensive Environmental Response, Compensation, and Liability Act.
   Oversight QAPP prepared following the "Uniform Federal Policy (UFP) for Quality Assurance Project Plans" (505-B-04-900A, Final Version March 2005).

2. Identify approval entity: USEPA Region 2

3. The QAPP is (select one): ☐Generic ☒Project Specific

4. List dates of scoping sessions that were held:
   June 11, 2009: Conference call with Partner Agencies, Malcolm Pirnie, Inc., and Battelle to review comments on QAPP documents prepared by CPG.
   June 30, 2009: Conference call with USEPA and Battelle to resolve issues on CPG response to comments.

5. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	Approval Date
Windward Environmental LLC. 2009. "Quality Assurance Project Plan Fish And Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey." Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG.	Awaiting approval (Revised Draft July 2009)
Windward Environmental LLC. 2009. "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing." Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG.	Awaiting approval (Draft May 2009)
Malcolm Pirnie, Inc. 2008. "Final Quality Assurance Project Plan CPG Oversight 2008 Sediment Sampling." Lower Passaic River Restoration Project. Prepared for USEPA and USACE.	July 2008
ENSR Environmental Consultants and Engineers. 2008. "Quality Assurance Project Plan RI Low Resolution Corning/Sediment Sampling." Lower Passaic River Restoration Project. Prepared by ENSR.	May 2008
Malcolm Pirnie, Inc. 2007. "Quality Assurance Project Plan/Field Sampling Plan Addendum for Empirical Mass Balance Evaluation." Lower Passaic River Restoration Project. Prepared for USEPA and USACE.	December 2007

Malcolm Pirnie, Inc., Earth Tech, Inc., and Battelle. 2006. "Draft Field Sampling Plan. Volume 2." Lower Passaic River Restoration Project. Prepared for USEPA, USACE, and NJDOT.	June 2006
Malcolm Pirnie, Inc. 2005. "Final Quality Assurance Project Plan for Lower Passaic River Restoration Project." Prepared for USEPA and USACE.	August 2005

6. List organizational partners (stakeholders) and connection with lead organization:
   USACE (Kansas City District) performs contract management for USEPA (Region 2). Malcolm Pirnie, Inc. and CDM provide consulting services under contract to USACE. Battelle is Malcolm Pirnie, Inc.'s team sub-consultant. The Lower Passaic River CPG retained de maximis, inc. to manage the RI/FS. AECOM and Windward Environmental LLC are implementing the RI/FS under de maximis, inc.'s oversight and direction.

7. List data users:
   Partner Agencies, Malcolm Pirnie, Inc., CDM, Battelle, and stakeholders.

8. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusions below: Worksheet 22 (Field Equipment Calibration and Maintenance) is omitted because the oversight program will not employ field equipment.

QAPP Worksheet #2
QAPP Identifying Information
(continued)

Identify where each required QAPP element is located in the QAPP (provide section, worksheet, table, or figure number) or other project planning documents (provide complete document title, date, section number, page numbers, and location of the information in the document). Type "NA" for the QAPP elements that are not applicable to the project. Provide an explanation in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	WS#1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	WS#2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	WS#3 WS#4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	WS#5 (Figure 1) WS#6 Attachment 5 (Field Modification Form) WS#7 WS#8
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	WS#9 WS#9 WS#10 (Figure 2)
2.6 Project Quality Objectives (PQOs) and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	WS#11 WS#12

QAPP Worksheet #2
QAPP Identifying Information
(continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	WS#13
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	WS#14 WS#15 WS#16
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.3 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.4 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/Standard Operating Procedure (SOP) Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	WS#17 Attachment 6 (Oversight Forms) WS#18 WS#19 Attachment 7 (Laboratory SOPs) WS#20 WS#21 Not applicable (WS 22)
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	WS#23 WS#24 WS#25

QAPP Worksheet #2
QAPP Identifying Information
(continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Required Documents
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	WS#26 Attachment 1 (SOP No. 1) WS#27 Attachment 2 and Attachment 3
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	WS#28
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	WS#29 WS#30
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	WS#31 Attachment 2 (SOP No. 2) WS#32
4.2 QA Management Reports	- QA Management Reports Table	WS#33
4.3 Final Project Report		

QAPP Worksheet #2
QAPP Identifying Information
(continued)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	WS#34 WS#35 WS#36 WS#37
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		WS#36

QAPP Worksheet #3 (UFP-QAPP Manual Section 2.3.1)
Distribution List

List those entities to whom copies of the approved QAPP, subsequent QAPP revisions, addenda, and amendments will be sent.

Distribution List

QAPP Recipients	Title	Organization	Telephone Number	E-mail Address	Document Control Number
Stephanie Vaughn	USEPA Project Manager	USEPA, Region 2	(212) 637-3914	vaughn.stephanie@epa.gov	P002
Alice Yeh	USEPA Project Manager	USEPA, Region 2	(212) 637-4427	yeh.alice@epa.gov	Electronic
William Sy	USEPA Quality Assurance Chemist	USEPA, Region 2	(732) 632-4766	sy.william@epa.gov	Electronic
Elizabeth Buckrucker	USACE Project Manager	USACE, Kansas City District	(816) 389-3581	elizabeth.a.buckrucker@usace.army.mil	Electronic
Lisa Baron	Partner Agency	USACE, New York District	(609) 530-4779	lisa.a.baron@usace.army.mil	Electronic
Peter Weppler	Partner Agency	USACE, New York District	(212) 264-4476	peter.m.weppler@nan02.usace.army.mil	Electronic
Elkins Green	Partner Agency	NJDOT	(609) 530-8075	elkins.green@dot.state.nj.us	Electronic
Reyhan Mehran	Partner Agency	NOAA	(212) 637-3257	reyhan.mehran@noaa.gov	Electronic
Tim Kubiak	Partner Agency	USFWS	(609) 646-9310 ext.26	tim.kubiak@fws.gov	Electronic
Janine MacGregor	Partner Agency	NJDEP	(609) 633-0784	janine.macgregor@dep.state.nj.us	Electronic
Len Warner	Malcolm Pirnie, Inc. Project Manager	Malcolm Pirnie, Inc.	(914) 641-2972	lwarner@pirnie.com	Electronic
James M. McCann	Malcolm Pirnie, Inc. Site Quality Control Officer	Malcolm Pirnie, Inc.	(201) 398-4310	jmccann@pirnie.com	Electronic
AmyMarie Accardi-Dey	Malcolm Pirnie, Inc. Oversight Field Leader	Malcolm Pirnie, Inc.	(914) 641-2699	aaccardi-dey@pirnie.com	Electronic
Frank Tsang	CDM Project Manager	CDM	(212) 377-4056	tsangc@cdm.com	Electronic
Norm Richardson	Risk Assessor	Battelle	(781) 869-1417	richardsonn@battelle.com	Electronic
Oversight Field Team Members	Malcolm Pirnie, Inc. Field Team	Malcolm Pirnie, Inc.			Electronic

QAPP Worksheet #4 (UFP-QAPP Manual Section 2.3.2)
Project Personnel Sign-Off Sheet

Have copies of this form signed by key project personnel from each organization to indicate that they have read the applicable sections of the QAPP and will perform the tasks as described. Ask each organization to forward signed sheets to the central project file.

Project Personnel Sign-Off Sheet[1]

Organization: Malcolm Pirnie, Inc.

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Len Warner	Malcolm Pirnie, Inc. Project Manager	(914) 641-2972		August 5, 2009
James M. McCann	Malcolm Pirnie, Inc. Site Quality Control Officer	(201) 398-4310		August 5, 2009
AmyMarie Accardi-Dey	Malcolm Pirnie, Inc. Oversight Field Leader	(914) 641-2699		August 5, 2009
Brian Gillen	Oversight Biologist	(914) 641-2408		
Dennis Corelli	Oversight Biologist	(914) 641-2687		
Julie Conklin	Oversight Biologist	(201) 398-4309		
Xiulan Wang	Sample Coordinator	(201) 398-4444		

1: By signing their respective task orders with Malcolm Pirnie, Inc., subcontractor laboratories have agreed to abide by the analytical requirements outlined in the Oversight QAPP.

QAPP Worksheet #5 (UFP-QAPP Manual Section 2.4.1)
Project Organization Chart

Refer to the Project Organization Chart attached in Figure 1.

QAPP Worksheet #6 (UFP-QAPP Manual Section 2.4.2)
Communication Pathway

Describe the communication pathways and modes of communication that will be used during the project, after the QAPP has been approved. Describe the procedures for soliciting and/or obtaining approval between project personnel, between different contractors, and between samplers and laboratory staff. Describe the procedure that will be followed when any project activity originally documented in an approved QAPP requires real-time modifications to achieve project goals or a QAPP amendment is required. Describe the procedures for stopping work and identify who is responsible.

Communication Pathways (Worksheet 6)

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Approval of amendments to the Oversight QAPP	Malcolm Pirnie, Inc.	Site Quality Control Officer with Project Manager approval	201-398-4310	Obtain initial approval from Project Manager. Submit documented amendments within 10 working days for transmittal to USACE and USEPA for approval.
Document control	Malcolm Pirnie, Inc.	Project Manager	914-641-2972	Project document preparation and distribution to USACE and USEPA for review and approval.
Stop work and initiation of corrective action	Malcolm Pirnie, Inc.	Project Manager	914-641-2972	The Project Manager communicates within 24 hours of stop work to the project organization by phone with confirming e-mail.
Real time modification, notifcations and approval	Malcolm Pirnie, Inc.	Site Quality Control Officer with Project Manager approval	201-398-4310	Real time modification to the project will require the approval of the Site Quality Control Officer and Project Manager and will be documented using the Field Modifications Form (attached to Oversight QAPP) within five working days.
Reporting of serious issues	Malcolm Pirnie, Inc.	Project Manager	914-641-2972	Field Team Members will report serious issues to the Project Manager. The Project Manager will report any serious issues to the USEPA and USACE and other concerned parties by e-mail or memo.
Corrective action and audit finding	Malcolm Pirnie, Inc.	Site Quality Control Officer	201-398-4310	Problems or negative audit finding are reported to the Project Manager by e-mail within a week.
Field oversight communication	Malcolm Pirnie, Inc.	Oversight Field Leader	914-641-2699	Communicate with oversight staff in the field to coordinate oversight activities and collection/shipment of split samples. Summarize daily activity in electronic mail format to Project Manager.

Communication Pathways (Worksheet 6)

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Field communication with the USEPA and USACE	Malcolm Pirnie, Inc.	Project Manager, Oversight Field Leader, and oversight field crew as necessary	914-641-2972 914-641-2699	As necessary, communicate with the USEPA and USACE on observations of CPG field decisions (*e.g.*, selected sampling locations and sample compositing scheme).
Communication with subcontract laboratories	Malcolm Pirnie, Inc.	Oversight Field Leader and Site Quality Control Officer	914-641-2699 201-398-4310	Communicate with laboratories to notify them of anticipated split sample shipment, verify receipt of split samples, and communicate any analytical issues. The Site Quality Control Officer will communicate with the Project Manager on any analytical issues that arise.
Communication with CPG-assigned laboratories	Malcolm Pirnie, Inc.	Oversight Field Leader and Site Quality Control Officer	914-641-2699 201-398-4310	Communicate with CPG-assigned laboratory to coordinate the generation and shipment of fish and benthic split samples and communicate analytical aspects of the toxicity split samples (*e.g.*, test conditions).

CPG = Cooperating Parties Group
QAPP = Quality Assurance Project Plan
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #7 (UFP-QAPP Manual Section 2.4.3)
Personnel Responsibilities and Qualification Table

Identify project personnel associated with each organization, contractor, and subcontractor participating in responsible roles. Include data users, decision-makers, project managers, quality assurance officers, project contacts for organizations involved in the project, project health and safety officers, geotechnical engineers and hydrogeologists, field operation personnel, analytical services, and data reviewers. Attach resume to this worksheet or note the location of the resumes.

Personnel Responsibilities and Qualification Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Stephanie Vaughn	USEPA Project Manager	USEPA-Region 2	USEPA Project Manager	NA
Alice Yeh	USEPA Project Manager	USEPA-Region 2	USEPA Project Manager	NA
Beth Buckrucker	USACE Project Manager	USACE, Kansas City District	USACE Project Manager	NA
Len Warner	Associate	Malcolm Pirnie, Inc.	Investigative Organization Project Manager	BS Engineering, 19+ years of experience in Environmental Engineering, specifically contaminated site investigation and remedial planning
James McCann	Project Chemist	Malcolm Pirnie, Inc.	Site Quality Control Officer/Chemist	MA/BS in Chemistry, 40+ years of experience in analytical chemistry, environmental testing, and quality assurance
AmyMarie Accardi-Dey	Project Engineer	Malcolm Pirnie, Inc.	Oversight Field Leader	PhD Environmental Engineering/Chemical Oceanography, 5+ years of experience in Environmental Engineering, specifically geochemistry, environmental chemistry, and the study of contaminant fate and transport.
Charles Myers	Senior Associate	Malcolm Pirnie, Inc.	Corporate Health and Safety Manager	MA in Industrial Hygiene, 30+ years of experience in environmental health and safety. Certified Hazardous Materials Manager; Certified Industrial Hygienist; Certified Infrastructure Preparedness Specialist; Certified Mold Remediation Contractor; Certified Professional Environmental Auditor (Health and Safety).

Resumes and copies of certifications are on file at Malcolm Pirnie, Inc. corporate office in White Plains, New York.

BS = Bachelor of Science
MA = Master of Art and Science
Phd = Doctor of Philosophy
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #8 (UFP-QAPP Manual Section 2.4.4)
Special Personnel Training Requirements Table

Provide the following information for those projects requiring personnel with specialized training. Attach training records and/or certificates to the QAPP or note their location.

Special Personnel Training Requirements Table

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date [1]	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates
Field oversight and on-site personnel	Safety and OSHA training as specified in the Health and Safety Plan[2]	Malcolm Pirnie, Inc.	Training dates kept in company/project training records	All field team members working on-site	Malcolm Pirnie, Inc.	Malcolm Pirnie, Inc. Project Files
Sample management and creation of COC records[3]	Forms II Lite software training for any applicable CLP laboratories	USEPA on-line training for any applicable CLP laboratories	Training dates kept in company/project training records	Malcolm Pirnie, Inc. Sample Management Officer or designee assigned to log samples into Forms II Lite for applicable CLP laboratories	Malcolm Pirnie, Inc.	Malcolm Pirnie, Inc. Project Files

1: Training records are on file at Malcolm Pirnie, Inc. corporate office in White Plains, New York.
2: The Site-Specific Health and Safety Plan is being provided to the USEPA and the USACE under separate cover.
3: Forms II Lite software will be used to manage samples and create COC; however, depending on field conditions, oversight staff can generate a hand-written COC for sample shipment.

CLP = Contract Laboratory Program
COC = Chain of Custody
OSHA = Occupational Safety & Health Administration
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #9 (UFP-QAPP Manual Section 2.5.1)
Project Scoping Session Participants Sheet

Complete this worksheet for each project scoping session held. Identify project team members who are responsible for planning the project.

Project Scoping Session Participants Sheet

Project Name: Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing Projected Date(s) of Sampling: Summer 2009, Winter 2009, and Spring 2010 Project Manager: Elizabeth Buckrucker (USACE) Stephanie Vaughn and Alice Yeh (USEPA) Len Warner (Malcolm Pirnie, Inc.)	Site Name: Lower Passaic River Restoration Project Site Location: New Jersey

Date of Session: June 11, 2009
Scoping Session Purpose: Conference call with Partner Agencies, Malcolm Pirnie, Inc., and Battelle to review concerns on QAPP documents prepared by CPG

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Elizabeth Buckrucker	USACE Project Manager	USACE	(816) 389-3581	elizabeth.a.buckrucker@usace.army.mil	USACE Project Manager
Stephanie Vaughn	USEPA Project Manager	USEPA	(212) 637-3914	stephanie.vaughn@epa.gov	Lead Agency Project Manager
Alice Yeh	USEPA Project Manager	USEPA	(212) 637-4427	alice.yeh@epa.gov	Lead Agency Project Manager
Chuck Nace	Partner Agency	USEPA	(212) 637-4164	nace.charles@epamail.epa.gov	USEPA Ecological Risk Assessor
Marian Olsen	Partner Agency	USEPA	(212) 637-4313	olsen.marian@epa.gov	USEPA Human Health Risk Assessor
Janine MacGregor	Partner Agency	NJDEP	(609) 633-0784	janine.macgregor@dep.state.nj.us	Partner Agency
Anne Hayton	Partner Agency	NJDEP	(609) 984-9772	anne.hayton@dep.state.nj.us	Partner Agency
Allan Motter	Partner Agency	NJDEP	(609) 984-4532	allan.motter@dep.state.nj.us	Partner Agency
Nancy Hamill	Partner Agency	NJDEP	(609) 633-1353	nancy.hamill@dep.state.nj.us	Partner Agency
Linda Cullen	Partner Agency	NJDEP	(609) 984-9778	linda.cullen@dep.state.nj.us	Partner Agency
Reyhan Mehran	Partner Agency	NOAA	(212) 637-3257	reyhan.mehran@noaa.gov	Partner Agency
Tim Kubiak	Partner Agency	USFWS	(609) 646-9310 ext. 26	tim_kubiak@fws.gov	Partner Agency
Lisa Baron	Partner Agency	USACE	(917) 790-8306	Lisa.a.baron@usace.army.mil	Partner Agency
AmyMarie Accardi-Dey	Oversight Field Leader	Malcolm Pirnie, Inc.	(914) 641-2699	aaccardi-dey@pirnie.com	Oversight Field Leader
Norm Richardson	Risk Assessor	Battelle	(781) 869-1417	richardsonN@battelle.org	Ecological Risk Assessor

Worksheet 9 (continued)

Comments/Decisions: Conference call with Partner Agencies, Malcolm Pirnie, Inc., and Battelle to review concerns on QAPP documents prepared by CPG [specifically the "Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" (revised draft version, July 2009)]. Concerns:

- Oversight required when CPG selects final sampling location in the field.
- Oversight required when CPG determines species for composite.
- Requirements for compositing biota tissues.
- Proposed statistical analyses.

Action Items:

- Malcolm Pirnie, Inc. will discuss proposed CPG statistics and applicability of compositing biological samples with John Kern (subcontractor to Malcolm Pirnie, Inc.).
- USEPA will compile comments and provide them to CPG for review.

Consensus Decisions: Oversight required when CPG selects final sampling location in the field, and oversight required when CPG determines species for composite.

QAPP Worksheet #9 (UFP-QAPP Manual Section 2.5.1)
Project Scoping Session Participants Sheet

Complete this worksheet for each project scoping session held. Identify project team members who are responsible for planning the project.

Project Scoping Session Participants Sheet

Project Name: Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing Projected Date(s) of Sampling: Summer 2009, Winter 2009, and Spring 2010 Project Manager: Elizabeth Buckrucker (USACE) Stephanie Vaughn and Alice Yeh (USEPA) Len Warner (Malcolm Pirnie, Inc.)	Site Name: Lower Passaic River Restoration Project Site Location: New Jersey

Date of Session: June 30, 2009
Scoping Session Purpose: Conference call with USEPA and Battelle to resolve issues on CPG response to comments

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Stephanie Vaughn	USEPA Project Manager	USEPA	(212) 637-3914	stephanie.vaughn@epa.gov	Lead Agency Project Manager
Alice Yeh	USEPA Project Manager	USEPA	(212) 637-4427	alice.yeh@epa.gov	Lead Agency Project Manager
Chuck Nace	Partner Agency	USEPA	(212) 637-4164	nace.charles@epamail.epa.gov	USEPA Ecological Risk Assessor
Marian Olsen	Partner Agency	USEPA	(212) 637-4313	olsen.marian@epa.gov	USEPA Human Health Risk Assessor
Norm Richardson	Risk Assessor	Battelle	(781) 869-1417	richardsonN@battelle.org	Ecological Risk Assessor
Pam Rodgers	Risk Assessor	Battelle	(614) 424-4624	rodgersp@battelle.org	Human Health Risk Assessor

Worksheet 9 (continued)

Comments/Decisions: Conference call with USEPA and Battelle to resolve issues on CPG response-to-comments on the "Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" (revised draft version, July 2009). Concerns:

- Partner Agency request to include herbicides on the parameter list.
- Partner Agency request to include histopathology as part of the community survey and assessment of fish health.
- Partner Agency request to include fish egg count (as an alternative to early-life stage studies).
- Selected analytical method for alkylated PAH compounds.

Action Items and Consensus Decisions:

- Herbicides: USEPA will request that the CPG prepare a screening-assessment memorandum to summarize the potential risk of herbicides to fish and fish-consumers. If necessary, herbicides will be added to the parameter list in the 2010 sampling event.
- Histopathology: USEPA will request that the CPG conduct histopathology on fish species that have lesions as well as fish that appear to be healthy. Discrepancy remains on the number of species that will be analyzed.
- Egg Count: USEPA will request that the CPG conduct a fish egg count on mummichog during the 2010 sampling event.
- Alkylated PAH: Selected low resolution analytical method should be appropriate since the method has minimal impacts from lipids.

QAPP Worksheet #10 (UFP-QAPP Manual Section 2.5.2)
Problem Definition

Clearly define the problem and the environmental questions that should be answered for the current investigation and develop the project decision "If…, then…" statements in the QAPP, linking data results with possible actions. The prompts below are meant to help the project team define the problem. They are not comprehensive.

Problem Definition (Worksheet 10)

The problem to be addressed by the project:

Oversight Activities

As part of the Lower Passaic River Restoration Project, the CPG is implementing a biological field sampling program to support the ecological risk assessment and the human health risk assessment. On behalf of the USACE and USEPA, Malcolm Pirnie, Inc. will provide oversight and will collect and analyze government split samples. The oversight program is designed to provide technical review and evaluation of the CPG-implemented field sampling plan. Oversight will observe the following field tasks:

- Benthic community survey: Oversight will include field observation of the benthic community survey and review of CPG-selected sampling locations (as necessary, oversight staff will communicate with USEPA on sampling locations).
- Fish community survey and fish health evaluation: Oversight will include field observation of the fish community survey and review of CPG-selected sampling locations (and as necessary communication with USEPA on sampling locations). As part of the fish community survey, oversight staff will also observe fish health evaluation that is documented by the CPG field laboratory. No oversight is anticipated at this time for the histopathology component of the fish health evaluation.
- Fish egg count: No oversight is anticipated at this time for the fish egg count of gravid mummichogs, which is anticipated to occur during the 2010 sampling event.
- Fish tissue samples: Oversight will include field observations, review of CPG-selected sampling locations, review of species "catches" and CPG-selected receptor species, and review of individual species selected by CPG field crew for compositing (as necessary, oversight staff will communicate with USEPA on selected sampling locations, selected receptor species, and selected compositing schemes). Oversight will also include coordination with the CPG-designated laboratory to collect government split samples of fish tissue (refer to Worksheet 11 for details on split samples and refer to Worksheet 19 for minimum mass requirements).
- Fish stomach content taxonomy samples: Oversight will include field observations of fish stomach content taxonomy at the CPG field laboratory.
- Laboratory toxicity testing: Oversight will include collection of sediment split samples to conduct split-sample toxicity tests at a government laboratory (refer to Worksheet 11 for details).
- Laboratory bioaccumulation testing: Oversight will include coordination with the CPG-designated laboratory to collect split samples of benthic tissue from laboratory bioaccumulation tests for analysis at a government laboratory (refer to Worksheet 11 for details on split samples and refer to Worksheet 19 for minimum mass requirements).
- *In-situ* bioaccumulation testing: Oversight will include field observation of deployment of *in-situ* bioaccumulation tests and coordination with the CPG-designated laboratory to collect government tissue split samples of benthic tissue from *in-situ* bioaccumulation tests (refer to Worksheet 11 for details on split samples and refer to Worksheet 19 for minimum mass requirements).
- Surface sediment samples: Oversight will include field observation and collection of sediment split samples as part of the triad approach to benthic organism evaluation.

Oversight Program (summer 2009)

The oversight program for summer 2009 will include the following level of effort (USEPA reserves the right to modify program as necessary):

- Benthic community survey: 40 days of oversight with one oversight staff on the river observing the benthic community survey.
- Fish community survey and fish health evaluation: 40 days of oversight with one oversight staff on the river observing the fish community survey and fish health evaluation.
- Fish egg count: No oversight is anticipated for summer 2009 sampling event.
- Fish tissue samples: 40 days of oversight with one oversight staff at the CPG field laboratory facility observing CPG fish tissue collection and compositing. The split sample program will include approximately 40 fish tissue split samples plus QC samples (refer to Worksheet 20). Target fish tissue species may consist of the following types:

Problem Definition (Worksheet 10)

mummichog (whole body), white perch (skinless fillet and carcass), brown bullhead (skinless fillet and carcass), American eel (skinless fillet and carcass), largemouth bass (skinless fillet and carcass), blue crab (muscle), and crayfish (whole body). However, the fish tissue samples will depend on the "catch," as necessary alternative fish species may be analyzed.

- Fish stomach content taxonomy samples: Oversight of fish stomach content will be incorporated into the fish community survey effort and fish tissue sampling effort.
- Laboratory toxicity testing: Sediment split samples to conduct the toxicity tests will be collected during the benthic community survey. The split sample program will include approximately 10 sampling locations. Each location will be evaluated for 28-day survival and growth of *Hyalella azteca*. Half of the locations (5 freshwater locations) will also be evaluated for 10-day survival and growth of *Chironomus dilutus* and the other half (5 estuarine locations) will also be evaluated for 10-day survival of *Ampelisca abdita* (total of 20 toxicity tests). Selection of *Chironomus dilutus* or *Ampelisca abdita* will depend on salinity of interstitial water.
- Laboratory and *In-situ* bioaccumulation testing: Oversight of the *in-situ* bioaccumulation testing will be incorporated into the benthic community survey. The split sample program will include approximately10 benthic tissue split samples plus QC samples (refer to Worksheet 20) from the bioaccumulation testing. Target benthic species include: *Lumbriculus variegatus, Corbicula fluminea, Neanthes virens*, and *Macoma nasula*.
- Surface sediment samples: Sediment split samples will be collected during the benthic community survey. The split sample program will include approximately10 sediment split samples plus QC samples (refer to Worksheet 20).

Oversight Locations (summer 2009)

Potential sampling locations are described in the RI/FS QAPP documents (draft version May 2009 and revised draft version July 2009) prepared by Windward Environmental LLC; refer to Figure 2 of the Oversight QAPP for a map of the study area.

As necessary, the Oversight QAPP will be modified to account for the subsequent winter 2009 and spring 2010 oversight programs.

The environmental questions being asked:

The oversight program is designed to provide technical and quality controls on the CPG-implemented field sampling plan and laboratory analyses. Split samples will ba analyzed to evaluate potential bias in the CPG data. Field activities will be observed for adherence to the approved RI/FS QAPP documents (draft version May 2009 and revised draft version July 2009) prepared by Windward Environmental LLC.

Observations from any site reconnaissance reports:

A site reconnaissance survey has not been performed to support this effort.

A synopsis of secondary data or information from site reports:

A summary of secondary data is provided in the following documents:

- Windward Environmental LLC. 2009. "Quality Assurance Project Plan Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Revised Draft July 2009.
- Windward Environmental LLC. 2009. "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Draft May 2009.

The possible classes of contaminants and the affected matrices:

Sediment and Tissue (fish or benthic): Government split samples will be analyzed for the following parameters:

- PCB congeners
- PCDD/F congeners
- Pesticides
- PAH and SVOC

Problem Definition (Worksheet 10)

- Metals and Methylmercury
- Inorganic arsenic (tissue samples only)
- Percent lipid (tissue samples only)
- TOC and percent moisture (sediment samples only)

The CPG is analyzing sediment and tissue samples with an extended analytical list; however, government split samples will not be analyzed for this extended list. Consequently, the parent samples will be analyzed for more parameters than the split samples. Government split samples will not be analyzed for the following parameters: butyltins, total petroleum hydrocarbons, total sulfides, total phosphorous, total Kjeldahl nitrogen, cyanide, ammonia, acid volatile sulfides – simultaneously extracted metals, grain size, alkylated PAH, PCB Aroclors, herbicides, and volatile organic compounds.

Sediment split samples will be analyzed for chemical concentration and be used to conduct laboratory toxicity tests, including: 28-day survival and growth of *Hyalella azteca*, 10-day survival and growth of *Chironomus dilutus*; and 10-day survival of *Ampelisca abdita*.

The rationale for inclusion of chemical and nonchemical analyses:
Split samples will be collected to support the oversight program, which is designed to provide technical review and evaluation on the CPG-implemented field sampling program and laboratory analyses.

Project decision conditions ("If..., then..." statements):
Depending on the fish catch and tissue mass available, the oversight crew will request that the CPG field crew (either in the field or in the field facility) collect extra tissue mass to generate a government split sample. Receptor species caught by the CPG and available mass will determine the number of split samples and species/matrix type collected by the oversight crew (refer to Worksheet 11 for details on split sample program and refer to Worksheet 19 for minimum mass requirements). If the CPG adhere to the approved RI/FS QAPP documents, then the oversight staff will collect split samples and document observations. If the CPG deviate from the approved RI/FS QAPP documents, then the oversight staff will notify USEPA and USACE.

CPG = Cooperating Parties Group
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
QAPP = Quality Assurance Project Plan
QC = Quality control
RI/FS = Remedial Investigation / Feasibility Study
SVOC = Semivolatile organic Compounds
TOC = Total organic carbon
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #11 (UFP-QAPP Manual Section 2.6.1)
Project Quality Objectives/Systematic Planning Process Statements

Use this worksheet to develop project quality objectives (PQOs) in terms of type, quantity, and quality of data determined using a systematic planning process. Provide a detailed discussion of PQOs in the QAPP. List PQOs in the form of qualitative and quantitative statements. These statements should answer questions such as those listed below. These questions are examples only, however; they are neither inclusive nor appropriate for all projects.

Project Quality Objectives /Systematic Planning Process Statements (Worksheet 11)

Who will use the data? Partner Agencies, Malcolm Pirnie, Inc., CDM, Battelle, and stakeholders (as necessary).
What will the data be used for? Oversight activities will monitor the CPG-implemented field sampling program to verify that elements of the approved RI/FS QAPP are fulfilled. Any deviations observed during the field program will be documented in the oversight forms. The oversight field crew will also review the CPG-selected sampling locations and review species that were selected by the CPG for compositing. Government split sample data will be compared to the parent samples collected by the CPG to determine if a bias exists in the data produced by the CPG. A data comparison of government split sample data to the CPG parent sample data will only be completed for parameters that were analyzed and detected by both the CPG program and the oversight program. This comparison will be presented graphically as bivariate scatter plots relative to a 1:1 line and a table of relative percent difference for values that are 5 times the quantitation limits. (Data comparison will not be conducted on concentrations that are considered non-detect by either the CPG validators or oversight validators.) For analytical groups that contain multiple parameters (*e.g.*, congeners), the data comparison will be completed on select parameters per chemical class. Comparison of toxicity test data will be based on the "percent survival" obtained for the CPG and government split samples. The results of the toxicity test will be statistically compared to comparable tests conducted with control sediment for control survival and/or growth. Because of the overlap of the SVOC and PAH chemical classes, some analytes will be reported twice in the split sample program. For the data comparison, PAH results reported by Axys Analytical Services using the HRGC/LRMS method will take precedence over the PAH data generated by Accutest Laboratories using SW846 Method 8270C for SVOC analysis.
What type of data is needed? Data needs include: analyses of split samples and records of observed field sampling activities and fish/benthic community surveys.
How "good" do the data need to be in order to support the environmental decision? The government split sample data must be suitable for comparison to the parent samples collected by the CPG. Refer to Worksheet 12, Worksheet 15, and Worksheet 28, which summarize data quality (including measurement performance, project quantitation limits, and quality control measures for each parameter). Certification: Chemistry analyses will be performed by subcontract laboratories qualified in the analytical methods and, where applicable, certified through NELAC..

Project Quality Objectives /Systematic Planning Process Statements (Worksheet 11)

How much data are needed? (number of samples for each analytical group, matrix, and concentration)

Government split samples will be collected from approximately 10 percent of the samples to determine if a bias exists in the data produced by the CPG. Oversight activities are listed in Worksheet 10. The government split sample program includes: fish tissue split samples, laboratory toxicity testing, benthic tissue split samples from laboratory and *in-situ* bioaccumulation testing, and sediment split samples. (Refer to Worksheet 19 for minimum mass requirements.) As necessary, the Oversight QAPP will be modified to account for the subsequent winter 2009 and spring 2010 oversight programs.

Oversight Split Sample Program (summer 2009)

The oversight program for summer 2009 will include the following level of effort (USEPA reserves the right to modify program as necessary):

- Benthic community survey: 40 days of oversight with one oversight staff on the river observing the benthic community survey.
- Fish community survey and fish health evaluation: 40 days of oversight with one oversight staff on the river observing the fish community survey and fish health evaluation.
- Fish egg count: No oversight is anticipated for summer 2009 sampling event.
- Fish tissue samples: 40 days of oversight with one oversight staff at the CPG field laboratory facility observing CPG fish tissue collection and compositing. The split sample program will include approximately 40 fish tissue split samples plus QC samples (refer to Worksheet 20). Target fish tissue species may consist of the following types: mummichog (whole body), white perch (skinless fillet and carcass), brown bullhead (skinless fillet and carcass), American eel (skinless fillet and carcass), largemouth bass (skinless fillet and carcass), blue crab (muscle), and crayfish (whole body). However, the fish tissue samples will depend on the "catch," as necessary alternative fish species may be analyzed.
- Fish stomach content taxonomy samples: Oversight of fish stomach content will be incorporated into fish community survey effort and fish tissue sampling effort.
- Laboratory toxicity testing: Sediment split samples to conduct the toxicity tests will be collected during the benthic community survey. The split sample program will include approximately 10 sampling locations. Each location will be evaluated for 28-day survival and growth of *Hyalella azteca*. Half of the locations (5 freshwater locations) will also be evaluated for 10-day survival and growth of *Chironomus dilutus* and the other half (5 estuarine locations) will also be evaluated for 10-day survival of *Ampelisca abdita* (total of 20 toxicity tests). Selection of *Chironomus dilutus* or *Ampelisca abdita* will depend on salinity of interstitial water.
- Laboratory and *In-situ* bioaccumulation testing: Oversight of the *in-situ* bioaccumulation testing will be incorporated into the benthic community survey. The split sample program will include 10 benthic tissue split samples plus QC samples (refer to Worksheet 20) from the bioaccumulation testing. Target benthic species include: *Lumbriculus variegatus, Corbicula fluminea, Neanthes virens,* and *Macoma nasula*.
- Surface sediment samples: Sediment split samples will be collected during the benthic community survey. The split sample program will include approximately 10 sediment split samples plus QC samples (refer to Worksheet 20).

Logistics for Split Sample Collection

- Fish Tissue Split Samples: Special arrangements will be made by the USEPA and Malcolm Pirnie, Inc. with the CPG for the collection of fish tissue split samples. It has been proposed that prior to sampling, Malcolm Pirnie, Inc. oversight staff will notify the CPG field crew that extra mass is necessary to support the split sample program (refer to Worksheet 19 for minimum mass requirements). The fish tissue samples will be collected by the CPG field team, shipped to the CPG-assigned laboratory, and processed and homogenized by the CPG-assigned laboratory. Malcolm Pirnie, Inc. oversight staff will coordinate with the CPG-assigned laboratory, which will ship a portion of the homogenized fish tissue split sample from the CPG-assigned laboratory to the assigned government oversight laboratory. Alternately, if these arrangements cannot be made with the CPG laboratories, portions of the biota collected by the CPG field crew will be divided in the field and transferred to Malcolm Pirnie, Inc. oversight staff. The biota will be shipped to the assigned government laboratory for homogenization and split sample analyses.
- Laboratory Toxicity Testing: At selected locations, Malcolm Pirnie, Inc. oversight staff will request that the CPG field team collect additional sediment mass for a laboratory toxicity split sample test, including: 28-day survival and growth of *Hyalella azteca*, 10-day survival and growth of *Chironomus dilutus*, and 10-day survival of *Ampelisca abdita*. It is anticipated that oversight staff will target 5 locations in the estuarine section of the river and 5 locations in the freshwater section of the river. [The

government-assigned laboratory will be prepared with sufficient numbers of organisms for all tests (*e.g.*, if salinity is higher than expected).] The government-assigned laboratory will follow their laboratory SOP to conduct the toxicity test, but will modify their procedure so that test conditions are comparable to the CPG-assigned laboratory SOP. Malcolm Pirnie, Inc. oversight staff will coordinate with the CPG-assigned laboratory to verify test conditions, as necessary. Refer to Worksheet 19 on sampling mass requirements and Worksheet 23 on details for toxicity test SOP modifications. (Site-specific reference sediment will not be collected from the Lower Passaic River.)

- Benthic Tissue Split Samples from Bioaccumulation Tests (Laboratory and *In-situ*): Benthic tissue split samples will be collected from the *in-situ* bioaccumulation tests and the laboratory bioaccumulation tests. Special arrangements will be made by the USEPA and Malcolm Pirnie, Inc. with the CPG for the collection of benthic tissue split samples. It has been proposed that prior to sampling, Malcolm Pirnie, Inc. oversight staff will notify the CPG field crew that extra mass is necessary to support the split sample program (refer to Worksheet 19 for minimum mass requirements). The benthic tissue samples from the *in-situ* bioaccumulation tests will be collected by the CPG field team and will be shipped to the CPG-assigned laboratory. The CPG-assigned laboratory will then process and homogenize the benthic tissue generated from the *in-situ* bioaccumulation test. For the laboratory bioaccumulation test, the CPG-assigned laboratory will process and homogenize the benthic tissue at the completion of the laboratory test. Malcolm Pirnie, Inc. oversight staff will coordinate with the CPG-assigned laboratory, which will ship a portion of the homogenized benthic tissue split samples (from the *in-situ* and laboratory bioaccumulation tests) to the assigned government oversight laboratory. Alternately, if these arrangements cannot be made with the CPG laboratories, portions of the biota collected by the CPG field crew (for the *in-situ* bioaccumulation test only) will be divided in the field and transferred to Malcolm Pirnie, Inc. oversight staff. The biota will be shipped to the assigned government laboratory for homogenization.
- Sediment Split Samples: At selected locations, Malcolm Pirnie, Inc. oversight staff will request that the CPG field team collect additional sediment mass to generate a sediment split sample.

Where, when, and how should the data be collected/generated?
The CPG-implemented field program is anticipated to include biological sampling and community surveys in summer 2009, winter 2009, and spring 2010. This Oversight QAPP addresses split sample collection and oversight activities that will occur during summer 2009 (August-October 2009). Subsequent field modifications and addendums to this Oversight QAPP will address future oversight for the winter 2009 and spring 2010 field programs.

Who will collect and generate the data?
Malcolm Pirnie, Inc. oversight staff will record field observations and obtain split samples from the CPG while the field sampling program is being conducted.

How will the data be reported?
The analytical data will be reported according to the requirements in Worksheet 29. The field observations will be recorded using field oversight forms provided in the Oversight QAPP. An Oversight Report will be prepared to compare the split sample laboratory data and the CPG parent sample data.

Project Quality Objectives /Systematic Planning Process Statements (Worksheet 11)

How will the data be archived?
Electronic data (MEDD deliverables and applicable MS Excel spreadsheets containing validated data) and hard copies of laboratory reports will be kept in the Malcolm Pirnie, Inc. project files. Electronic data will be provided to the Partner Agencies in USEPA Region 2 MEDD format. The MEDD will also be uploaded to the project database for stakeholder accessibility. The length of time that records will be archived will be at the discretion of the USACE and USEPA.

CPG = Cooperating Parties Group
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectrometry
MEDD = Multimedia Electronic Data Deliverable
NELAC = National Environmental Laboratory Accreditation Conference
PAH = Polycyclic Aromatic Hydrocarbon
PQO = Project Quality Objectives
QAPP = Quality Assurance Project Plan
QC = Quality control
RI/FS = Remedial Investigation / Feasibility Study
SOP = Standard Operating Procedure
SVOC = Semivolatile Organic Compounds
USEPA = United States Environmental Protection Agency

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – PCB Congeners

Matrix	Sediment and Tissue
Analytical Group	PCB Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	USEPA Method 1668A (For the Axys Analytical Services SOP MSU-020 which follows USEPA 1668A, refer to Attachment 7)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicate	S & A
		Precision	Must agree to within ±20% of the mean (applicable to concentration >10 times the DL)	Laboratory duplicate	A
		Accuracy/Bias	Per USEPA Method 1668A and the criteria in the Axys Analytical Services SOP MSU-020	Initial Calibration	A
		Accuracy/Bias	Per USEPA Method 1668A and the criteria in the Axys Analytical Services SOP MSU-020 (warning 75-125%, acceptance 70-130%)	Calibration Verification	A
		Accuracy/Bias	Per recoveries given in laboratory SOP MSU-020 (RSD 40%, recovery 60-140%)	Initial Precision and Recovery	A
		Accuracy/Bias	Per recoveries given in laboratory SOP MSU-020 (warning 70-130%, acceptance 50-150%)	On-going Precision and Recovery	A

Measurement Performance Criteria Table – PCB Congeners

Matrix	Sediment and Tissue
Analytical Group	PCB Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
		Sensitivity	Per USEPA Method 1668A and the criteria in the Axys Analytical Services SOP MSU-020	Method Blank (MB)	A
		Sensitivity	Per USEPA Method 1668A (Axys Analytical Services SOP MSU-020)	Method Detection Limits (MDL)	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1.The assigned laboratory must perform and meet all quality assurance requirements specified in USEPA Method 1668A, including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks, and determination of detection limits.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – PCDD/F Congeners

Matrix	Sediment and Tissue
Analytical Group	PCDD/F Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	USEPA Method 1613B (For the Axys Analytical Services SOP MSU-018 which follows USEPA Method 1613B, refer to Attachment 7)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicates	S & A
		Precision	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)	Laboratory duplicate	A
		Accuracy/Bias	Per USEPA Method 1613B and the criteria in the Axys Analytical SOP MSU-018	Initial Calibration	A
		Accuracy/Bias	Per recoveries given in Axys Analytical SOP MSU-018 Table 1 and USEPA Method 1613B	Calibration Verification	A
		Accuracy/Bias	Per recoveries given in Axys Analytical SOP MSU-018 Table 1 and USEPA Method 1613B	Initial Precision and Recovery	A
		Accuracy/Bias	Per recoveries given in Axys Analytical SOP MSU-018 Table 1 and USEPA Method 1613B	On-going Precision and Recovery	A
		Sensitivity	Per USEPA Method 1613B and the criteria in the Axys Analytical SOP MSU-018	MB	A

Measurement Performance Criteria Table – PCDD/F Congeners

Matrix	Sediment and Tissue
Analytical Group	PCDD/F Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
		Sensitivity	Per USEPA Method 1613B (Axys Analytical SOP MSU-018)	MDL	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1. The assigned laboratory must perform and meet all quality assurance requirements specified in USEPA Method 1613B, including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - Pesticides

Matrix	Sediment and Tissue
Analytical Group	Chlorinated Pesticides
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria [1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	Axys Analytical Services Method MLA-028 (Refer to Attachment 7 for SOP)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the QL	Field Duplicates	S & A
		Precision	Must agree to within ±20% of the mean (applicable to concentration >10 times the DL)	Laboratory Duplicates	A
		Accuracy/Bias	Per Axys MLA-028	Initial Calibration	A
		Accuracy/Bias	Per Axys MLA-028 must be within ±20%	Calibration Verification	A
		Accuracy/Bias	Per recoveries given in MLA-028 (tables 4 and 5)	On-going Precision and Recovery	A
		Sensitivity	Less then QLs	MB	A
		Sensitivity	Per Axys MLA-028	MDL	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1. The assigned laboratory must perform and meet all the quality assurance requirements specified in MLA-028 including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - PAH

Matrix	Sediment and Tissue
Analytical Group	PAH
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria [1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split sample	Axys Analytical Services Method MLA-021 based on GC/MS isotope dilution (Refer to Attachment 7 for SOP)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicates	S & A
		Precision	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)	Lab Duplicates	A
		Accuracy/Bias	Recovery 40-120%	Laboratory Control Standard	A
		Accuracy/Bias /Precision	Per recovery per Axys Analytical MLA-021 Table 2. RPD within ±20%	MS/MSD	A
		Accuracy/Bias	Deuterated Monitoring Compound recoveries per SOP	Deuterated Monitoring Compounds	A
		Sensitivity	Per requirements in Axys Analytical Services SOP MLA-021	MDL	A
		Sensitivity	Per Axys Analytical Services SOP MLA-021	MB	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1. The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - SVOC

Matrix	Sediment and Tissue
Analytical Group	SVOC
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[1]	Data Quality Indicators (DQIs)	Measurement Performance Criteria [1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	SW846 Method 8270C (Accutest SOP EMS8270-15/ EOPGPC-04)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicates	S & A
		Accuracy	The percent difference for the continuing calibration compounds must be less than 20%.	Continuing Calibration	A
		Accuracy	Recoveries per SW846 Method 8270C and the criteria in laboratory SOP	Surrogates	A
		Accuracy/Bias /Precision	Recovery and RPD per laboratory control limits for individual compounds	MS/MSD	A
		Sensitivity	Low enough to support QL	MDL	A
		Sensitivity	Less than QL	MB	
		Completeness	>90% soil collection, >90% laboratory analysis	Data Completeness Check	S & A

1. The assigned laboratory must perform and meet all the measurement performance criteria to assess the analytical DQIs as specified in SW846 Method 8270C, such as laboratory duplicates and matrix spike duplicates for precision, matrix spikes, Deuterated Monitoring Compounds for accuracy, and blanks and method detection limits for sensitivity. If DESA or CLP laboratories perform the analysis, they will meet the measurement performance and QC criteria in their SOP or Statement of Work.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - TOC

Matrix	Sediment
Analytical Group	Total Organic Carbon
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	USEPA Method Lloyd Kahn	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicate	S & A
		Precision	RPD ≤30%	Laboratory Duplicate	A
		Precision and Accuracy	Per USEPA Method Lloyd Kahn, Recovery 75-125%, RPD 20%	MS/MSD	A
		Sensitivity	Sufficient to support QLs	MDL	A
		Sensitivity	Less than QLs	MB	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1. The assigned laboratory must perform and meet all quality assurance requirements specified in USEPA Method Lloyd Kahn.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - Metals

Matrix	Sediment and Tissue
Analytical Group	Metals
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria [1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	SW846 Method 6010B and 6020	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicates	S & A
		Precision	RPD <20% for duplicate values greater than or equal to 5 times the QL	Lab Duplicate	A
		Accuracy/Bias	± 10 percent of the true value	Calibration Check Standard	A
		Accuracy/Bias	Recovery 75-125% or per lab control charts	MS/MSD	A
		Accuracy/Bias	± 10 percent of the true value	Laboratory Control Sample	A
		Sensitivity	Less than CRQLs	MB	A
		Sensitivity	Low enough to support the QLs	MDLs	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1 The assigned laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable SW846 methods. If DESA performs the analysis they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table - Methylmercury

Matrix	Sediment and Tissue
Analytical Group	Methylmercury
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	USEPA Method 1630 (Battelle Marine Sciences Laboratory SOP MSL-I-015-08)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicate	S & A
		Precision	RPD <35% for values >5 times the MDL. No more than 35% of all relative standard deviations can be >35%	Laboratory Duplicates	A
		Accuracy	67-133% of certified value	Certified Reference Material or On-going Precision and Recovery Sample	A
		Precision and Accuracy	Recovery 65-135%, RPD ≤35%	MS/MSD	A
		Sensitivity	<5 times the MDL	Laboratory Reagent Blank	A
		Accuracy	<20% of initial calibration	Initial and Continuing Calibration Verification	A
		Sensitivity	Low enough to support QLs	MDL	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	A

1. The assigned laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1630. If DESA performs the analysis, they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Total Mercury

Matrix	Sediment and Tissue
Analytical Group	Total Mercury
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	USEPA Method 1631 (Battelle Marine Sciences Laboratory SOP MSL-I-013)	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicate	S & A
		Precision	RPD <25% for values >10 times the MDL. No more than 35% of all relative standard deviations can be >25%	Laboratory Duplicates	A
		Accuracy	77-123% of certified value	Certified Reference Material or On-going Precision and Recovery Sample	A
		Precision and Accuracy	Recovery 71-125%, RPD ≤24%	MS/MSD	A
		Sensitivity	<5 times the MDL	Laboratory Reagent Blank	A
		Accuracy	<15% of initial calibration	Initial and Continuing Calibration Verification	A
		Sensitivity	Low enough to support QLs	MDL	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	A

1. The assigned laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1631. If DESA performs the analysis, they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Inorganic Arsenic

Matrix	Tissue
Analytical Group	Inorganic arsenic
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria [1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	Battelle Marine Sciences Laboratory SOP MSL-I-037-01	Precision	RPD< 40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicates	S & A
		Precision	RPD <20% for duplicate values greater than or equal to 5 times the QL	Laboratory Duplicate (or Matrix Duplicate)	A
		Accuracy/Bias	Initial calibration <10% Calibration Verification <15% of initial calibration	Calibration Check Verification	A
		Accuracy/Bias	Within ±15%	Laboratory Control Sample	A
		Accuracy/Bias	Recovery ±25% or per lab control charts, RPD <20%	MS/MSD	A
		Sensitivity	Less than 5 times the MDL	MB	A
		Sensitivity	Low enough to support the QLs	MDLs	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1 The assigned laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable USEPA method. If DESA performs the analysis they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Percent Lipid

Matrix	Tissue
Analytical Group	Percent Lipid
Concentration Level	Unknown

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	Laboratory SOP based on SM2540B or equivalent laboratory SOP such as Accutest EGN273-01	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL	Field Duplicate	S & A
		Accuracy	Per Laboratory SOP	Balance Calibration	A
		Precision and Accuracy	Recovery 75-125%, RPD <20%	MS/MSD	A
		Completeness	>90% collection, >90% laboratory analysis	Data Completeness Check	S & A

1. If DESA performs the analysis, they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Toxicity Test

Matrix	Sediment
Analytical Group	Toxicity (*Chironomus dilutus*)
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407	Health of test organisms	Survival: ≥ 70% Average ash free dry weight: ≥ 0.48 mg per surviving individual	Laboratory negative control	A
		Health of test organisms	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Laboratory positive control (Reference toxicant)	A
		Acceptability of test conditions	Test conditions: Dissolved oxygen: ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, Hardness, and Ammonia: Should not vary by more than 50% during the test	Monitor overlying water: dissolved oxygen, pH, conductivity, and temperature daily in one surrogate test vessel for each treatment. Monitor temperature hourly in separate test vessel. Analyze alkalinity, hardness, and ammonia in one replicate of each treatment at test start and in each test vessel at test termination.	A

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Toxicity Test

Matrix	Sediment
Analytical Group	Toxicity (*Hyalella azteca)*
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split Sample	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467	Health of test organisms	Survival: ≥ 80% Average dry weight: ≥ 0.15 mg per surviving individual	Laboratory negative control	A
		Health of test organisms	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Laboratory positive control (Reference toxicant)	A

Measurement Performance Criteria Table – Toxicity Test

Matrix	Sediment
Analytical Group	Toxicity (*Hyalella azteca)*
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
		Acceptability of test conditions	Test conditions: Dissolved oxygen: ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, Hardness, and Ammonia: Should not vary by more than 50% during the test.	Monitor overlying water prior to renewal: temperature, dissolved oxygen, specific conductance, and pH daily during test in one surrogate test vessel for each treatment. Monitor temperature hourly in separate test vessel. Analyze alkalinity, hardness, and ammonia in a surrogate test vessel for each treatment at test start and weekly thereafter. Total organic carbon is to be measured in surrogate container at test start and end.	A

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

QAPP Worksheet #12
(UFP-QAPP Manual Section 2.6.2)

Measurement Performance Criteria Table – Toxicity Test

Matrix	Sediment
Analytical Group	Toxicity *(Ampelisca abdita)*
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
Split sample	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426	Health of test organisms	Average survival: ≥ 90% Individual replicate survival: ≥ 80%	Laboratory negative control	A
		Health of test organisms	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Laboratory positive control (Reference toxicant)	A
		Acceptability of test conditions	Test conditions: Dissolved oxygen: ≥ 6.0 mg/L Temperature (daily mean): 15ºC±1ºC Salinity: 30±2 ppt	Monitor overlying water: dissolved oxygen, temperature, pH, and salinity in every test vessel at test start and end; daily during test in surrogate test vessel for each treatment. Monitor overlying and porewater ammonia in surrogate test vessel at test start, day 3, and end.	A

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

Acronyms (for previous Worksheet 12)

A = Analytical
CRQL = Contract-Required Quantification Limit
DESA = Division of Environmental Science and Assessment
DL = Detection Limit
DQI = Data Quality Indicators
LCS = Laboratory Control Samples
MB = Method Blank
MDL = Method Detection Limits
MS = Matrix Spike
MSD = Matrix Spike Duplicate
PAH = Polycyclic Aromatic Hydrocarbon
PCB = Polychlorinated Biphenyls
PCDD/F = Polychlorodibenzodioxin/furans
QC = Quality Control
QL = Quantitation Limit
RPD = Relative Percent Difference
RSD = Relative Standard Deviation
S = Sampling
SOP Standard Operating Procedure
SVOC = Semivolatile Organic Compounds
USEPA = United States Environmental Protection Agency

QAPP Worksheet #13 (UFP-QAPP Manual Section 2.7)
Secondary Data Criteria and Limitations Table

Identify all secondary data and information that will be used for the project and their originating sources. Specify how the secondary data will be used and the limitations on their use.

Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/ Collection Dates)	How Data Will Be Used	Limitations on Data Use
Lower Passaic River Restoration Project - Fish/decapod tissue chemistry analysis and fish community survey	Windward Environmental LLC. 2009. "Quality Assurance Project Plan Fish And Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Revised Draft version July 2009.	Sampling activities anticipated to occur in summer 2009, winter 2009, and spring 2010 by the CPG field team.	Parent sample data generated by the CPG will be compared to the government split sample data (only for parameters with detected concentrations in both datasets; refer to Worksheet 11 for details).	Any uncertainty or error associated with the parent sampling data will affect the usability of the data (refer to the RI/FS QAPP prepared by Windward Environmental LLC for uncertainty).
Lower Passaic River Restoration Project - Benthic invertebrate toxicity, community survey, and bioaccumulation testing	Windward Environmental LLC. 2009. "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Draft version May 2009.	Sampling activities anticipated to occur in summer 2009, winter 2009, and spring 2010 by the CPG field team.	Parent sample data generated by the CPG will be compared to the government split sample data (only for parameters with detected concentrations in both datasets; refer to Worksheet 11 for details).	Any uncertainty or error associated with the parent sampling data will affect the usability of the data (refer to the RI/FS QAPP prepared by Windward Environmental LLC for uncertainty).

CPG = Cooperating Parties Group
QAPP = Quality Assurance Project Plan
RI/FS = Remedial Investigation / Feasibility Study

QAPP Worksheet #14 (UFP-QAPP Manual Section 2.8.1)
Summary of Project Tasks

Provide a brief overview of the listed project activities.

Summary of Project Tasks (Worksheet 14)

Sampling Tasks: As part of the Lower Passaic River Restoration Project, the CPG is implementing a biological field sampling program to support the ecological risk assessment and the human health risk assessment. On behalf of the USACE and USEPA, Malcolm Pirnie, Inc. will provide oversight and will collect and analyze government split samples. The oversight program is designed to provide technical review and evaluation of the CPG-implemented field sampling plan. Worksheet 10 lists the oversight activities that will occur; Worksheet 11 provides details on the collection of government split samples; and Worksheet 17 provides a list of required oversight forms and other documentation.
Analysis Tasks: USEPA CLP laboratories, the DESA laboratory, and/or subcontracted laboratories will be assigned to conduct analyses on split samples. Analyses performed on sediments will include parameters such as PCB congeners, PCDD/F congeners, pesticides, PAH compounds, SVOC compounds, metals (including mercury and methylmercury), TOC, and percent moisture. Sediment split samples will also be used to conduct laboratory toxicity tests, including: 28-day survival and growth of *Hyalella azteca*, 10-day survival and growth of *Chironomus dilutus*; and 10-day survival of *Ampelisca abdita*. Analyses on tissue (fish and benthic) samples will include PCB congeners, PCDD/F congeners, pesticides, PAH compounds, SVOC compounds, metals (mercury, methylmercury, and inorganic arsenic), and percent lipids. Oversight forms documenting field observations will be completed by oversight staff.
Quality Control Tasks: The analytical and testing laboratories will be required to analyze quality control samples listed in this document (refer to Worksheet 28) via the applicable laboratory methods.
Secondary Data: Parent sample data generated during the CPG-implemented field sampling program (outlined in the QAPP prepared by Windward Environmental LLD, revised draft version July 2009)
Data Management Tasks: All analytical data and field notes will be maintained in the Malcolm Pirnie, Inc. corporate office in White Plains, New York. See Worksheet 29 for discussion of data management.
Documentation and Records: All hardcopy data (field notebooks, photographs, and oversight forms) will be maintained in the Malcolm Pirnie, Inc. corporate office in White Plains, New York and kept in the project files. Electronic scans of hardcopy data will be provided to the Partner Agencies in PDF-format and posted on the project database.
Assessment/Audit Tasks: Senior staff conducting the field audits will review Oversight QAPP and SOP prior to the performance of audits. Technical System Audits will be performed on the split sample collection activities (refer to Worksheet 31).

Summary of Project Tasks (Worksheet 14)

Data Review Tasks:
Laboratory data produced by subcontracted laboratories will be validated by Malcolm Pirnie, Inc. data validators based on the criteria in the applicable analytical SOPs. Non-chemical data will not be validated. (If DESA or CLP laboratories perform the analyses, laboratory data produced by USEPA CLP or DESA laboratories will be validated by USEPA.) Data verification and validation are described in Worksheets 34, 35, and 36.

CLP = Contract Laboratory Program
CPG = Cooperating Parties Group
DESA = Division of Environmental Science and Assessment
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
PDF = Portable Document Format
QAPP = Quality Assurance Project Plan
SOP = Standard Operating Procedure
SVOC = Semivolatile organic compounds
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: PCB Congeners by USEPA Method 1668A
Concentration Level: Low

Analyte[1]	Chemical Abstracts Services (CAS) Number [1]	Project Action Limit (pg/g)	Project Quantitation Limit (pg/g)	Analytical Method		Achievable Laboratory Limits Axys Analytical [3,4]	
				MDLs	QLs	MDLs (pg/g)	QLs (pg/g)
All individual Congeners PCB-1 through PCB-209	List is provided in Attachment 8	Note 2	Equal to the lab achievable QLs for each congener	See USEPA Method 1668A	See USEPA Method 1668A	Sees summary in Attachment 8 based on Axys Analytical MDLs for 10 gram sample.	0.1 to 0.2

1 See Attachment 8 for a list of PCB Congener statistically-derived MDLs determined by Axys Analytical Services and the list of co-eluting PCB congeners.
2 Project-specific screening levels have not been approved by the USEPA for this project. Data Quality Levels (DQLs) for the individual PCB Congeners are listed by the CPG RI/FS QAPP in the *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing QAPP*, May 2009. The QLs listed in the draft QAPP for individual PCB congeners for sediments ranged from 1.11 to 9.9 pg/g. The laboratory QLs are set low enough to support the split sample comparison.
3 Achievable QLs based on typical Axys Analytical Services detection limits are expected to range from 0.1 to 2.0 pg/g with exceptions (particularly for co-eluting congeners). The laboratory will report the PCB congeners to sample specific detection limits, which may be different depending upon the samples. The Axys Analytical Services laboratory achievable QLs are generally below the QLs listed in the CPG RI/FS QAPP, so that split sample data should be suitable for comparison.
4 Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
PCB = Polychlorinated biphenyls
pg/g = picogram per gram of solids
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: PCDD/F by USEPA Method 1613B
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (ng/kg)	Project Quantitation Limit[2] (ng/kg)	Analytical Method		Achievable Laboratory Limits Quantitation Limits (QLs)	
				MDLs (ng/kg)[3]	QLs (ng/kg)[3]	MDLs (ng/kg)[4]	QLs (ng/kg)[4]
2,3,7,8-TCDD	1746-01-6	Note 1	1.0	NA	1	0.031	0.05
1,2,3,7,8-PeCDD	40321-76-4	Note 1	5.0	NA	5	0.13	0.10
1,2,3,6,7,8-HxCDD	57653-85-7	Note 1	5.0	NA	5	0.19	0.10
1,2,3,4,7,8-HxCDD	39227-28-6	Note 1	5.0	NA	5	0.18	0.10
1,2,3,7,8,9-HxCDD	19408-74-3	Note 1	5.0	NA	5	0.17	0.10
1,2,3,4,6,7,8-HpCDD	35822-46-9	Note 1	5.0	NA	5	0.17	0.10
OCDD	3268-87-9	Note 1	10	NA	10	0.83	0.5
2,3,7,8-TCDF	51207-31-9	Note 1	1.0	NA	1	0.015	0.05
1,2,3,7,8-PeCDF	57117-41-6	Note 1	5.0	NA	5	0.095	0.10
2,3,4,7,8-PeCDF	57117-31-4	Note 1	5.0	NA	5	0.096	0.10
1,2,3,6,7,8-HxCDF	57117-44-9	Note 1	5.0	NA	5	0.091	0.10
1,2,3,7,8,9-HxCDF	72918-21-9	Note 1	5.0	NA	5	0.12	0.10
1,2,3,4,7,8-HxCDF	70648-26-9	Note 1	5.0	NA	5	0.093	0.10
2,3,4,6,7,8-HxCDF	60851-34-5	Note 1	5.0	NA	5	0.12	0.10
1,2,3,4,6,7,8-HpCDF	67562-39-4	Note 1	5.0	NA	5	0.099	0.10
1,2,3,4,7,8,9-HpCDF	55673-89-7	Note 1	5.0	NA	5	0.088	0.10
OCDF	39001-02-0	Note 1	10	NA	10	0.28	0.50

1. Project-specific screening levels have not been approved by the USEPA for this project. Data Quality Levels (DQLs) for the individual PCDD/F Congeners are listed by the CPG RI/FS QAPP in the *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing QAPP*, May 2009. The DQLs proposed by the CPG ranged down to as low as 0.000039 mg/kg for 2,3,7,8-TCDD. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are target reporting limit goals based on minimum levels published in Table 2 of USEPA Method1613B.
3. Specific MDLs for solids are not given in USEPA Method 1613B, but the QLs listed are the minimum levels published in Table 2 of USEPA Method 1613B. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.
4. The MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services' typical sample specific detection limits. Results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Levels

MDL = Method detection limit
NA = Not available
ng/g = nanogram per gram of solids
PCDD/F = Polychlorinated biphenyls
PQL = Project Quantitation Limit
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: Chlorinated Pesticides (Axys Analytical Services MLA-028)
Concentration Level: Low

Analyte	CAS Number	Action Levels[1]	Project Quantitation Limit Goal (ng/g) [2]	Analytical Method		Achievable Laboratory Limits	
				MDL (ng/g)	Method QL (ng/g)	MDLs (ng/g) [3]	QLs (ng/g) [3]
2,4'-DDD	53-19-0	2.0	2.0	NA	NA	0.008	0.02
2,4'-DDE	3424-82-6	1.42	1.42	NA	NA	0.006	0.02
2,4'-DDT	789-02-6	1.0	1.0	NA	NA	0.008	0.02
4,4'-DDD	72-54-8	2.0	2.0	NA	NA	0.008	0.02
4,4'-DDE	72-55-9	1.42	1.42	NA	NA	0.009	0.02
4,4'-DDT	50-29-3	1.0	1.0	NA	NA	0.010	0.02
Aldrin	309-00-2	2.0	2.0	NA	NA	0.079	0.02
alpha-BHC	319-84-6	0.940	0.940	NA	NA	0.027	0.02
beta-BHC	319-85-7	0.940	0.940	NA	NA	0.015	0.02
cis-Chlordane	5103-71-9	0.0200	0.0200	NA	NA	0.024	0.02
cis-Nonachlor	5103-73-1	0.0200	0.0200	NA	NA	0.027	0.02
delta-BHC	319-86-8	0.0940	0.0940	NA	NA	0.007	0.02
Dieldrin	60-57-1	0.0200	0.0200	NA	NA	0.019	0.05
Endosulfan I	959-98-8	0.0400	0.0400	NA	NA	0.029	0.05
Endosufan II	33213-65-9	0.0400	0.0400	NA	NA	0.057	0.05
Endosulfan sulfate	1031-07-8	36,700	36,700	NA	NA	0.052	0.05
Endrin	72-20-8	2.67	2.67	NA	NA	0.031	0.05
Endrin aldehyde	7421-93-4	2.67	2.67	NA	NA	0.027	0.05
Endrin ketone	53494-70-5	2.67	2.67	NA	NA	0.029	0.05
gamma-BHC (Lindane)	58-89-9	0.940	0.940	NA	NA	0.012	0.02
Hexachlorobenzene	118-74-1	2.00	2.00	NA	NA	0.009	0.02
Heptachlor	76-44-8	0.60	0.60	NA	NA	0.024	0.02
Heptachlor epoxide	1024-57-3	0.60	0.60	NA	NA	0.014	0.05
Methoxychlor	72-43-5	6.0	6.0	NA	NA	0.005	0.10
Oxychlordane	27304-13-8	0.020	0.020	NA	NA	0.043	0.02
trans-Chlordane	5103-74-2	0.020	0.020	NA	NA	0.015	0.02

Analyte	CAS Number	Action Levels[1]	Project Quantitation Limit Goal (ng/g) [2]	Analytical Method		Achievable Laboratory Limits	
				MDL (ng/g)	Method QL (ng/g)	MDLs (ng/g) [3]	QLs (ng/g) [3]
trans-Nonachlor	3734-49-4	0.020	0.020	NA	NA	0.021	0.02

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP for *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing*, May 2009, Revision 0, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the lower method calibration limits. Actual QLs should be lower since the lab reports to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services' typical sample specific detection limits. Results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
ng/g = nanogram per gram of solids
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: PAH (Axys Analytical Services MLA-021)
Concentration Level: Low

Analyte	CAS Number	Action Levels[1]	Project Quantitation Limit Goal (ug/kg) [2]	Analytical Method		Achievable Laboratory Limits[c]	
				MDL (ug/kg)	Method QL (ug/kg)	MDLs (ug/kg)	QLs (ug/kg) [3]
Anthracene	120-12-7	46.9	2.5	NA	2.5	0.41	0.5
Pyrene	129-00-0	53.0	2.5	NA	2.5	0.18	0.5
Benzo[g,h,i]perylene	191-24-2	170	2.5	NA	2.5	0.21	1.0
Benzo[e]pyrene	192-97-2	170000	2.5	NA	2.5	0.17	0.5
Indeno[1,2,3-c,d]-pyrene	193-39-5	150	2.5	NA	2.5	0.17	1.0
Perylene	198-55-0	170000	2.5	NA	2.5	0.18	1.0
Fluoranthene	206-44-0	111	2.5	NA	2.5	0.17	0.5
Acenaphthylene	208-96-8	5.87	2.5	NA	2.5	0.20	0.5
Chrysene	218-01-9	57.1	2.5	NA	2.5	0.20	0.5
2,3,5-Trimethylnaphthalene	2245-38-7	3900	2.5	NA	2.5	0.60	1.0
Benzo[a]pyrene	50-32-8	15.0	2.5	NA	2.5	0.14	0.5
Dibenzo[a,h]anthracene	53-70-3	6.22	2.5	NA	2.5	0.23	1.0
Benzo[a]anthracene	56-55-3	31.7	2.5	NA	2.5	0.18	0.5
2,6-Dimethylnaphthalene	581-42-0	3900	2.5	NA	2.5	0.25	1.0
Acenaphthene	83-32-9	6.71		NA		0.16	0.5
1-Methylphenanthrene	832-69-9	1700000	2.5	NA	2.5	0.28	1.0
Phenanthrene	85-01-8	41.9	2.5	NA	2.5	0.13	0.5
Fluorene	86-73-7	19.0	2.5	NA	2.5	0.17	0.5
1-Methylnaphthalene	90-12-0	5590	2.5	NA	2.5	NA	1.0
Naphthalene	91-20-3	34.6	2.5	NA	2.5	1.55	0.5
2-Methylnaphthalene	91-57-6	20.2	2.5	NA	2.5	0.29	1.0
Benzo[b]fluoranthene	205-99-2	150.0	2.5	NA	2.5	0.6 1	
Benzo[j/k]fluoranthene	205-82-3, and 207-08-9	240 (for k)	2.5	NA	2.5	0.10	0.5
Dibenzothiophene	135-65-0	NA	2.5	NA	2.5	0.23	1.0

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP for *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing*, May 2009, Revision 0, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs listed are based on the lower method calibration limits. Actual QLs may be lower, since the lab reports to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services' typical sample specific detection limits. Results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
PAH = Polycyclic aromatic hydrocarbon
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
ug/g =microgram per gram of solids
USEPA = United States Environmental Protection Agency

Worksheet #15 Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: SVOC, SW846 Method 8270C
Concentration Level: Low

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit[c]	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
1,1'-Biphenyl	92-52-4	262	0.067	NA	NA	0.017	0.067
2,2'-Oxybis (1-Chloropropane)	108-60-1	3.50	0.067	NA	0.66	0.017	0.067
2,4,5-Trichlorophenol	95-95-4	610	0.170	NA	0.66	0.036	0.170
2,4,6-Trichlorophenol	88-06-2	0.610	0.170	NA	0.66	0.044	0.170
2,4-Dichlorophenol	120-83-2	18.0	0.70	NA	0.66	0.041	0.70
2,4-Dimethylphenol	105-67-9	120	0.170	NA	0.66	0.041	0.170
2,4-Dinitrophenol	51-28-5	12.0	0.670	NA	3.3	0.360	0.670
2,4-Dinitrotoluene	121-14-2	0.70	0.067	NA	0.66	0.015	0.067
2,6-Dinitrotoluene	606-20-2	0.70	0.067	NA	0.66	0.015	0.067
2-Chloronaphthalene	91-58-7	494	0.067	NA	0.66	0.015	0.067
2-Chlorophenol	95-57-8	6.34	0.170	NA	0.66	0.028	0.170
2-Methylnaphthalene[4]	91-57-6	0.0202	0.067	NA	0.66	0.015	0.067
2-Methylphenol	95-48-7	306	0.067	NA	0.66	0.036	0.067
2-Nitroaniline	88-74-4	18.0	0.170	NA	3.3	0.024	0.170
2-Nitrophenol	88-75-5	1800[e]	0.170	NA	0.66	0.035	0.170
3,3'-Dichlorobenzidine	91-94-1	1.00	0.170	NA	1.3	0.058	0.170
3-Nitroaniline	99-09-2	1.83	0.170	NA	3.3	0.013	0.170
4,6-Dinitro-2-methylphenol	534-52-1	0.610	0.670	NA	3.3	0.035	0.670
4-Bromophenyl-phenylether	101-55-3	NA[f]	0.067	NA	0.66	0.022	0.067
4-Chloro-3-methylphenol	59-50-7	10000	0.170	NA	1.3	0.040	0.170
4-Chloroaniline	106-47-8	24.4	0.170	NA	1.3	0.014	0.170
4-Chlorophenyl-phenyl ether	7005-72-3	NA[f]	0.067	NA	0.66	0.022	0.067

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit[c]	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
4-Methylphenol	106-44-5	30.6	0.067	NA	0.66	0.045	0.067
4-Nitroaniline	100-01-6	23.2	0.170	NA	NA	0.021	0.170
4-Nitrophenol	100-02-7	1800[e]	0.330	NA	3.3	0.043	0.330
Acenaphthene[4]	83-32-9	0.0067	0.033	NA	0.66	0.018	0.033
Acenaphthylene[4]	208-96-8	0.0059	0.033	NA	0.66	0.014	0.033
Acetophenone	98-86-2	2.00	0.170	NA	NA	0.016	0.170
Anthracene[4]	120-12-7	0.0469	0.170	NA	0.66	0.014	0.170
Atrazine	1912-24-9	2.10	0.170	NA	NA	0.021	0.170
Benzaldehyde	100-52-7	611	0.170	NA	NA	0.097	0.170
Benzo(a)anthracene[4]	56-55-3	0.0317	0.033	NA	0.66	0.020	0.033
Benzo(a)pyrene[4]	50-32-8	0.015	0.033	NA	0.66	0.014	0.033
Benzo(b)fluoranthene[4]	205-99-2	0.150	0.033	NA	0.66	0.018	0.033
Benzo(g,h,i)perylene[4]	191-24-2	0.170	0.033	NA	0.66	0.016	0.033
Benzo(k)fluoranthene[4]	207-08-9	0.240	0.033	NA	0.66	0.017	0.033
bis-(2-Chloroethoxy)methane	111-91-1	18.0	0.067	NA	0.66	0.017	0.067
bis-(2-Chloroethyl)ether	111-44-4	0.190	0.067	NA	0.66	0.016	0.067
bis(2-Ethylhexyl)phthalate	117-81-7	2.00	0.067	NA	0.66	0.017	0.067
Butylbenzylphthalate	85-68-7	46.0	0.067	NA	0.66	0.017	0.067
Caprolactam	105-60-2	3060	0.067	NA	NA	0.027	0.067
Carbazole	86-74-8	24.0	0.067	NA	NA	0.014	0.067
Chrysene[4]	218-01-9	0.0571	0.033	NA	0.66	0.015	0.033
Dibenzo(a,h)-anthracene[4]	53-70-3	0.00622	0.033	NA	0.66	0.016	0.033
Dibenzofuran	132-64-9	14.5	0.067	NA	0.66	0.016	0.067
Diethylphthalate	84-66-2	46.0	0.067	NA	0.66	0.015	0.067
Dimethylphthalate	131-11-3	46.0	0.067	NA	0.66	0.016	0.067
Di-n-butylphthalate	84-74-2	46.0	0.067	NA	NA	0.021	0.067

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit[c]	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
Di-n-octylphthalate	117-84-0	46.0	0.067	NA	0.66	0.015	0.067
Fluoranthene[4]	206-44-0	0.111	0.033	NA	0.66	0.015	0.033
Fluorene[d]	86-73-7	0.0190	0.033	NA	0.66	0.016	0.033
Hexachlorobenzene[5]	118-74-1	0.00200	0.067	NA	0.66	0.019	0.067
Hexachlorobutadiene	87-68-3	0.0160	0.033	NA	0.66	0.016	0.033
Hexachloroethane	67-72-1	6.00	0.170	NA	0.66	0.022	0.170
Hexchlorocyclopentadiene	77-47-4	0.00700	0.670	NA	0.66	0.031	0.670
Indeno(1,2,3-cd)-pyrene[4]	193-39-5	0.200	0.033	NA	0.66	0.012	0.033
Isophorone	78-59-1	510	0.067	NA	0.66	0.029	0.067
Naphthalene[4]	91-20-3	0.0346	0.033	NA	0.66	0.013	0.033
Nitrobenzene	98-95-3	1.96	0.067	NA	0.66	0.015	0.067
n-Nitroso-di-n-propylamine	621-64-7	0.0690	0.067	NA	0.66	0.021	0.067
n-Nitrosodiphenylamine	86-30-6	99.0	0.170	NA	0.66	0.022	0.170
Pentachlorophenol	87-86-5	0.400	0.330	NA	3.3	0.043	0.330
Phenanthrene	85-01-8	0.0419	0.033	NA	0.66	0.013	0.033
Phenol	108-95-2	1800	0.067	NA	0.66	0.025	0.067
Pyrene[4]	129-00-0	0.0530	0.033	NA	0.66	0.015	0.033

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP for *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing*, May 2009, Revision 0, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the achievable laboratory QLs.
3. Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method. Actual MDLs and QLs will vary based on sample-specific factors. The QLs listed are based on detection limits achieved by Accutest Laboratories.
4. Analyte may also be reported from the PAH analysis by the Axys Analytical GC/MS method and the PAH method results will take precedence over SW846 Method 8270C results. The analytes 1-methylnaphthalene,1-methylphenanthrene, 2,3,5-trimethylnaphthalene, 2,6-dimethylnaphthalene, benzo(e)pyrene, dibenzothiophene, and perylene, originally listed under this method, will be reported by the PAH method only.

5. Analyte will also be reported from the Organochlorine Pesticide HRGC/HRMS method, the results from the HRGC/HRMS will take precedence over SW846 Method 8270C results.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
GCMS = Gas Chromatography / Mass Spectrometry
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry
MDL = Method detection limit
mg/kg =milligram per kilogram of solids
NA = Not available
PAH = Polycyclic aromatic hydrocarbon
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
SVOC = Semivolatile Organic Compounds
USEPA = United States Environmental Protection Agency

Worksheet #15 – Reference Limits and Evaluation Tables
Matrix: Sediment
Analytical Group: TOC, Lloyd Kahn Method
Concentration Level: Low

Analyte	CAS Number	Project Action Limits[1] (mg/kg)	Project Quantitation Limit[2] (mg/kg)	Analytical Method		Achievable Laboratory Limit[3,4]	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)
TOC	D3590-89-02	NA	500	Not Listed	Note Listed	25.15	100

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this parameter for this project. Differences in laboratory detection limits will be considered when comparing the data.
2. The target PQL listed is based on the lab achievable QL.
3. The QL and MDL are based on Accutest Laboratories data. The lab's QL is anticipated to be low enough to allow comparison of the split sample data to the CPG data. If another lab were assigned to perform this test their detection limits may differ.
4. Lab results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
mg/kg =milligram per kilogram of solids
NA = Not available
PQL = Project Quantitation Limit
QL = Quantitation limit
TOC = Total Organic Carbon
USEPA = United States Environmental Protection Agency

Worksheet #15 – Reference Limits and Evaluation Tables
Matrix: Sediment
Concentration Level: Low
Analytical Group: Metals

Analyte	CAS Number	Project Limit (Data Quality Limit) (mg/kg) [1]	Project Quantitation Limit[2,5] (mg/kg)	Analytical Method Methods		Achievable Laboratory Limits	
				MDLs (mg/kg)	Method QLs(mg/kg)	MDLs (mg/kg)	QLs (mg/kg)[4,5]
Aluminum	7429-90-5	7610	20.0	NA	20.0	3.150	20.0
Antimony	7440-36-0	2.0	2.0	NA	2.0	0.400	2.0
Arsenic	7440-38-2	0.390	0.5	NA	0.5	0.250	0.5
Barium	7440-39-3	537	20.0	NA	20.0	0.080	20.0
Beryllium	7440-41-7	2.00	0.5	NA	0.5	0.020	0.5
Cadmium	7440-43-9	0.596	0.4	NA	0.4	0.030	0.4
Calcium	7440-70-2	NA	500	NA	500	7.480	500
Chromium	7440-47-3	32.0	1.0	NA	1.0	0.090	1.0
Cobalt	7440-48-4	2.30	5.0	NA	5.0	0.030	5.0
Copper	7440-50-8	34.0	2.5	NA	2.5	0.160	2.5
Iron	7439-89-6	2350	10.0	NA	10.0	0.580	10.0
Lead	7439-92-1	35.0	2.0	NA	2.0	0.170	2.0
Magnesium	7439-95-4	NA	500	NA	500	4.810	500
Manganese	7439-96-5	176	1.5	NA	1.5	0.060	1.5
Nickel	7440-02-0	18.0	4.0	NA	4.0	0.060	4.0
Potassium	7440-09-7	NA	1000	NA	1000	8.56	1000
Selenium	7782-49-2	13.0	2.0	NA	2.0	0.370	2.0
Silver	7440-22-4	1.00	1.0	NA	1.0	0.110	1.0
Sodium	7440-23-5	NA	NA	NA	NA	3.470	1000
Thallium	7440-28-0	0.510	0.5	NA	0.5	0.196	0.5
Titanium	7440-28-0	100,000	1.0	NA	1.0	0.060	1.0
Vanadium	7440-62-2	7.82	5.0	NA	5.0	0.090	5.0
Zinc	7440-66-6	123	2.0	NA	2.0	0.330	2.0

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP for *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing*, May 2009, Revision 0, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.

2. The PQLs are based on the laboratory achievable quantitation limits and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Accutest Laboratories by ICP-AES. If another laboratory is assigned it may be necessary to also employ ICP-MS and the detection limits will differ.
5. Lab results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
ICP-AES = Inductively Couple Plasma – Atomic Emission Spectrometry
ICP-MS = Inductively Couple Plasma –Mass Spectrometry
MDL = Method detection limit
mg/kg =milligram per kilogram of solids
NA = Not available
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: Mercury and Methylmercury by USEPA 1631/1630
Concentration: Trace

Analyte	CAS Number	Project Limits (Data Quality Limit) ng/g [1]	Project Quantitation Limit (ng/g)[2]	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs (ng/g)	QLs (ng/g)[4,5]
Mercury	7439-97-6	150 ng/g	1	NA	See USEPA Method 1631	0.04	1
Methylmercury	22967-92-6	611 ng/g	0.05	NA	See USEPA Method 1630	0.02	0.05

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP for *Draft Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing*, May 2009, Revision 0, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the laboratory achievable quantitation limits and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Accutest Laboratories. If another laboratory is assigned the detection limits will differ.
5. Lab results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
ng/g = nanogram per gram of solids
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: PCB Congeners by USEPA Method 1668A
Concentration Level: Low

Analyte[1]	Chemical Abstracts Services (CAS) Number [1]	Project Action Limit (pg/g)	Project Quantitation Limit (pg/g)	Analytical Method		Achievable Laboratory Limits Axys Analytical Services [3,4]	
				MDLs	QLs	MDLs (pg/g)	QLs (pg/g)
All individual Congeners PCB-1 through PCB-209	List is provided in Attachment 8	Note 2	Equal to the lab achievable QLs for each congener	See USEPA Method 1668A	See USEPA Method 1668A	See summary in Attachment 8 based on Axys MDLs for 10 gram sample.	0.1 to 0.2

1. See Attachment 8 for a list of PCB Congener statistically-derived MDLs determined by Axys Analytical Services and the list of co-eluting PCB congeners.
2. Project-specific screening levels have not been approved by the USEPA for this project. Data Quality Levels (DQLs) for the individual PCB Congeners were listed by the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009. They ranged for 0.00158 mg/kg for the majority of the PCB congeners to 2.43E-07 mg/kg for PCB 126. The QLs listed in the CPG draft QAPP for individual PCB congeners for sediments ranged from 1.11 to 9.9 pg/g. The laboratory QLs are set low enough to support the split sample comparison.
3. Achievable QLs based on typical Axys Analytical Services detection limits are expected to range from 0.1 to 2.0 pg/g with some exceptions in particular for the co-eluting PCB congeners. The lab will report the PCB congeners to sample specific detection limits, which may be different depending upon the samples. The Axys Analytical Services lab achievable QLs are generally below the QLs listed in the CPG RI/FS QAPP. Therefore the split sample data should be suitable for comparison.
4. Actual QLs may be higher and are dependent on matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
PCB = Polychlorinated biphenyls
pg/g = picogram per gram of solids
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: PCDD/F by USEPA 1613B
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (ng/kg)	Project Quantitation Limit[2] (ng/kg)	Analytical Method		Achievable Laboratoire Limits Quantitation Limits (QLs)	
				MDLs (ng/kg)[3]	QLs (ng/kg)[3]	MDLs (ng/kg)[4]	QLs (ng/kg)[4]
2,3,7,8-TCDD	1746-01-6	Note 1	1.0	NA	1	0.043	0.05
1,2,3,7,8-PeCDD	40321-76-4	Note 1	5.0	NA	5	0.13	0.10
1,2,3,6,7,8-HxCDD	57653-85-7	Note 1	5.0	NA	5	0.20	0.10
1,2,3,4,7,8-HxCDD	39227-28-6	Note 1	5.0	NA	5	0.124	0.10
1,2,3,7,8,9-HxCDD	19408-74-3	Note 1	5.0	NA	5	0.089	0.10
1,2,3,4,6,7,8-HpCDD	35822-46-9	Note 1	5.0	NA	5	0.112	0.10
OCDD	3268-87-9	Note 1	10	NA	10	0.337	0.5
2,3,7,8-TCDF	51207-31-9	Note 1	1.0	NA	1	0.027	0.05
1,2,3,7,8-PeCDF	57117-41-6	Note 1	5.0	NA	5	0.096	0.10
2,3,4,7,8-PeCDF	57117-31-4	Note 1	5.0	NA	5	0.102	0.10
1,2,3,6,7,8-HxCDF	57117-44-9	Note 1	5.0	NA	5	0.075	0.10
1,2,3,7,8,9-HxCDF	72918-21-9	Note 1	5.0	NA	5	0.86	0.10
1,2,3,4,7,8-HxCDF	70648-26-9	Note 1	5.0	NA	5	0.093	0.10
2,3,4,6,7,8-HxCDF	60851-34-5	Note 1	5.0	NA	5	0.077	0.10
1,2,3,4,6,7,8-HpCDF	67562-39-4	Note 1	5.0	NA	5	0.128	0.10
1,2,3,4,7,8,9-HpCDF	55673-89-7	Note 1	5.0	NA	5	0.107	0.10
OCDF	39001-02-0	Note 1	10	NA	10	0.099	0.50

1. Project-specific screening levels have not been approved by the USEPA for this project. Data Quality Levels (DQLs) for the individual PCDD/F Congeners are listed by the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009.They ranged down to 2.43E-08 mg/kg for 2,3,7,8-TCDD. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are target reporting limit goals based on minimum levels published in Table 2 of USEPA Method 1613B.
3. Specific MDLs for solids are not given in USEPA 1613B, but the QLs listed are the minimum levels published in Table 2 of USEPA Method 1613B. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.
4. The MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services typical sample specific detection limits. Actual QLs may be higher and are dependent on the sample matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group

DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
ng/kg =nanogram per kilogram of solids
PCDD/F = Polychlorodibenzodioxin/furan
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: Chlorinated Pesticides (Axys Analytical Services MLA-028)
Concentration Level: Low

Analyte	CAS Number	Action Levels[1]	Project Quantitation Limit Goal (ng/g) [2]	Analytical Method		Achievable Laboratory Limits	
				MDL (ng/g)	Method QL (ng/g)	MDLs (ng/g) [3]	QLs (ng/g) [3]
2,4'-DDD	53-19-0	2.0	0.2	NA	NA	0.016	0.02
2,4'-DDE	3424-82-6	1.42	0.2	NA	NA	0.007	0.02
2,4'-DDT	789-02-6	1.0	0.2	NA	NA	0.013	0.02
4,4'-DDD	72-54-8	2.0	0.2	NA	NA	0.018	0.02
4,4'-DDE	72-55-9	1.42	0,2	NA	NA	0.008	0.02
4,4'-DDT	50-29-3	1.0	0.2	NA	NA	0.013	0.02
Aldrin	309-00-2	2.0	0.4	NA	NA	0.017	0.02
alpha-BHC	319-84-6	0.940	0.4	NA	NA	0.022	0.02
beta-BHC	319-85-7	0.940	0.4	NA	NA	0.010	0.02
cis-Chlordane	5103-71-9	0.0200	0.4	NA	NA	0.017	0.02
cis-Nonachlor	5103-73-1	0.0200	0.4	NA	NA	0.023	0.02
delta-BHC	319-86-8	0.0940	0.2	NA	NA	0.012	0.02
Dieldrin	60-57-1	0.0200	0.16	NA	NA	0.018	0.05
Endosulfan I	959-98-8	0.0400	0.16	NA	NA	0.035	0.05
Endosufan II	33213-65-9	0.0400	0.16	NA	NA	0.050	0.05
Endosulfan sulfate	1031-07-8	36,700	0,16	NA	NA	0.015	0.05
Endrin	72-20-8	2.67	0.16	NA	NA	0.009	0.05
Endrin aldehyde	7421-93-4	2.67	0.16	NA	NA	0.017	0.05
Endrin ketone	53494-70-5	2.67	0.16	NA	NA	0.017	0.05
gamma-BHC (Lindane)	58-89-9	0.940	0.16	NA	NA	0.139	0.02
Hexachlorobenzene	118-74-1	2.00	0.2	NA	NA	0.008	0.02
Heptachlor	76-44-8	0.60	0.16	NA	NA	0.013	0.02
Heptachlor epoxide	1024-57-3	0.60	0.16	NA	NA	0.009	0.05
Methoxychlor	72-43-5	6.0	0.16	NA	NA	0.010	0.10
Oxychlordane	27304-13-8	0.020	0.4	NA	NA	0.030	0.02
trans-Chlordane	5103-74-2	0.020	0.4	NA	NA	0.011	0.02

Analyte	CAS Number	Action Levels[1]	Project Quantitation Limit Goal (ng/g) [2]	Analytical Method		Achievable Laboratory Limits	
				MDL (ng/g)	Method QL (ng/g)	MDLs (ng/g) [3]	QLs (ng/g) [3]
trans-Nonachlor	3734-49-4	0.020	0.4	NA	NA	0.012	0.02

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009 but these DQLs are not approved action levels.
2. The PQLs are based on the lower method calibration limits. Actual QLs maybe lower, since the lab reports results to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services typical sample specific detection limits. Actual QLs may be higher and are dependent on the sample matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
ng/g =nanogram per gram of solids
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 - Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: PAH (Axys Analytical Services MLA-021)
Concentration Level: Low

Analyte	CAS Number	Project Action Levels[1]	Project Quantitation Limit Goal (ug/kg) [2]	Analytical Method		Achievable Laboratory Limits	
				MDL (ug/kg)	Method QL (ug/kg)	MDLs (ug/kg)	QLs (ug/kg) [3]
Anthracene	120-12-7	40600	0.5	NA	0.5	0.32	0.1
Pyrene	129-00-0	4060	0.5	NA	0.5	0.38	0.1
Benzo[g,h,i]perylene	191-24-2	4060	0.5	NA	0.5	0.18	0.2
Benzo[e]pyrene	192-97-2	4060	0.5	NA	0.5	0.33	0.1
Indeno[1,2,3-c,d]-pyrene	193-39-5	4.32	0.5	NA	0.5	0.1	0.2
Perylene	198-55-0	4060	0.5	NA	0.5	0.91	0.2
Fluoranthene	206-44-0	5410	0.5	NA	0.5	0.54	0.1
Acenaphthylene	208-96-8	8110	0.5	NA	0.5	0.32	0.1
Chrysene	218-01-9	432	0.5	NA	0.5	0.17	0.1
2,3,5-Trimethylnaphthalene[4]	2245-38-7	NA	0.5	NA	0.5	1.1	0.2
Benzo[a]pyrene	50-32-8	0.432	0.5	NA	0.5	0.59	0.1
Dibenzo[a,h]anthracene	53-70-3	0.432	0.5	NA	0.5	0.66	0.2
Benzo[a]anthracene	56-55-3	4.32	0.5	NA	0.5	0.28	0.1
2,6-Dimethylnaphthalene[4]	581-42-0	NA	0.5	NA	0.5	0.74	0.2
Acenaphthene	83-32-9	8110	0.5	NA	0.5	0.24	0.1
1-Methylphenanthrene[4]	832-69-9	NA	0.5	NA	0.5	0.2	0.2
Phenanthrene	85-01-8	40600	0.5	NA	0.5	0.67	0.1
Fluorene	86-73-7	5410	0.5	NA	0.5	0.54	0.1
1-Methylnaphthalene[4]	90-12-0	NA	0.5	NA	0.5	0.5	0.1
Naphthalene	91-20-3	2700	0.5	NA	0.5	0.70	0.1
2-Methylnaphthalene	91-57-6	5421	0.5	NA	0.5	NA	0.2
Benzo[b]fluoranthene	205-99-2	4.32	0.5	NA	0.5	0.8	0.1
Benzo[j/k]fluoranthene	205-82-3, and 207-08-9	43.2 (for k)	0.5	NA	0.5	0.8	0.1
Dibenzothiophene[4]	135-65-0	NA	0.5	NA	0.5	0.36	0.2

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009 but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the lower method calibration limits. Actual QLs should be lower since the lab reports to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services typical sample specific detection limits.. Actual QLs may be higher and are dependent on the sample matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.
4. This analyte was not included on the PAH list in the CPG RI/FS QAPP *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
PAH = Polycyclic aromatic hydrocarbon
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
ug/kg = microgram per kilogram of solids
USEPA = United States Environmental Protection Agency

Worksheet #15 Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: SVOC, SW846 Method 8270C
Concentration Level: Low

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
1,1'-Biphenyl	92-52-4	6.76	0.067	NA	NA	0.017	0.067
2,2'-Oxybis (1-Chloropropane)	108-60-1	NA	0.067	NA	0.66	0.017	0.067
2,4,5-Trichlorophenol	95-95-4	13.5	0.170	NA	0.66	0.036	0.170
2,4,6-Trichlorophenol	88-06-2	0.135	0.170	NA	0.66	0.044	0.170
2,4-Dichlorophenol	120-83-2	0.406	0.70	NA	0.66	0.041	0.70
2,4-Dimethylphenol	105-67-9	2.70	0.170	NA	0.66	0.041	0.170
2,4-Dinitrophenol	51-28-5	0.270	0.670	NA	3.3	0.360	0.670
2,4-Dinitrotoluene	121-14-2	0.270	0.067	NA	0.66	0.015	0.067
2,6-Dinitrotoluene	606-20-2	0.135	0.067	NA	0.66	0.015	0.067
2-Chloronaphthalene	91-58-7	10.8	0.067	NA	0.66	0.015	0.067
2-Chlorophenol	95-57-8	0.676	0.170	NA	0.66	0.028	0.170
2-Methylnaphthalene[4]	91-57-6	0.541	0.067	NA	0.66	0.015	0.067
2-Methylphenol	95-48-7	6.76	0.067	NA	0.66	0.036	0.067
2-Nitroaniline	88-74-4	0.0406	0.170	NA	3.3	0.024	0.170
2-Nitrophenol	88-75-5	40.6[e]	0.170	NA	0.66	0.035	0.170
3,3'-Dichlorobenzidine	91-94-1	0.00701	0.170	NA	1.3	0.058	0.170
3-Nitroaniline	99-09-2	0.0406	0.170	NA	3.3	0.013	0.170
4,6-Dinitro-2-methylphenol	534-52-1	0.0135	0.670	NA	3.3	0.035	0.670
4-Bromophenyl-phenylether	101-55-3	NA	0.067	NA	0.66	0.022	0.067
4-Chloro-3-methylphenol	59-50-7	NA	0.170	NA	1.3	0.040	0.170
4-Chloroaniline	106-47-8	0.0584	0.170	NA	1.3	0.014	0.170
4-Chlorophenyl-phenyl ether	7005-72-3	NA	0.067	NA	0.66	0.022	0.067
4-Methylphenol	106-44-5	0.676	0.067	NA	0.66	0.045	0.067
4-Nitroaniline	100-01-6	0.0150	0.170	NA	NA	0.021	0.170

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
4-Nitrophenol	100-02-7	40.6	0.330	NA	3.3	0.043	0.330
Acenaphthene[4]	83-32-9	8.11	0.033	NA	0.66	0.018	0.033
Acenaphthylene[4]	208-96-8	8.11	0.033	NA	0.66	0.014	0.033
Acetophenone	98-86-2	13.5	0.170	NA	NA	0.016	0.170
Anthracene[4]	120-12-7	40.6	0.170	NA	0.66	0.014	0.170
Atrazine	1912-24-9	0.0137	0.170	NA	NA	0.021	0.170
Benzaldehyde	100-52-7	13.5	0.170	NA	NA	0.097	0.170
Benzo(a)anthracene[4]	56-55-3	0.00432	0.033	NA	0.66	0.020	0.033
Benzo(a)pyrene[4]	50-32-8	0.000432	0.033	NA	0.66	0.014	0.033
Benzo(b)fluoranthene[4]	205-99-2	0.00432	0.033	NA	0.66	0.018	0.033
Benzo(g,h,i)perylene[4]	191-24-2	4.06	0.033	NA	0.66	0.016	0.033
Benzo(k)fluoranthene[4]	207-08-9	0.0432	0.033	NA	0.66	0.017	0.033
bis-(2-Chloroethoxy)methane	111-91-1	0.406	0.067	NA	0.66	0.017	0.067
bis-(2-Chloroethyl)ether	111-44-4	0.00287	0.067	NA	0.66	0.016	0.067
bis(2-Ethylhexyl)phthalate	117-81-7	0.225	0.067	NA	0.66	0.017	0.067
Butylbenzylphthalate	85-68-7	1.66	0.067	NA	0.66	0.017	0.067
Caprolactam	105-60-2	67.6	0.067	NA	NA	0.027	0.067
Carbazole	86-74-8	NA	0.067	NA	NA	0.014	0.067
Chrysene[4]	218-01-9	0.432	0.033	NA	0.66	0.015	0.033
Dibenzo(a,h)-anthracene[4]	53-70-3	0.000432	0.033	NA	0.66	0.016	0.033
Dibenzofuran	132-64-9	NA	0.067	NA	0.66	0.016	0.067
Diethylphthalate	84-66-2	108	0.067	NA	0.66	0.015	0.067
Dimethylphthalate	131-11-3	NA	0.067	NA	0.66	0.016	0.067
Di-n-butylphthalate	84-74-2	13.5	0.067	NA	NA	0.021	0.067
Di-n-octylphthalate	117-84-0	13.5[f]	0.067	NA	0.66	0.015	0.067
Fluoranthene[4]	206-44-0	5.41	0.033	NA	0.66	0.015	0.033
Fluorene[4]	86-73-7	5.41	0.033	NA	0.66	0.016	0.033
Hexachlorobenzene[5]	118-74-1	0.00197	0.067	NA	0.66	0.019	0.067

Analyte	CAS Number	Project Limits (Data Quality Limits) (mg/kg)[1]	Project Quantitation Limit Goal (mg/kg)[2]	Analytical Method		Achievable Laboratory Limit	
				MDL (mg/kg)	Method QL (mg/kg)	MDL (mg/kg)	QL (mg/kg)[3]
Hexachlorobutadiene	87-68-3	0.0404	0.033	NA	0.66	0.016	0.033
Hexachloroethane	67-72-1	0.135	0.170	NA	0.66	0.022	0.170
Hexchlorocyclopentadiene	77-47-4	0.811	0.670	NA	0.66	0.031	0.670
Indeno(1,2,3-cd)-pyrene[4]	193-39-5	0.00432	0.033	NA	0.66	0.012	0.033
Isophorone	78-59-1	3.32	0.067	NA	0.66	0.029	0.067
Naphthalene[4]	91-20-3	2.70	0.033	NA	0.66	0.013	0.033
Nitrobenzene	98-95-3	0.0676	0.067	NA	0.66	0.015	0.067
n-Nitroso-di-n-propylamine	621-64-7	0.000451	0.067	NA	0.66	0.021	0.067
n-Nitrosodiphenylamine	86-30-6	0.644	0.170	NA	0.66	0.022	0.170
Pentachlorophenol	87-86-5	0.0263	0.330	NA	3.3	0.043	0.330
Phenanthrene	85-01-8	40.6	0.033	NA	0.66	0.013	0.033
Phenol	108-95-2	40.6	0.067	NA	0.66	0.025	0.067
Pyrene[4]	129-00-0	4.06	0.033	NA	0.66	0.015	0.033

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009 but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the achievable laboratory QLs.
3. Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method. Actual MDLs and QLs will vary based on sample-specific factors. The QLs listed are based on detection limits achieved by Accutest Laboratories.
4. Analyte may also be reported from the PAH analysis and will take precedence over SW846 Method 8270C data.
5. Hexachlorobenzene will also be reported from the Pesticide HRGC/HRMS method and the results from the HRGC/HRMS will take precedence over SW846 Method 8270C results.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry
MDL = Method detection limit

mg/kg = milligram per kilogram of solids
NA = Not available
PAH = Polycyclic aromatic hydrocarbon
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
SVOC = Semivolatile Organic Compounds
USEPA = United States Environmental Protection Agency

Worksheet #15 – Reference Limits and Evaluation Tables
Matrix: Tissue
Analytical Group: Metals
Concentration Level: Low

Analyte	CAS Number	Project Limit (Data Quality Limit) (mg/kg) [1]	Project Quantitation Limit Goals[2,5] (mg/kg)	Analytical Method Methods		Achievable Laboratory Limits	
				MDLs (mg/kg)	Method QLs(mg/kg)	MDLs (mg/kg)	QLs (mg/kg)[4,5]
Aluminum	7429-90-5	135	20.0	NA	NA	3.150	20.0 (ICP-AES)
Antimony	7440-36-0	0.541	0.4	NA	NA	0.033	0.40 (ICP-MS)
Arsenic[6,7]	**7440-38-2**	**0.0021**	**0.4**	**NA**	NA	**0.089**	**0.40 (ICP-MS)**
Barium	7440-39-3	27.0	5	NA	NA	0.047	5.0 (ICP-MS)
Beryllium	7440-41-7	0.270	0.2	NA	NA	0.032	0.20(ICP-MS)
Cadmium[6]	**7440-43-9**	**0.135**	**0.2**	**NA**	NA	**0.017**	**0.2 (ICP-MS)**
Calcium	7440-70-2	NA	500	NA	NA	7.480	500 (ICP-AES)
Chromium[6]	**7440-47-3**	**0.406**	**1.0**	**NA**	**NA**	**0.044**	**1.0(ICP-MS)**
Cobalt[6]	**7440-48-4**	**0.0406**	**0.2**	**NA**	**NA**	**0.0043**	**0.20(ICP-MS)**
Copper	7440-50-8	5.41	1.0	NA	NA	0.098	1.0 (ICP-MS)
Iron	7439-89-6	94.6	10.0	NA	NA	0.580	10.0 (ICP-AES)
Lead	7439-92-1	1.5	0.10	NA	NA	0.0047	0.10(ICP-MS)
Magnesium	7439-95-4	NA	500	NA	NA	4.810	500 (ICP-AES)
Manganese	7439-96-5	18.9	0.2	NA	NA	0.015	0.2(ICP-MS)
Nickel	7440-02-0	2.70	4.0	NA	NA	0.033	1.0(ICP-MS)
Potassium	7440-09-7	NA	1000	NA	NA	8.56	1000(ICP-AES)
Selenium[6]	**7782-49-2**	**0.676**	**1.0**	**NA**	**NA**	**0.094**	**1.0(ICP-MS)**
Silver[6]	**7440-22-4**	**0.676**	**1.0**	**NA**	**NA**	**0.0038**	**1.0 (ICP-MS)**
Sodium	7440-23-5	NA	NA	NA	NA	3.470	1000 (ICP-AES)
Thallium[6]	**7440-28-0**	**0.00876**	**0.1**	**NA**	**NA**	**0.016**	**0.10(ICP-MS)**
Titanium	7440-28-0	NA	1.0	NA	NA	0.060	1.0 (ICP-AES)
Vanadium[6]	**7440-62-2**	**0.946**	**5.0**	**NA**	**NA**	**0.090**	**5.0 (ICP-AES)**
Zinc	7440-66-6	40.6	1.0	NA	NA	0.14	1.0 (ICP-MS)

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.

2. The PQLs are based on the laboratory achievable quantitation limits and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Accutest Laboratories by ICP-AES and or ICP-MS. The lab will use a combination of these methods. If positive detections are made by ICP-AES, the lab may not have to employ ICP-MS. If another laboratory is assigned the detection limits will differ.
5. Actual QLs may be higher and are dependent on the sample matrix effects.
6. The laboratory QLs are above the CPG target DQLs, but the lab will report the metals data to the MDLs. Differences in laboratory method sensitivity must be considered when evaluating the split sample results.
7. Inorganic arsenic will also be determined by an alternative, more sensitive method (Battelle Marine Science Laboratory SOP MSL-I-037-01).

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
ICP-AES = Inductively Coupled Plasma – Atomic Emission Spectrometry
ICP-MS = Inductively Coupled Plasma – Mass Spectrometry
MDL = Method detection limit
mg/kg = milligram per kilogram of solids
NA = Not available
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: Inorganic arsenic by Battelle Marine Science Laboratory SOP MSL-I-037-01
Concentration: Trace

Analyte	CAS Number	Project Limits (Data Quality Limit) (ug/g) [1]	Project Quantitation Limit (ug/g)[2]	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs (ug/g)	QLs (ug/g)[4,5]
Inorganic arsenic	7440-38-2	0.0021	0.0123	NA	NA	0.0123	0.05

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQLs are based on the laboratory achievable quantitation limits and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Battelle Marine Sciences Laboratories. If another laboratory is assigned the detection limits will differ.
5. Actual QLs may be higher and are dependent on the sample matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
ug/kg = microgram per kilogram of solids
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: Mercury by USEPA Method 1631
Concentration: Trace

Analyte	CAS Number	Project Limits (Data Quality Limit) (ug/g) [1]	Project Quantitation Limit (ug/g)[2]	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs (ug/g)	QLs (ug/g)[4,5]
Mercury	7439-97-6	13.5	1	NA	See USEPA Method 1631	0.3	1

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQL is based on the laboratory achievable quantitation limit and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Battelle Marine Sciences Laboratories. If another laboratory is assigned the detection limits will differ.
5. Actual QLs may be higher and are dependent on the sample matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
ug/g = microgram per gram of solids
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: Methylmercury by USEPA 1630
Concentration: Trace

Analyte	CAS Number	Project Limits (Data Quality Limit) (ng/g) [1]	Project Quantitation Limit (ng/g)[2]	Analytical Method[1]		*Achievable Laboratory Limits*	
				MDLs	Method QLs	MDLs (ng/g)	QLs (ng/g)[4,5]
Methylmercury	22967-92-6	13.5	5	NA	See USEPA Method 1630	1	5

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The values listed are the Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP in the *Revised Draft Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey*, July 2009, but these DQLs are not approved action levels. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
2. The PQL is based on the laboratory achievable quantitation limit and should be adequate for data comparison.
3. Method MDLs are not specified.
4. The achievable QLs listed are for Battelle Marine Sciences Laboratories. If another laboratory is assigned the detection limits will differ.
5. . Actual QLs may be higher and are dependent on the sample matrix effects.

CAS = Chemical Abstract Services
CPG = Cooperating Parties Group
DQL = Data Quality Level
MDL = Method detection limit
NA = Not available
PQL = Project Quantitation Limits
QAPP = Quality Assurance Project Plan
QL = Quantitation limit
RI/FS = Remedial Investigation and Feasibility Study
ug/g = microgram per gram of solids
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Tissue
Analytical Group: Percent Lipids by SM240B or equivalent
Concentration: Trace

Analyte	CAS Number	Project Limits (Data Quality Limit) (%) [1]	Project Quantitation Limit (%)	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Lipids	NA	NA	NA	NA	NA	NA	NA

1. At this time, there are no project-specific screening levels or action levels approved by the USEPA for this project. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.

CAS = Chemical Abstract Services
MDL = Method detection limit
NA = Not available
QL = Quantitation Limits
USEPA = United States Environmental Protection Agency

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: Toxicity Test (*Chironomus dilutus*)
Concentration: Low

Analyte	CAS Number	Project Limits (Data Quality Limit) (%) [1]	Project Quantitation Limit (%)	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Survival	NA	NA	NA	NA	NA	NA	1%

CAS = Chemical Abstract Services
MDL = Method detection limit
NA = Not available
QL = Quantitation Limits

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: Toxicity Test (*Hyalella azteca*)
Concentration: Low

Analyte	CAS Number	Project Limits (Data Quality Limit) (%) [1]	Project Quantitation Limit (%)	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Survival	NA	NA	NA	NA	NA	NA	1%

CAS = Chemical Abstract Services
MDL = Method detection limit
NA = Not available
QL = Quantitation Limits

QAPP Worksheet #15 Reference Limits and Evaluation Table
Matrix: Sediment
Analytical Group: Toxicity Test (*Ampelisca abdita*)
Concentration: Low

Analyte	CAS Number	Project Limits (Data Quality Limit) (%) [1]	Project Quantitation Limit (%)	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Survival	NA	NA	NA	NA	NA	NA	1%

CAS = Chemical Abstract Services
MDL = Method detection limit
NA = Not available
QL = Quantitation Limits

QAPP Worksheet #16 (UFP-QAPP Manual Section 2.8.2)
Project Schedule Timeline Table

Project Schedule Timeline Table (Worksheet 16)

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Prepare and submit draft version of "Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing" to USACE and USEPA	Malcolm Pirnie, Inc.	June 24, 2009	July 22, 2009	Draft Oversight QAPP	July 22, 2009
Request DESA and USEPA CLP assignments and complete subcontract laboratory selection	Malcolm Pirnie, Inc.	June 26, 2009	July 10, 2009: received DESA and USEPA CLP response on CLP/DESA request August 10, 2009: complete laboratory subcontract, as necesssary	Subcontract laboratories and USEPA CLP/DESA laboratory assignments	August 10, 2009
Prepare and submit final version of "Oversight Quality Assurance Project Plan for Biological Sampling, Community Surveys, and Toxicity and Bioaccumulation Testing" to USACE and USEPA	Malcolm Pirnie, Inc.	July 30, 2009	August 5, 2009	Final Oversight QAPP	August 6, 2009 (Final Oversight QAPP will be submitted once comments are received from the USEPA.)
Receive approval from USACE and USEPA to begin oversight program	USACE and USEPA	August 10, 2009	August 10, 2009	Approval on oversight program	August 10, 2009

Project Schedule Timeline Table (Worksheet 16)

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Oversight of field activities and audits	Malcolm Pirnie, Inc. and CDM	Summer 2009, Winter 2009, and Spring 2010 Anticipated the summer 2009 program will last approximately 80 days starting August 10, 2009. Fish sampling will occur first (approximately 40 days) followed by the benthic sampling (approximately 40 days.	Summer 2009, Winter 2009, and Spring 2010	Oversight forms and associated photos and field notes (provided to the Partner Agencies electronically in PDF-format and posted on project database)	To be determined
Collection of split samples and submission for analysis	Malcolm Pirnie, Inc.	August 10, 2009	To be determined (Collection of benthic and fish tissue split samples will be dependent on the CPG-assigned laboratories' schedule to generate split samples. Refer to Worksheet 11 for logistics.)	Samples obtained per Oversight QAPP and shipped to assigned laboratories.	Split samples will be collected during the CPG-implemented field sampling program
Laboratory data analyses	Assigned laboratories	August 10, 2009	To be determined (Collection of benthic and fish tissue split samples will be dependent on the CPG-assigned laboratories' schedule to generate split samples. Refer to Worksheet 11 for logistics.)	Send analytical data to Malcolm Pirnie, Inc. data validator. If DESA or USEPA CLP laboratories conduct the analyses, send analytical data to USEPA for validation.	For standard parameters, 21 days after last sample is received. For specialized organic analyses (PCB, PCDD/F, PAH, and pesticides), 35 days[1] after last sample is received. For toxicity testing, 60 days after last sample is received.

Project Schedule Timeline Table (Worksheet 16)

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Validation and verification of sample data	Malcolm Pirnie, Inc.	To be determined	To be determined	Validated data reported	For standard parameters and toxicity data[2], 30 days after last sample is received. For specialized organic analyses (PCB, PCDD/F, PAH, and pesticides), 30 days after last sample is received.
Evaluation of split sample data	Malcolm Pirnie, Inc.	To be determined	To be determined	Oversight Report (comparison of split sample data to CPG parent sample data and evaluation of toxcitiy tests)	To be determined

1: Subcontract laboratories will communicate with the Site Quality Control Officer on split sample status and potential analytical difficulties (if any arise). With the approval of the Site Quality Control Officer and Project Manager, the turn-around-time for the laboratory data package deliverable can be adjusted to account for re-analysis or additional quality control as necessary.
2: Toxicity testing data will not require full data validation. Toxicity data will only be reviewed against the acceptance limits provided in Worksheets 12 and 28.

CLP = Contract Laboratory Program
CPG = Cooperating Parties Group
DESA = Division of Environmental Science and Assessment
PAH = Polycyclic aromatic hydrocarbons
PCB = Polychlorinated biphenyls
PCDD/F = Polychlorodibenzodioxins/furans
PDF = Portable Document Format
QAPP = Quality Assurance Project Plan
SOP = Standard Operating Procedure
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #17 (UFP-QAPP Manual Section 3.1.1)
Sampling Design and Rationale

Describe the project sampling approach. Provide the rationale for selecting sample locations and matrices for each analytical group and concentration level.

Sampling Design and Rationale (Worksheet 17)

Sampling Process Design

As part of the Lower Passaic River Restoration Project, the CPG is implementing a biological field sampling program to support the ecological risk assessment and the human health risk assessment. On behalf of the USACE and USEPA, Malcolm Pirnie, Inc. will provide oversight and will collect and analyze government split samples. The oversight program is designed to provide technical review and evaluation of the CPG-implemented field sampling plan. Worksheet 10 lists the oversight activities that will occur during the field sampling program, and Worksheet 11 provides details on the collection of government split samples.

Oversight staff will complete oversight forms each day oversight is conducted. Oversight forms are provided in Attachment 6 and described below:

- Oversight Form LPR001 "Fish Community Survey" – documenting field observation of the fish community survey and review of CPG-selected sampling locations and equipment deployment/retrieval based on criteria provided in the CPG RI/FS QAPP documents and professional judgment.
- Oversight Form LPR002 "Fish Tissue Sampling" – documenting field observations of fish health and fish stomach content, review of CPG-selected receptor species, and review of sample processing based on criteria provided in the CPG RI/FS QAPP documents and professional judgment. Oversight form will also document where oversight staff requested a fish split sample.
- Oversight Form LPR003 "Benthic Community Survey" – documenting field observations of the benthic community survey, field observation on *in-situ* bioaccumulation test deployment, and review of CPG-selected sampling locations based on criteria provided in the CPG RI/FS QAPP documents and professional judgment. Oversight form will also document when split samples were collected for laboratory toxicity tests and sediment chemistry as well as document when a split sample from bioaccumulation testing (laboratory or *in-situ*) was requested.

No oversight is anticipated at this time for the histopathology component of the fish health evaluation and fish egg count of gravid mummichogs.

Observations and information collected during the field oversight program will be used to evaluate whether the CPG adhered to their approved RI/FS QAPP. Government split sample data will be compared to the parent samples collected by the CPG to determine if a bias exists in the data produced by the CPG. Refer to Worksheet 11 on details on requirements for the data comparison. Comparison of toxicity test data will be based on the "percent survival" obtained for the CPG and government split samples. The results of the toxicity test will be statistically compared to comparable tests conducted with control sediment for control survival and/or growth.

Sampling Design and Rationale (Worksheet 17)

Sampling Methods

The sampling procedures for the biological field sampling program are provided in the RI/FS QAPP documents (draft version May 2009 and revised draft version July 2009) submitted by Windward Environmental LLC. Under the planned oversight program split samples will be collected judgmentally by the on-site oversight personnel. SOPs associated with the collection and shipping of government split samples are attached to the Oversight QAPP. Worksheet 11 provides details on the collection of government split samples.

Potential sampling locations are described in the RI/FS QAPP documents (draft version May 2009 and revised draft version July 2009) prepared by Windward Environmental LLC; refer to Figure 2 of the Oversight QAPP for a map of the study area.

CPG = Cooperating Parties Group
QAPP = Quality Assurance Project Plan
RI/FS = Remedial Investigation / Feasibility Study
SOP = Standard Operating Procedures
RI/FS = Remedial Investigation and Feasibility Study
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

QAPP Worksheet #18 (UFP-QAPP Manual Section 3.1.1)
Sampling Locations and Methods/SOP Requirements Table

List all site locations that will be sampled and include sample/ID number, if available. (Provide a range of sampling locations and ID numbers if a site has a large number.) Specify matrix and, if applicable, depth at which samples will be taken. Only a short reference for the sampling location rationale is necessary for the table. The text of the QAPP should clearly identify the detailed rationale associated with each reference. Complete all required information, using additional worksheets if necessary

Sampling Locations and Methods/SOP Requirements Table (Worksheet 18)

Sampling Location/ID Number	Matrix	Depth	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference[1]	Rationale for Sampling Location
Refer to QAPP prepared by Windward Environmental LLC for CPG.[1]	Fish tissue split samples	Refer to QAPP prepared by Windward Environmental LLC for CPG.[1]	Analytical group for split samples includes: PCB congeners, PCDD/F congeners, pesticides, PAH and SVOC, metals (including mercury, methylmercury, and inorganic arsenic), and percent lipid	Low	40 split samples plus QC samples (refer to Worksheet 20). Target fish tissue species may consist of the following types: mummichog (whole body), white perch (skinless fillet and carcass), brown bullhead (skinless fillet and carcass), American eel (skinless fillet and carcass), largemouth bass (skinless fillet and carcass), blue crab (muscle), and crayfish (whole body). However, the fish tissue samples will depend on the "catch," as necessary alternative fish species may be analyzed.	Refer to QAPP prepared by Windward Environmental LLC for CPG.[1]	Split samples will be collected judgmentally by the on-site oversight staff. Selection may be restricted by the species "caught" during sampling and the amount of tissue mass available.

Sampling Locations and Methods/SOP Requirements Table (Worksheet 18)

Sampling Location/ID Number	Matrix	Depth	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference[1]	Rationale for Sampling Location
Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Benthic tissue split samples from *in-situ* and laboratory bioaccumulation tests	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Analytical group for split samples includes: PCB congeners, PCDD/F congeners, pesticides, PAH and SVOC, metals (including mercury, methylmercury, and inorganic arsenic), and percent lipid	Low	10 benthic tissue split samples plus QC samples (refer to Worksheet 20). Target benthic species include: *Lumbriculus variegatus*, *Corbicula fluminea*, *Neanthes virens*, and *Macoma nasula*. The distribution of benthic tissue samples will depend on available tissue mass (anticipate 5 split samples from the *in-situ* bioaccumulation tests and 5 split samples from the laboratory bioaccumulation tests).	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Oversight staff will coordinate with the CPG-assigned laboratory to collect a homogenized split sample of the benthic tissue sample.
Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Sediment	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Analytical group for split samples includes: PCB congeners, PCDD/F congeners, pesticides, PAH and SVOC, metals (including mercury, and methylmercury), percent moisture, and TOC	Low	10 sediment split samples plus QC samples (refer to Worksheet 20).	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Sediment split samples will be collected judgmentally by the on-site oversight staff.

Sampling Locations and Methods/SOP Requirements Table (Worksheet 18)

Sampling Location/ID Number	Matrix	Depth	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference[1]	Rationale for Sampling Location
Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Sediment (Toxicity testing)	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Toxicity (*Chironomus dilutus*, *Hyalella azteca*, and *Ampelisca abdita*)	Low	10 sediment split samples will be collected for toxicity testing. Each sediment split sample will be evaluated for 28-day survival and growth of *Hyalella azteca*. Half of the locations (5 freshwater locations) will also be evaluated for 10-day survival and growth of *Chironomus dilutus* and the other half (5 estuarine locations) will also be evaluated for 10-day survival of *Ampelisca abdita* (total of 20 toxicity tests). Selection of *Chironomus dilutus* or *Ampelisca abdita* will depend on salinity of interstitial water. (No field duplicates are required.)	Refer to QAPP prepared by Windward Environmental LLC for CPG [2]	Sediment split samples will be collected judgmentally by the on-site oversight staff. Sediment will be shipped to government designated laboratory for toxicity testing.

1: Windward Environmental LLC. 2009. "Quality Assurance Project Plan Fish and Decapod Crustacean Tissue Collection for Chemical Analysis and Fish Community Survey" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Revised Draft version July 2009.
2: Windward Environmental LLC. 2009. "Quality Assurance Project Plan Surface Sediment Chemical Analyses and Benthic Invertebrate Toxicity and Bioaccumulation Testing" Lower Passaic River Restoration Project. Prepared for the Lower Passaic River CPG. Draft version May 2009.

CPG = Cooperating Parties Group
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
QAPP = Quality Assurance Project Plan
QC = Quality control
SVOC = Semivolatile organic compounds
TOC = Total organic carbon

QAPP Worksheet #19 (UFP-QAPP Manual Section 3.1.1)
Analytical SOP Requirement Table

Analytical SOP Requirements Table (Worksheet 19)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference [2]	Sample Volume	Containers (number, size, and type) [3]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Sediment	Pesticides	Low	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Maintain in the dark at less than 4 degrees Celsius from time of collection until receipt at the laboratory	14 days to extraction, 40 days to analysis at 4 degrees Celsius (For this study pesticide samples can be stored 299 days if frozen.)
Sediment	PCB Congeners	Low	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP:MSU-020 R06)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Maintain in the dark at less than 4 degrees Celsius from time of collection until receipt at the laboratory	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to one year. Sample extracts can be stored at less than -10 degrees Celsius for up to one year
Sediment	PCDD/F Congeners	Low	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP:MSU-018 R05)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Maintain in the dark at less than 4 degrees Celsius from time of collection until receipt at the laboratory	If stored at less than -10°C, solid multiphase samples can be stored up to one year. Sample extracts can be stored at less than -10°C for up to one year
Sediment	PAH	Low	Laboratory SOP for HRGC/LRMS (Laboratory SOP: MLA-021 R09)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Maintain in the dark at less than 4 degrees Celsius from time of collection until receipt at the laboratory	14 days to extraction, 40 days to analysis at 4 degrees Celsius (For this study PAH samples can be stored 199 days if frozen.)

Analytical SOP Requirements Table (Worksheet 19)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference [2]	Sample Volume	Containers (number, size, and type) [3]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Sediment	TCL SVOC	Low	SW846 Method 8270C (Laboratory SOP: EMS8270-15/ EOPGPC-04)	Minimum mass = 30 grams	One 8 oz glass jar (ship one jar for SVOC, metals, TOC, and percent moisture)	Cool to 4 degrees Celsius ± 2 degrees Celsius	14 days to extraction; 40 days to analysis at 4 degrees Celsius
Sediment	Metals	Low	SW846 Method 6010B/6020 (Laboratory SOPs: EMA217-08, EMA222-04)	Minimum mass = 2 grams	One 8 oz glass jar (ship one jar for SVOC, metals, TOC, and percent moisture)	Cool to 4 degrees Celsius ± 2 degrees Celsius	6 months at 4 degrees Celsius
Sediment	Total Mercury and Methyl-mercury	Low	USEPA Method 1630/1631 (Laboratory SOPs: MSL-I-013-09 and MSL-I-015-08)	Minimum mass = 1 gram	One 4oz pre-tared polyethylene bottle	Cool to 4 degrees Celsius ± 2 degrees Celsius and freeze as soon as possible	1 year at 4 degrees Celsius
Sediment	TOC	Low	Lloyd Kahn and (Laboratory SOP: EGN233-07)	Minimum mass = 1 gram	One 8 oz glass jar (ship one jar for SVOC, metals, TOC, and percent moisture)	Cool to 4 degrees Celsius ± 2 degrees Celsius	14 days at 4 degrees Celsius
Sediment	Percent Moisture	Unknown	Laboratory SOP: EGN007-07	Minimum mass = 10 gram	One 8 oz glass jar (ship one jar for SVOC, metals, TOC, and percent moisture)	Cool to 4 degrees Celsius ± 2 degrees Celsius	Analyze as soon as possible
Tissue	Pesticides	Low	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Freeze to 0 degrees Celsius to -20 degrees Celsius	14 days to extraction, 40 days to analysis at 4 degrees Celsius (For this study pesticide samples can be stored 299 days if frozen.)

Analytical SOP Requirements Table (Worksheet 19)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference [2]	Sample Volume	Containers (number, size, and type) [3]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Tissue	PCB Congeners	Low	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP:MSU-020 R06)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Freeze to 0 degrees Celsius to -20 degrees Celsius	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to one year. Sample extracts can be stored at less than -10 degrees Celsius for up to one year
Tissue	PCDD/F Congeners	Low	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP:MSU-018 R05)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Freeze to 0 degrees Celsius to -20 degrees Celsius	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to one year. Sample extracts can be stored at less than -10 degrees Celsius for up to one year
Tissue	PAH	Low	Laboratory SOP for HRGC/LRMS (Laboratory SOP: MLA-021 R09)	Minimum mass = 50 grams (combine mass for pesticide, PCB, PCDD/F, and PAH)	One 4 oz amber glass jar (ship one jar for pesticide, PCB, PCDD/F, and PAH)	Freeze to 0 degrees Celsius to -20 degrees Celsius	14 days to extraction, 40 days to analysis (For this study PAH samples can be stored 199 days if frozen.)
Tissue	TCL SVOC	Low	SW846 Method 8270C (Laboratory SOP: EMS8270-15/ EOPGPC-04)	Minimum mass = 30 grams	One 8 oz glass jar (ship one jar for SVOC, metals, and percent lipid)	Freeze to 0 degrees Celsius to -20 degrees Celsius	14 days to extraction; 40 days to analysis at 4 degrees Celsius
Tissue	Metals	Low	SW846 Method 6010B/6020 (Laboratory SOPs: EMA217-08, EMA222-04)	Minimum mass = 2 grams	One 8 oz glass jar (ship one jar for SVOC, metals, and percent lipid)	Freeze to 0 degrees Celsius to -20 degrees Celsius	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to 6 months.

Analytical SOP Requirements Table (Worksheet 19)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference [2]	Sample Volume	Containers (number, size, and type) [3]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Tissue	Inorganic arsenic	Low	Battelle Marine Sciences Laboratory SOP MSL-I-037-01	Minimum mass = 1 gram	One 4oz pre-tared polyethylene bottle filled 2/3 full	Freeze to 0 degrees Celsius to -20 degrees Celsius	28 days at 4 degrees Celsius. If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to 180 days.
Tissue	Total Mercury and Methyl-mercury	Low	USEPA Method 1630/1631 (Laboratory SOPs: MSL-I-013-09 and MSL-I-015-08)	Minimum mass = 1 gram	One 4oz pre-tared polyethylene bottle	Freeze to 0 degrees Celsius to -20 degrees Celsius	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to one year.
Tissue	Percent Lipid	Unknown	SM 2540B or equivalent (Laboratory SOP: EGN273-01)	Minimum mass = 1 gram	One 8 oz glass jar (ship one jar for SVOC, metals, and percent lipid)	Freeze to 0 degrees Celsius to -20 degrees Celsius	If stored at less than -10 degrees Celsius solid multiphase samples can be stored for up to one year.
Sediment	Toxicity *Chironomus dilutus*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407	Two gallons unsieved[4]	Two gallon HDPE bucket with lid	≤ 4 degrees Celsius	≤8 weeks, preferably ≤14 days[5]
Sediment	Toxicity *Hyalella azteca*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467	Two gallons unsieved[4]	Two gallon HDPE bucket with lid	≤ 4 degrees Celsius	≤8 weeks, preferably ≤14 days [5]

Analytical SOP Requirements Table (Worksheet 19)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference [2]	Sample Volume	Containers (number, size, and type) [3]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Sediment	Toxicity *Ampelisca abdita*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426	Two gallons unsieved[4]	Two gallon HDPE bucket with lid	≤ 4 degrees Celsius	≤8 weeks, preferably ≤14 days[5]

1: Sediment matrix refers to sediment split sample analyzed for sediment chemical concentration.
Tissue matrix refers to fish tissue split sample and benthic tissue split sample from *in-situ* and laboratory bioaccumulation tests.

2: Laboratory SOPs are provided in Attachment 7. The actual jar size may vary depending on the need of the assigned laboratory.

3: The minimum tissue mass to complete the required analyses is 85 grams. One tissue split sample shipment will include four containers: one 8 oz glass jar with a minimum mass of 33 grams for SVOC, metals, and percent lipid (Accutest Laboratories); one 4 oz pre-tared polyethylene bottle with a minimum mass of 1 gram for methylmercury and mercury (Accutest Laboratories); one 4 oz pre-tared polyethylene bottle with a minimum mass of 1 gram for inorganic arsenic (Accutest Laboratories); and one 8 oz glass amber jar with a minimum mass of 50 grams for PCB, PCDD/F, PAH, and pesticides (Axys Analytical Services).

4: All toxicity testing will be performed using the same two gallons of unsieved sediment. Accutest Laboratories' subcontractor (American Aquatic Testing, Inc.) performing toxicity tests will thoroughly mix each sample and sieve sediment through ≥2 millimeter mesh (*Ampelisca abdita* and *Chironomus dilutus*) or ≥ 3 millimeter mesh (*Hyalella azteca*) to remove large organisms and debris prior to conducting toxicity test.

5: To ensure timely acquisition of test organisms and laboratory space the CPG-assigned toxicology laboratory must notify Accutest Laboratories' subcontractor (American Aquatic Testing, Inc.) preferably 10 days before they start exposures so that they can start testing on, or as closely as possible, the same date as the CPG-assigned laboratory.

ASTM = American Society for Testing and Materials
HDPE = High density polyethylene
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectroscopy
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectroscopy
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
oz = ounce
SOP = Standard Operating Procedure
SVOC = Semivolatile organic compounds
TCL = Target Compound List
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #20 (UFP-QAPP Manual Section 3.1.1)
Field Quality Control Sample Summary Table

Summarize by matrix, analytical group, and concentration level the number of field quality control samples that will be collected and sent to the laboratory.

Field Quality Control Sample Summary Table (Worksheet 20)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Estimated No. of Sampling Locations	No. of Field Duplicate Pairs	No. of MS/MSD Samples	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Estimated Total No. of Samples to Lab
Sediment	Pesticides	Low	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate)	0	0	0	0	10 sediment split samples plus duplicate
Sediment	PCB Congeners	Low	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP: MSU-020 R06)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	0	0	0	0	10 sediment split samples plus duplicate
Sediment	PCDD/F Congeners	Low	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP: MSU-018 R05)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	0	0	0	0	10 sediment split samples plus duplicate
Sediment	PAH	Low	Laboratory SOP for HRGC/LRMS (Laboratory SOP: MLA-028 R05)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	1 pair per 20 or less (total of 2 samples)	0	0	0	10 sediment split samples plus duplicate. Extra mass for MS sample and MSD sample.
Sediment	TCL SVOC	Low	SW846 Method 8270C (Laboratory SOP: EMS8270-15/ EOPGPC-04)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	1 pair per 20 or less (total of 2 samples)	0	0	0	10 sediment split samples plus duplicate. Extra mass for MS sample and MSD sample.

Field Quality Control Sample Summary Table (Worksheet 20)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Estimated No. of Sampling Locations	No. of Field Duplicate Pairs	No. of MS/MSD Samples	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Estimated Total No. of Samples to Lab
Sediment	Metals	Low	SW846 Method 6010B/6020 (Laboratory SOP: EMA217-08, EMA222-04)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate)	1 MS sample only per 20 or less (total of 1 sample)	0	0	0	10 sediment split samples plus duplicate. Extra mass for MS sample only.
Sediment	Total Mercury and Methyl mercury	Low	USEPA Method 1630/1631 (Laboratory SOP: MSL-I-013-09 and MSL-I-015-08)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	1 MS sample only per 20 or less (total of 1 sample)	0	0	0	10 sediment split samples plus duplicate. Extra mass for MS sample only
Sediment	TOC	Low	USEPA Method Lloyd Kahn (Laboratory SOP: EGN233-07)	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 or less (total of 1 duplicate	1 pair per 20 or less (total of 1 sample)	0	0	0	10 sediment split samples plus duplicate. Extra mass for MS sample and MSD sample
Sediment	Percent Moisture	Low	Laboratory SOP: EGN007-07	10 sediment split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	0	0	0	0	0	10 sediment split samples.
Tissue	Pesticides	Low	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	0	0	0	0	50 tissue split samples plus duplicates

Field Quality Control Sample Summary Table (Worksheet 20)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Estimated No. of Sampling Locations	No. of Field Duplicate Pairs	No. of MS/MSD Samples	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Estimated Total No. of Samples to Lab
Tissue	PCB Congeners	Low	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP: MSU-020 R06)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	0	0	0	0	50 tissue split samples plus duplicates
Tissue	PCDD/F Congeners	Low	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP: MSU-018 R05)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	0	0	0	0	50 tissue split samples plus duplicates
Tissue	PAH	Low	Laboratory SOP for HRGC/LRMS (Laboratory SOP: MLA-028 R05)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	1 pair per 20 (total of 4 samples)	0	0	0	50 tissue split samples plus duplicates. Extra mass for MS sample and MSD sample.
Tissue	TCL SVOC	Low	SW846 Method 8270C (Laboratory SOP: EMS8270-15/ EOPGPC-04)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	1 pair per 20 (total of 4 samples)	0	0	0	50 tissue split samples plus duplicates. Extra mass for MS sample and MSD sample.

Field Quality Control Sample Summary Table (Worksheet 20)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Estimated No. of Sampling Locations	No. of Field Duplicate Pairs	No. of MS/MSD Samples	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Estimated Total No. of Samples to Lab
Tissue	Metals	Low	SW846 Method 6010B/6020 (Laboratory SOP: EMA217-08, EMA222-04)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	1 MS sample per 20 (total of 2 samples)	0	0	0	50 tissue split samples plus duplicates. Extra mass for MS sample only.
Tissue	Inorganic arsenic	Low	Battelle Marine Sciences Laboratory SOP MSL-I-037-01	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	1 MS sample per 20 (total of 2 samples)	0	0	0	50 tissue split samples plus duplicates. Extra mass for MS sample only.
Tissue	Total Mercury and Methyl mercury	Low	USEPA Method 1630/1631 (Laboratory SOP: MSL-I-013-09 and MSL-I-015-08)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	1 MS sample per 20 (total of 2 samples)	0	0	0	50 tissue split samples plus duplicates. Extra mass for MS sample only.
Tissue	Percent Lipid	Unknown	SM2540B or equivalent (Laboratory SOP: EGN273-01)	40 fish tissue split samples and 10 benthic tissue split samples Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	1 per 20 (total of 2 duplicates)	0	0	0	0	50 tissue split samples plus duplicates.

Field Quality Control Sample Summary Table (Worksheet 20)

Matrix [1]	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Estimated No. of Sampling Locations	No. of Field Duplicate Pairs	No. of MS/MSD Samples	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Estimated Total No. of Samples to Lab
Sediment	Toxicity Testing *Hyalella azteca*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467	10 sediment split samples used for toxicity testing. Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	0	0	0	0	0	10 sediment split samples used for toxicity testing.
Sediment	Toxicity Testing *Chironomus dilutus*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407	5 sediment split samples used for toxicity testing from the freshwater section of the river. Sampling locations to be determined by the oversight staff (refer to Worksheet 18).	0	0	0	0	0	5 sediment split samples used for toxicity testing.
Sediment	Toxicity Testing *Ampelisca abdita*	Low	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426	5 sediment split samples used for toxicity testing from the estuarine section of the river. Sampling locations to be determined by the oversight staff (refer to Worksheet 18)	0	0	0	0	0	5 sediment split samples used for toxicity testing.

1: Sediment matrix refers to sediment split sample analyzed for sediment chemical concentration, and sediment material used for toxicity testing
Tissue matrix refers to fish tissue split sample and benthic tissue split sample from *in-situ* and laboratory bioaccumulation tests.

2: The split sample program will include toxicity split samples for 10 sampling locations. Each location will be evaluated for 28-day survival and growth of *Hyalella azteca*. Half of the locations (5 locations) will also be evaluated for 10-day survival and growth of *Chironomus dilutus* and the other half (5 locations) will also be evaluated for 10-day survival of *Ampelisca abdita* (total of 20 toxicity tests). Selection of *Chironomus dilutus* or *Ampelisca abdita* will depend on salinity of interstitial water.

Acronyms (for previous Worksheet 20)

ASTM = American Society for Testing and Materials
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectroscopy
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectroscopy
MS = Matrix Spike
MSD = Matrix Spike Duplicate
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
PT = Performance Test
QAPP = Quality Assurance Project Plan
SOP = Standard Operating Procedure
SVOC = Semivolatile organic compounds
TCL = Target Compound List
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #21 (UFP-QAPP Manual Section 3.1.2)
Project Sampling SOP Reference Table

List all SOPs associated with project sampling including, but not limited to, sample collection, sample preservation, equipment cleaning and decontamination, equipment testing, inspection and maintenance, supply inspection and acceptance, and sample handling and custody. Include copies of the SOPs as attachments or reference all in the QAPP. Sequentially number sampling SOP references in the Reference Number column. The reference number can be used throughout the QAPP to refer to a specific SOP.

Project Sampling SOP References Table

Reference Number[1]	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work?	Comments
SOP No. 1	Procedure to Conduct Sample Management for CLP and Non-CLP Samples, August 2009, Revision No. 0	Malcolm Pirnie, Inc.	Note book, personal computer, PPE, sample coolers, ice, sample management material	No	Attachment 1
SOP No. 2	Procedure to Conduct a Technical System Field Audit, August 2009, Revision No. 0	Malcolm Pirnie, Inc.	Note book, camera, PPE, and check list	No	Attachment 2
Oversight Forms	Oversight Forms	Malcolm Pirnie, Inc.	Note book, camera, PPE and oversight forms	Yes –developed for this project	Attachment 6
EPA540-R -07-06	USEPA Contract Laboratory Program Guidance for Field Samplers, EPA540-R-07-06, July 2007	USEPA	Note book, personal computer, PPE sample coolers, ice, sample management material	No	To be used by the field team as a guide for collecting and preparing samples (refer to SOP No. 1).
Form II Lite User's Guide	Forms II Lite, Version 5.1 User's Guide, Version 5.1	USEPA	Personal computer, printer, Forms II Lite software	No	Forms II Lite software will be used to manage samples and create COC; however, depending on field conditions, oversight staff can generate a hand-written COC for sample shipment.
SOP No. HW-32	Standard Operating Procedure For Implementing The National Strategy For Procuring Analytical Services for All OSWER Programs (Superfund, RCRA, Brownfields), Revision 5, March 17, 2005	USEPA	Refer to referenced document	No	Refer to referenced document

1. Laboratory SOPs are provided in Attachment 7.

CLP = Contract Laboratory Program
COC = Chain of Custody
OSWER = Office of Solid Waste and Emergency Response
PPE = Personal Protection Equipment
QAPP = Quality Assurance Project Plan
RCRA = Resource Conservation and Recovery Act
SOP = Standard Operating Procedure
USEPA = United States Environmental Protection Agency

QAPP Worksheet #22 (UFP-QAPP Manual Section 3.1.2.4)
Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Identify all field equipment and instruments (other than analytical instrumentation) that require calibration, maintenance, testing, or inspection and provide the SOP reference number for each type of equipment. In addition, document the frequency of activity, acceptance criteria, and corrective action requirements on the worksheet.

This Worksheet is not applicable, since the oversight project will not require any field instrumentation.

QAPP Worksheet #23 (UFP-QAPP Manual Section 3.2.1)
Analytical SOP Reference Table

List all SOPs that will be used to perform on-site or off-site analysis. Indicate whether the procedure produces screening or definitive data. Sequentially number analytical SOP reference in the Reference Number column. Include copies of the SOPs as attachments or reference in the QAPP. The reference number can be used throughout the QAPP to refer to a specific SOP.

Analytical SOP References Table (Worksheet 23)

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
USEPA Method 1613B Modified	Axys Analytical Services: Analysis of Organochlorine Pesticides by HRGC/HRMS by Method MLA-028, February 2009 (Laboratory SOP: MLA-028 R05)	Definitive	Pesticides	HRGC/HRMS	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	No
USEPA Method 1668A	Axys Analytical Services: Analysis of PCB Congeners by USEPA Method 1668A, May 2006 (Laboratory SOP: MSU-020 R06)	Definitive	PCB Congeners	HRGC/HRMS	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	No
USEPA Method 1613B	Axys Analytical Services: Analysis of Polychlorinated Dioxins and Furans By USEPA Method 1613B, June 2005 (Laboratory SOP: MSU-018 R05)	Definitive	PCDD/F Congeners	HRGC/HRMS	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	No
Laboratory SOP for HRGC/HRMS	Axys Analytical Services: Analysis of Polycyclic Aromatic Hydrocarbons (PAH) and Alkylated PAH By Method MLA-021, February 2009 (Laboratory SOP: MLA-021 R09)	Definitive	PAH	HRGC/LRMS	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	No

Analytical SOP References Table (Worksheet 23)

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
SW846 Method 8270C	Accutest Laboratories: Method 8270C Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry. January 2009. (Laboratory SOP: EMS8270-15) Cleanup of Organic Extracts by Gel Permeation Chromoatography. May 2006. (Laboratory SOP: EOPGPC-04)	Definitive	TCL SVOC	GC/MS	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	No (Refer to footnote 1 on additional analytical clean-up of split samples)
SW846 Method 6010B/6020	Accutest Laboratories: Metals by Inductively Coupled Plasma Atomic Emission Spectrometry using Solid State ICP. August 2008 (Laboratory SOP: EMA222-04) Accutest Laboratories: Metals by Inductively Coupled Plasma – Mass Spectrometry. July 2008. (Laboratory SOP: EMA-217-08)	Definitive	Metals	ICP-AES and ICP-MS	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	No
USEPA Method 1631	Battelle Marine Sciences Laboratory: Total Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence. March 2009 (Laboratory SOP: MSL-I-013-09)	Definitive	Total Mercury	CVAFS	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382 Phone: 360-683-4151	No
USEPA Method 1630	Battelle Marine Sciences Laboratory: Methylmercury in Tissue and Sediment by Cold Vapor Atomic Fluorescence. August 2007 (Laboratory SOP: MSL-I-015-08)	Definitive	Methylmercury	CVAFS	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382 Phone: 360-683-4151	No

Analytical SOP References Table (Worksheet 23)

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
Battelle Marine Science Laboratory SOP MSL-I-037-01	Battelle Marine Sciences Laboratory: Arsenic Speciation Using High-Pressure Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry June 2009 (Laboratory SOP MSL-I-037-01)	Definitive	Inorganic arsenic	ICP-MS	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382 Phone: 360-683-4151	Yes Per Battelle Marine Sciences laboratory SOP MSL-I-037-01, HPLC-ICP-MS will be employed instead of AAS. Results obtained are comparable to USEPA Method 1632.
ASTM 2007; USEPA 2000	American Aquatic Testing, Inc.: 10-Day static whole sediment bioassay using *Chironomus dilutus* or *Chironomus riparius*. (Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407)	Definitive	Toxicity (*Chironomus dilutus)*	Toxicity testing equipment	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Phone: 610 434 9015 office	Yes (Refer to footnote 2 on details of SOP modification and logistics for testing)
ASTM 2007; USEPA 2000	American Aquatic Testing, Inc.: 28-Day static whole sediment bioassay using *Hyalella azteca*. (Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467)	Definitive	Toxicity (*Hyalella azteca)*	Toxicity testing equipment	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Phone: 610 434 9015 office	Yes (Refer to footnote 2 on details of SOP modification and logistics for testing)
ASTM 2007; USEPA 2000	American Aquatic Testing, Inc.: 10-Day static whole sediment bioassay using the amphipod *Ampelisca abdita*. (Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426)	Definitive	Toxicity *(Ampelisca abdita)*	Toxicity teting equipment	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Phone: 610 434 9015 office	Yes (Refer to footnote 2 on details of SOP modification and logistics for testing)

1: As necessary, Accutest Laboratories will perform additional clean-up of split samples (via gel permeation chromatography) prior to analysis of organic compounds.
2: Toxicity Test SOP Modification: At selected locations based (in part) on field-measured salinity values, Malcolm Pirnie, Inc. oversight staff will request that the CPG field team collect additional sediment mass for laboratory toxicity split sample tests (refer to Worksheet 19 for sample mass requirements). It is anticipated that approximately 10 sampling locations will be sampled – approximately 5 locations in the estuarine section of the river and approximately 5 locations in the freshwater section of the river. Malcolm Pirnie, Inc. oversight staff will coordinate with the CPG-assigned laboratory to confirm salinity of interstitial water, selected organism for toxicity test for each sampling location, and start time of toxicity tests (refer Worksheet 19 for holding times). A *Chironomus dilutus* growth and toxicity test will be conducted if the interstitial salinity is <5 ppt and an *Ampelisca abdita*

toxicity test will be conducted if the interstitial salinity is ≥5 ppt. A *Hyalella azteca* growth and toxicity test will be conducted for all sampling locations (yielding two toxicity tests per sampling location). Malcolm Pirnie, Inc. will also verify that test conditions between the parent toxicity test and split-sample toxicity test (*e.g*., dissolved oxygen, temperature, salinity, or any other test conditions that could impact the sensitivity of the test organisms) are similar. The toxicity tests must meet the performance standards for these tests provided by ASTM (2007) and USEPA (2000). Worksheets 12 and 28 define the criteria that will be used to evaluate toxicity test acceptability. The government-assigned laboratory will follow their own laboratory SOPs to perform toxicity testing but modify them according to the CPG-laboratory SOP to ensure comparability on test conditions. Areas of test flexibility within the SOPs [*e.g*., test renewal (frequency and methods) and optional water quality measurements] or areas where specific directions is omitted (*e.g*., water hardness) will be established by the CPG-assigned laboratory and communicated to the government-assigned laboratory via Malcolm Pirnie, Inc. oversight staff prior to testing. Prior to testing, the government-assigned laboratory will thoroughly mix each sample, remove the sediment volume needed for testing, and sieve it to remove large organisms and debris: sediment for *Hyalella azteca* testing will be sieved using a ≥3 millimeter screen and sediment for *Chironomus dilutus* and *Ampelisca abdita* testing will be sieved using a ≥2 millimeter screen. Due to concern regarding the usability of *Hyalella azteca* toxicity data from the estuarine section of the river where salinity levels are >15 ppt, the government-assigned laboratory will use the same approach defined in the CPG RI/FS QAPP: the interstitial salinity in the sediment samples will be measured in the laboratory, and the interstitial salinity > 8 ppt will be adjusted to a range of 5 to 7 ppt before test initiations. The adjustment will be performed by replacing the overlaying freshwater in each beaker (the sediments will not be manually mixed with fresh water) and incorporating a salinity control into the test design. The Hyalella toxicity test results from estuarine sampling areas will be evaluated by comparing the survival and growth results of the negative control with a salinity-adjusted control (the negative control sediment for the Ampelisca toxicity test).

References:

ASTM. 2007. “Standard Test Method for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates.” ASTM E 1706-05, West Conshohocken, PA.
USEPA. 2000. “Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates.” Second Edition. EPA/R-99/064. March 2000.

AAS = Atomic Absorption Spectrometry
ASTM = American Society for Testing and Materials
CPG = Cooperating Parties Group
CVAFS = Cold Vapor Atomic Fluorescence Spectrometry
DESA = Division of Environmental Science and Assessment
GC/MS = Gas Chromatography /Mass Spectrometry
HPLC = High Pressure Liquid Chromatography
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectroscopy
ICP-AES = Inductively Couple Plasma – Atomic Emission Spectrometry
ICP-MS = Inductively Couple Plasma – Mass Spectrometry
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
ppt = parts per thousand (salinity unit)
QAPP = Quality Assurance Project Plan
RI/FS = Remedial Investigation and Feasibility Study
SOP = Standard Operating Procedure
SVOC = Semivolatile organic compounds
TCL = Target Compound List
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #24 (UFP-QAPP Manual Section 3.2.2)
Analytical Instrument Calibration Table

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for Corrective Action	SOP Reference
CVAFS	Per vendor instrument manual and laboratory SOP	Per USEPA Method 1630/1631 and laboratory SOP	Per USEPA Method 1630/1631 and laboratory SOP	Correct and recalibrate	Assigned laboratory personnel	USEPA Method 1630/1631; refer to Attachment 7 for laboratory SOP
GC/MS	Per vendor instrument manual and laboratory SOP	Per SW846 Method 8270C and laboratory SOP	Per SW846 Method 8270C and laboratory SOP	Correct and recalibrate	Assigned laboratory personnel	SW846 Method 8270C; refer to Attachment 7 for laboratory SOP
HRGC/HRMS and HRGC/LRMS	Axys Analytical Services SOP	Axys Analytical Services SOP	Axys Analytical Services SOP	Correct and recalibrate	Assigned laboratory personnel	Refer to Attachment 7 for laboratory SOP
ICP-AES and ICP-MS	Per vendor instrument manual and laboratory SOP	Per SW846 Method 6010B/6020 and laboratory SOP	Per SW846 Method 6010B/6020 and laboratory SOP	Correct and recalibrate	Assigned laboratory personnel	SW846 Method 6010B/6020 and laboratory SOP; refer to Attachment 7 for laboratory SOP
TOC Instrument	Per vendor instrument manual and laboratory SOP	Check daily and laboratory SOP	Per USEPA Lloyd Kahn and laboratory SOP	Correct and recalibrate	Assigned laboratory personnel	USEPA Lloyd Kahn; refer to Attachment 7 for laboratory SOP

CVAFS = Cold Vapor Atomic Fluorescence Spectrometry
GC/MS = Gas Chromatography /Mass Spectrometry
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectrometry
ICP-AES = Inductively Couple Plasma – Atomic Emission Spectrometry
ICP-MS = Inductively Couple Plasma – Mass Spectrometry
SOP = Standard Operating Procedure
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #25 (UFP-QAPP Manual Section 3.2.3)
Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Identify all analytical instruments that require maintenance, testing, or inspection and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table (Worksheet 25)

Instrument/ Equipment [1,2,3]	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
CVAFS	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24
GC/MS	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24
HRGC/HRMS	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24
HRGC/LRMS	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24
ICP-AES and ICP-MS	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24
TOC Instrument	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Refer to Laboratory Quality Manual	Prior to analyzing samples per the laboratory procedures	Per the instrument manual and applicable laboratory SOPs	Correct the problem prior to analyzing samples	The assigned subcontract laboratory	Refer to USEPA, Standard Method, CLP SOW, and methods listed in Worksheet 23 and 24

1. The maintenance of the analytical instruments including the testing activity, inspection activity, frequency, acceptance criteria, responsible person, and SOP reference must be documented in the Laboratory Quality Manual.
2. If DESA laboratory or a contract laboratory performs analyses, the associated instrumentation must be maintained according to their SOPs and Laboratory Quality Manual. If a subcontract laboratory is assigned, the associated instrumentation must be maintained according to their SOPs and Laboratory Quality Manual. The subcontract laboratory(s) used for chemical analyses will be required to maintain and adhere to their quality manual which meets NELAC requirements.
3. Spare parts and maintenance of laboratory analytical instrumentation is the responsibility of the assigned USEPA CLP laboratory, the DESA laboratory, or the subcontract laboratory.

CLP = Contract Laboratory Program
CVAFS = Cold Vapor Atomic Fluorescence Spectrometry
DESA = Division of Environmental Science and Assessment
GC/MS = Gas Chromatography /Mass Spectrometry
HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS = High Resolution Gas Chromatography / Low Resolution Mass Spectrometry
ICP-AES = Inductively Couple Plasma – Atomic Emission Spectrometry
ICP-MS = Inductively Couple Plasma – Mass Spectrometry
NELAC = National Environmental Laboratory Accreditation Conference
SOP = Standard Operating Procedure
SOW = Scope of Work
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #26 (UFP-QAPP Manual Appendix A)
Sample Handling System

Use this worksheet to identify components of the project-specific sample handling system. Record personnel, and their organizational affiliations, who are primarily responsible for ensuring proper handling, custody, and storage of field samples from the time of collection, to laboratory delivery, to final sample disposal. Indicate the number of days field samples and their extracts/digestates will be archived prior to disposal.

Sample Handling System
SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Split samples will be collected by the CPG field crew, who will transfer custody to the Malcolm Pirnie, Inc. oversight field crew. For fish tissue samples and bioaccumulation testing (benthic tissue samples), the CPG-assigned laboratory will be responsible for homogenizing the tissue sample, generating a split sample, and shipping the sample to the assigned oversight laboratory. (Refer to Worksheet 11 for details on split sample coordination.)
Sample Packaging (Personnel/Organization): Malcolm Pirnie, Inc. oversight field crew
Coordination of Shipment (Personnel/Organization): Malcolm Pirnie, Inc. Sample Management Officer
Type of Shipment/Carrier: Federal Express for overnight delivery or courier to the laboratory
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Assigned USEPA CLP laboratory, DESA laboratory, or subcontract laboratory personnel
Sample Custody and Storage (Personnel/Organization): Assigned USEPA CLP laboratory, DESA laboratory, or subcontract laboratory personnel
Sample Preparation (Personnel/Organization): Assigned USEPA CLP laboratory, DESA laboratory, or subcontract laboratory personnel
Sample Determinative Analysis (Personnel/Organization): Assigned USEPA CLP laboratory, DESA laboratory, or subcontract laboratory personnel
SAMPLE ARCHIVING
Field Sample Storage (Number of days from sample collection): Split samples may be stored in the field according to preservation requirements in Worksheet 19. Split samples will preferably be shipped to government-assigned laboratories between Monday and Wednesday.
Sample Extract/Digestate Storage (Number of days from extraction/digestion): Sample extraction and digestion must be conducted according to any applicable USEPA CLP SOW. Subcontract laboratories should refer to Worksheet 19 for approved holding times of samples.
SAMPLE DISPOSAL
Personnel/Organization: Assigned USEPA CLP, DESA laboratory, or subcontract laboratory personnel
Number of Days from Analysis: At least 60 days

1: SOP No. 1 “Procedure to Conduct Sample Management for Contract Laboratory Program and Non-Contract Laboratory Program Samples” is provided in Attachment 1.
2: Example COC forms are provided in Attachment 3 and Attachment 4.

Acronym list for Worksheet 26 table presented on previous page:

CLP = Contract Laboratory Program
COC = Chain of Custody (see text below)
CPG = Cooperating Parties Group
DESA = Division of Environmental Science and Assessment
MS/MSD = Matrix Spike and Matrix Spike Duplicate
RCSS = Regional Sample Control Center (see text below)
SOP = Standard Operating Procedure (see text below)
SOW = Scope of Work (see text below)
USEPA = United States Environmental Protection Agency

Sample Handling and Custody

Sample custody procedures ensure the timely, correct, and complete analysis of each sample for all parameters requested. A sample is considered to be in someone's custody if it:

- Is in his/her possession.
- Is in his/her view, after being in his/her possession.
- Is in his/her possession and has been placed in a secured location.
- Is in a designated secure area.

Sample custody documentation provides a written record of sample collection and analysis. The sample custody procedures provide for specific identification of samples associated with an exact location, the recording of pertinent information associated with the sample, including time of sample collection and any preservation techniques, and a COC record that serves as physical evidence of sample custody. (Forms II Lite software will be used to manage samples and create COC; however, depending on field conditions, oversight staff can generate a hand-written COC for sample shipment.) Custody procedures will be similar to the procedures outlined in *USACE Requirements for the Preparation of Sampling and Analysis Plans* (USACE, 2001) and *USEPA CLP Guidance for Field Samplers* (USEPA, 2007). The COC documentation system provides the means to individually identify, track, and monitor each sample from the time of collection through final data reporting. Sample custody procedures are developed in three areas: sample collection, laboratory analysis, and final evidence files, which are described below.

Field Sample Handling and Custody

Field records provide a means of recording information for each field activity performed at the Site. COC procedures document pertinent sampling data and all

transfers of custody until the samples reach the analytical laboratory. The sample packaging and shipment procedures summarized below will ensure that the samples arrive at the laboratory with the COC intact. Refer to SOP No. 1 in Attachment 1 for sample management information. Worksheet 19 lists the specific sample preservation requirements for each test method.

Field Procedures

The general responsibilities of the field team are listed below:

- The field oversight crew is personally responsible for the care and custody of the samples until they are transferred to the Sample Management Officer or until they are properly dispatched. As few people as possible should handle the samples.
- The field oversight crew is responsible for entering the proper information on the oversight forms, including all pertinent information such as sample identification number, date and time of sample collection, type of analysis, and description of sample location. The information entered on the oversight form will be used to generate a COC.
- All sample containers will be labeled with the project identification, sample number, matrix, type of analysis required, and preservation requirements.
- The samples will be properly preserved, bagged, and packed into coolers. The original COC form will be placed into the lead cooler and will be shipped to the laboratory.
- The Sample Management Officer will review all field activities to determine whether proper custody procedures were followed during the field work and if additional samples are required.

Field Records

The oversight forms will provide the means of recording data collection activities. Entries will be described in as much detail as possible so that persons going to the Site can reconstruct a particular situation without reliance on memory. At the beginning of each day, the date, start time, weather, and names of all sampling team members present will be entered. The names of visitors to the Site and the purpose of their visit will also be recorded. All field measurements, as well as the

instrument(s), will be noted.

Split samples will be obtained from the CPG field crew or CPG-assigned laboratory. Sample identification numbers will be assigned at the time the data are entered on the field oversight form. MS/MSD samples for sediment and tissue split samples will not be noted on the COC forms as they will be collected after homogenization of the split samples in the analytical laboratory. The Sample Management Officer will coordinate with the CPG-assigned laboratory to expedite the shipment of split samples (fish tissue and benthic tissue from the *in-situ* and laboratory bioaccumulation tests) to the assigned USEPA laboratory or subcontract laboratory.

Sample Identification System

All samples collected from the Site must be identified with a sample label in addition to an entry on the COC. Indelible ink will be used to complete sample labels and handwritten COCs. All CLP samples must be generated using Forms II Lite software. Forms II Lite can also be used to create COCs for non-CLP samples. CLP samples will be assigned a CLP sample number by the Forms II Lite software. In addition, each sample shall be identified by a unique sample number. The sample identification scheme to be used will be the same identification number assigned by CPG with the letters “MP” at the end of the CPG identification. Note: Refer to the information in *USEPA CLP Guidance for Field Samplers* which can be found at http://www.epa.gov/superfund/programs/clp/guidance.htm for more detailed information on the proper collection, identification, handling and shipping of samples to a CLP laboratory.

Sample Labels/Tags

Sample labels will require the field team to complete the following information for each sample container:

1. Site Name
2. Sample Number
3. Sample Matrix
4. Parameters to be analyzed
5. Date of Collection
6. Time of Collection
7. Preservation Technique Employed (if applicable)

8. Sampler's Name

Sample Receipt

A designated sample custodian accepts custody of the samples and verifies that the information on the sample labels matches the information on the COC. The sample custodian will document any discrepancies and will sign and date all appropriate receiving documents. The sample custodian will also document the condition of the samples upon receipt at the laboratory. The CLP laboratories will send a copy of the sample receipt checklist to USEPA's Regional Sample Control Center (RSCC). Once the samples have been accepted by the laboratory, checked and logged in, they must be maintained in accordance with laboratory custody and security requirements. To ensure traceability of samples while in the possession of the laboratory, a method for sample identification that has been documented in a laboratory SOP will be used to assign sample numbers. The following stages of analysis must be documented by the laboratory: Sample Extraction/Preparation, Sample Analysis, Data Reduction, and Data Reporting. Laboratory personnel are responsible for the custody of samples until they are returned to the sample custodian.

When sample analyses and quality assurance checks have been completed in the laboratory, the used portion of the sample must be stored or disposed of in accordance with the protocols specified in the CLP SOW or the subcontract agreement. Identifying labels, data sheets, COCs, and laboratory records will be retained until analyses and quality assurance checks are completed in accordance with the protocols specified in the CLP SOW or the subcontract agreement.

QAPP Worksheet #27 (UFP-QAPP Manual Section 3.3.3)
Sample Custody Requirements

Describe the procedures that will be used to maintain sample custody and integrity. Include examples of chain-of-custody forms, traffic reports, sample identification, custody seals, laboratory sample receipt forms, and laboratory sample transfer forms. Attach or reference applicable SOPs.

Sample Custody Requirements (Worksheet 27)

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory): The CPG field crew or CPG-assigned laboratory will collect and process samples following the procedures described RI/FS QAPP. Split samples will be judgmentally selected by Malcolm Pirnie, Inc. oversight field crew. The CPG field crew will collect the split sample by transferring a representative portion of the selected split sample to the Malcolm Pirnie, Inc. oversight field crew, who will prepare the COC and prepare the split samples for shipment to the laboratory. The field sample custody procedures (including sample packing, shipment, and delivery requirements) are discussed in the text in Worksheet 26. For additional information, refer to SOP No. 1 in Attachment 1 and the *USEPA CLP Guidance for Field Samplers* for sample management information. For fish tissue samples and bioaccumulation testing (benthic tissue samples), the CPG-assigned laboratory will be responsible for homogenizing the tissue sample, generating a split sample, and shipping the sample to the assigned oversight laboratory. Refer to Worksheet 11 for details on split sample coordination.
Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal): Each laboratory (USEPA CLP laboratory, DESA laboratory, or the subcontract laboratory) will have a sample custodian, who accepts custody of the samples and verifies that the information on the sample labels matches the information on the COC. The sample custodian will document any discrepancies and will sign and date all appropriate receiving documents. The sample custodian will also document the condition of the samples upon receipt at the laboratory.
Sample Identification Procedures: The sample identification scheme to be used will be the same identification number assigned by CPG with the letters "MP" at the end of the CPG identification. Sample labeling procedures are discussed in the text in Worksheet 26.
COC Procedures: A COC record will accompany the samples from the time of sampling through all transfers of custody. Example COC forms are attached to the Oversight QAPP. The COC procedures are detailed in SOP No. 1 in Attachment 1. The COC procedures for CLP samples are detailed in *USEPA CLP Guidance for Field Samplers*. (Forms II Lite software will be used to manage samples and create COC; however, depending on field conditions, oversight staff can generate a hand-written COC for sample shipment.)

1: Example COC forms are provided in Attachment 3 and Attachment 4.

CLP = Contract Laboratory Program
COC = Chain of Custody
CPG = Cooperating Parties Group
DESA = Division of Environmental Science and Assessment
QAPP = Quality Assurance Project Plan
RCSS = Regional Sample Control Center (see text below)
RI/FS = Remedial Investigation / Feasibility Study
SOP = Standard Operating Procedure (see text below)
SOW = Scope of Work (see text below)
USEPA = United States Environmental Protection Agency

Chain of Custody Procedure

When samples are being submitted to a USEPA CLP laboratory, the COC must be generated using Forms II Lite software. Each CLP sample will have a CLP number assigned in addition to the field sample identification number. The following information is typically recorded on manual COC forms. All COC forms must be signed in ink:

- Project name and/or project number.
- Signature of Sample Management Officer or designee.
- Sampling location number.
- Date and time of collection.
- Grab or composite sample designation.
- Sample matrix.
- Sampling location description.
- Field identification number.
- Analyses required.
- Preservation technique.
- Signatures and dates for transfers of custody.
- Air express/shipper's bill of lading identification numbers.

The COC form serves as an official communication to the laboratory detailing the particular analyses required for each sample. The COC record will accompany the samples from the time of sampling through all transfers of custody. It will be kept on file at the laboratory where samples are analyzed and archived. Three copies of the COC form are created; one copy is retained by the Field Oversight Leader and two are sent to the laboratory. An electronic copy of each COC should be also made and kept in the project electronic-file directory. The Sample Management Officer or designee completes a COC record to accompany each shipment from the field to the laboratory. In the case of CLP samples a copy of the COC created by Forms

II Lite must be sent to the USEPA CLP Region 2 Coordinator. The completed COC is placed in a zip-lock bag and taped to the inside cover of the sample shipping container. If there is more than one container in a shipment, copies of the COC form will be placed in each container. Each container is then sealed with custody seals and custody is transferred to the laboratory. (Forms II Lite software will be used to manage samples and create COC; however, depending on field conditions, oversight staff can generate a hand-written COC for sample shipment.)

Transfer of Custody and Shipment

The custody of samples must be maintained from the time of sampling through shipment and relinquishment to the laboratory. Instructions for transferring custody are given below:

- All samples are accompanied by a COC. When transferring custody of samples, the individuals relinquishing and receiving will sign, date, and note the time on the COC. This form documents sample custody transfer from the Sample Management Officer or designee, through the shipper, to the analytical laboratory. Since a common carrier will usually not accept responsibility for handling COC forms, the name of the carrier is entered under "Received by," the bill-of-lading number is recorded in the comments section, and the COC form is placed in a zip-lock plastic bag and taped to the inside lid of the lead shipping cooler. Copies of the COC form will be placed in each additional cooler in a shipment.
- Samples will be packaged for shipment and either picked up at the Site by the laboratory or dispatched to the appropriate laboratory via overnight delivery service. SOP No. 1 in Attachment 1 contains the proper sample packaging techniques. A separate COC record must accompany each shipment. Shipping containers will be sealed for shipment to the laboratory. Two custody seals will be applied to each cooler to document that the container was properly sealed and to determine if the container was tampered with during shipment. The custody seals will be placed on the coolers in such a manner that the custody seal would be broken if the cooler were opened (*i.e.*, diagonally opposite corners of the cooler lid).
- The original COC (and a copy for CLP laboratories) will accompany the shipment. A copy will be retained by the Field Oversight Leader.

- If the samples are sent by common carrier or air freight, proper documentation must be maintained. For example, the bill of lading must be retained by the Field Oversight Leader.

Laboratory Custody Procedures

The laboratory custody procedures will be equivalent to those described in the latest edition of the CLP SOW or laboratory custody SOPs, including:

- A designated sample custodian accepts custody of the samples and verifies that the information on the sample labels matches the information on the COC. The sample custodian will document any discrepancies and will sign and date all appropriate receiving documents. The sample custodian will also document the condition of the samples upon receipt at the laboratory. The CLP laboratories will send a copy of the sample receipt checklist to USEPA's RSCC, while the subcontract laboratories will complete the form and return it electronically.
- Once the samples have been accepted by the laboratory, checked and logged in, they must be maintained in accordance with laboratory custody and security requirements.
- To ensure traceability of samples while in the possession of the laboratory, a method for sample identification that has been documented in a laboratory SOP will be used to assign sample numbers.
- The following stages of analysis must be documented by the laboratory:
    - Sample Extraction/Preparation.
    - Sample Analysis.
    - Data Reduction.
    - Data Reporting.
- Laboratory personnel are responsible for the custody of samples until they are returned to the sample custodian.
- When sample analyses and quality assurance checks have been completed in the laboratory, the used portion of the sample must be stored or disposed of in accordance with the protocols specified in the CLP SOW or the subcontract agreement. Identifying labels, data sheets, COCs,

and laboratory records will be retained until analyses and quality assurance checks are completed in accordance with the protocols specified in the CLP SOW or the subcontract agreement.

Final Evidence Files

In the final phase of sample custody, the COC records and sample analysis request form copies are archived in their respective project files. Laboratory custody forms, sample preparation and analysis logbooks, and data packages will become part of the laboratory final evidence file. Other relevant documentation including records, reports, and correspondence, logs, pictures, and data review reports will be archived by Malcolm Pirnie, Inc.

Sample Holding Times

Information on sample holding times and required preservation for each test method are provided in Worksheet 19.

Sample Packaging and Shipping Requirements

Custody of samples must be maintained through the shipment of samples to the selected laboratory. All samples will be packaged and shipped at the end of each day unless other arrangements are made with the laboratory. See SOP No. 1 in Attachment 1 for a description of the Sample Management and Custody Procedures as well as sample packing. Also refer to the *USEPA CLP Guidance for Field Samplers* for more details regarding shipment of CLP samples**.**

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for PCB Congeners (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1668A (Axys Analytical Services SOP MSU-020)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicate	1 per 20 field samples	USEPA 1668A (Axys SOP MSU-020)	Investigate and correct, if necessary repeat sample analysis	Assigned laboratory	Precision	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)

QC Samples Table for PCB Congeners (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1668A (Axys Analytical Services SOP MSU-020)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial Calibration	At initial set up or when corrective is taken, which may change calibration per USEPA 1668A	USEPA 1668A (Axys SOP MSU-020)	USEPA 1668A	Assigned laboratory	Accuracy	Per USEPA 1668A and the criteria in the Axys Analtyical Services SOP
Calibration Verification	Prior to every 12 hr. period, but following Column Performance Solution and at end of 12 hr. period per USEPA 1668A	USEPA 1668A (Axys SOP MSU-020)	USEPA 1668A	Assigned laboratory	Accuracy	Per USEPA 1668A
Initial Precision and Recovery	Prior to analyzing samples	USEPA 1668A (Axys SOP MSU-020)	Investigate and correct per USEPA 1668A	Assigned laboratory	Accuracy/Bias	USEPA 1668A (Axys SOP MSU-020) RSD 40%, recovery 60-140%

QC Samples Table for PCB Congeners (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCB Congeners
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1668A (Axys Analytical Services SOP MSU-020)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
On-going Precision and Recovery	Each group of samples digested	USEPA 1668A (Axys SOP MSU-020)	Redigest and reanalyze	Assigned laboratory	Accuracy/Bias	USEPA 1668A (Axys SOP MSU-020) warning 70-130%, acceptance 50-150%
Method Detection Limits (MDLs)	At instrument setup and at least annually and for a new operator	USEPA 1668A (Axys SOP MSU-020)	Re-determine when necessary	Assigned laboratory	Sensitivity	USEPA 1668A (Axys SOP MSU-020)
Method Blank	One per analytical batch of 20 or fewer samples	USEPA 1668A (Axys SOP MSU-020)	Investigate and correct	Assigned laboratory	Sensitivity	USEPA 1668A and the criteria in the Axys Analytical Services SOP MSU-020
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1668A, including initial and ongoing studies to demonstrate precision and accuracy, calibration verification, internal standards added to all extracts, cleanup standards and laboratory control standards for accuracy, and blanks and method detection limits for sensitivity.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for PCDD/F (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCDD/F
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1613B (Axys Analytical Services SOP MSU-018)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicate	1 per 20 field samples	Axys Analytical Laboratory SOP MSU-018	Investigate and correst, if necessary repeat sample analysis	Assigned laboratory	Precision	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)

QC Samples Table for PCDD/F (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCDD/F
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1613B (Axys Analytical Services SOP MSU-018)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial Calibration	At initial set up or when corrective is taken, which may change calibration per method 1613B	USEPA Method 1613B (Axys SOP MSU-018)	Per USEPA Method 1613B	Assigned laboratory	Accuracy	Per USEPA Method 1613B and the criteria in the Axys Analytical Services SOP (MSU-018)
Calibration Verification	Prior to every 12 hr. period, but following Column Performance Solution and at end of 12 hr. period per method 1613B	USEPA Method 1613B (Axys SOP MSU-018)	Investigate and correct problem. Recalibrate and if necessary re-analyze.	Assigned laboratory	Accuracy	Per USEPA Method 1613B and the criteria in the Axys Analytical Services SOP (MSU-018, Table 1)
Initial Precision and Recovery	Prior to analyzing samples	USEPA Method 1613B (Axys SOP MSU-018)	Investigate and correct by USEPA Method 1613B	Assigned laboratory	Accuracy	Per recoveries given in Analytical Services SOP (MSU-018, Table 1)

QC Samples Table for PCDD/F (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PCDD/F
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1613B (Axys Analytical Services SOP MSU-018)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
On-going Precision and Recovery	Each group of samples digested	USEPA Method 1613B (Axys SOP MSU-018)	Redigest and reanalyze	Assigned laboratory	Accuracy	Per recoveries given in Analytical Services SOP (MSU-018, Table 1)
Method Detection Limits (MDLs)	At instrument setup and at least annually and for a new operator	USEPA Method 1613B (Axys SOP MSU-018)	Re-determine when necessary	Assigned laboratory	Sensitivity	Per USEPA Method 1613B (Axys Analytical Services SOP MSU-018)
Method Blank	One per analytical batch of 20 or fewer samples	USEPA Method 1613B (Axys SOP MSU-018)	Investigate and correct	Assigned laboratory	Sensitivity	Less than QL
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1613B.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Pesticides (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Chlorinated Pesticides
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Axys MLA-028 (see Attachment 7 for summary)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	**Frequency/Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field Duplicates	1 per 20 field samples	QAPP	If the RPD exceeds limits for the field replicate, this will be addressed by the Malcolm Pirnie Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicate	1 per 20 field samples	Per Axys MLA-028	Investigate and correct, if necessary repeat analyses	Assigned laboratory	Accuracy	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)

QC Samples Table for Pesticides (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Chlorinated Pesticides
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Axys MLA-028 (see Attachment 7 for summary)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial Calibration	At initial set up or when corrective is taken, which may change calibration per Axys MLA-028	Per Axys MLA-028	Per Axys MLA-028	Assigned laboratory	Accuracy	Per Axys MLA-028
Calibration Verification	Prior to every 12 hr. period, but following Column Performance Solution and at end of 12 hr. period per Axys MLA-028	Per Axys SOP MLA-028	Per Axys SOP MLA-028 investigate and correct problem. Recalibrate and if necessary re-analyze samples.	Assigned laboratory	Accuracy	Per Axys SOP MLA-028 must be within ±20%
On-going Precision and Recovery	Each group of 20 samples or less prior to analysis of samples	Per Axys SOP MLA-028	Investigate and correct problem per Axys SOP MLA-028	Assigned laboratory	Accuracy	Per Axys SOP MLA-028 (tables 4 and 5)

QC Samples Table for Pesticides (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Chlorinated Pesticides
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Axys MLA-028 (see Attachment 7 for summary)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
MB	Each time samples are extracted	Per Axys SOP MLA-028	Per Axys SOP MLA-028 investigate and correct	Assigned laboratory	Sensitivity	Less than QLs
MDL	Annually	Per Axys SOP MLA-028	Per Axys SOP MLA-028	Assigned laboratory	Sensitivity	Low enough to support QLs
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in Axys MLA-028 including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits. Axys Analytical's requirements for MLA-028 are given in Attachment 7.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for PAH (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PAH
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	GC-MS Isotope Dilution Axys MLA-021
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the limits exceed limits for the field replicate, this will be addressed by the Malcolm Pirnie Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicates	1 per 20 field samples	Axys Analytical Services SOP MLA-021	Investigate and correct, if necessary reanalyze affected samples	Assigned laboratory	Precision	Must agree to within ±20% of the mean (applicable to concentration >10 times the DL)

QC Samples Table for PAH (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PAH
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	GC-MS Isotope Dilution Axys MLA-021
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
MS/MSD	Each group of field samples in an SDG, or each SDG, whichever is most frequent per Axys MLA-021	QAPP	Investigate and document in data summary	Assigned laboratory	Accuracy/Bias and Precision	Recovery per Axys SOP MLA-021(Table 2, RPD within ±20%)
Deuterated Monitoring Compounds	Each sample, standard, blank	Per Axys SOP MLA-021	Per Axys SOP MLA-021 investigate and reanalyze affected samples	Assigned laboratory	Accuracy/Bias	Recovery per Axys SOP MLA-021
MB	Once every 12 hours for each instrument per Axys MLA-021	Per Axys SOP MLA-021	Investigate and correct	Assigned laboratory	Sensitivity	Per Axys SOP MLA-021
MDL	Annual	Per Axys SOP MLA-021	Per Axys SOP MLA-021	Assigned laboratory	Sensitivity	Per Axys SOP MLA-021

QC Samples Table for PAH (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	PAH
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	GC-MS Isotope Dilution Axys MLA-021
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Axys Analytical Services
No. of Sample Locations	See Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in Axys MLA-021, such as laboratory duplicates and matrix spike duplicates for precision, matrix spikes, Deuterated monitoring compounds for accuracy, and blanks and method detection limits for sensitivity. The Axys Analytical lab personnel must follow all the corrective actions required by the laboratory SOP.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for SVOC (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	SVOC
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 8270C and Accutest SOP EMS8270-15/ EOPGPC-04
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Continuing Calibration	Every 12 hours of analysis	SW846 Method 8270C	Correct, re-calibrate if necessary	Assigned lab	Accuracy	The percent difference for the continuing calibration compounds must be less than 20%.

QC Samples Table for SVOC (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	SVOC
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 8270C and Accutest SOP EMS8270-15/ EOPGPC-04
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Surrogate	With every sample	SW846 Method 8270C and Accutest SOP EMS8270-15/EOP GPC-04	Investigate and correct per laboratory SOP re-analyze samples if necessary	Assigned laboratory	Accuracy/Bias	Recoveries per SW846 Method 8270C and the criteria in laboratory SOP (Accutest EMS8270-15/EOPGPC-04)
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	Each batch of 20 or less	SW846 Method 8270C and Accutest SOP EMS8270-15/EOP GPC-04	Investigate matrix effects, record in case narrative	Assigned laboratory	Accuracy/Bias/Precision	Recovery and RPD per lab control limits for individual compounds
Method Detection Limits (MDLs)	Annual	SW846 Method 8270C and Accutest SOP EMS8270-15/EOP GPC-04	Determine before analyzing samples	Assigned laboratory	Sensitivity	Low enough to support QLs

QC Samples Table for SVOC (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	SVOC
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 8270C and Accutest SOP EMS8270-15/ EOPGPC-04
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per analytical batch of 20 or fewer samples	SW846 Method 8270C and Accutest SOP EMS8270-15/EOP GPC-04	Investigate and correct	Assigned laboratory	Sensitivity	Less than QLs
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable SW846 methods. If DESA or CLP laboratories perform the analyses, they will follow the QC requirements in the laboratory SOP or Statement of Work.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for TOC (Worksheet 28)

Matrix	Sediment
Analytical Group	Total Organic Carbon
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method Lloyd Kahn
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicates	One per analytical batch of 20 or fewer samples	Per laboratory SOP	Identify problem and correct	Assigned laboratory	Precision	RPD ≤30% for duplicate values
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	One per analytical batch of 20 or fewer samples	Per laboratory SOP	Investigate	Assigned laboratory	Precision and accuracy	Per USEPA Method Lloyd Kahn, recovery 75-125%, RPD 20%

QC Samples Table for TOC (Worksheet 28)

Matrix	Sediment
Analytical Group	Total Organic Carbon
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method Lloyd Kahn
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet #20

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Detection Limits (MDLs)	At instrument setup and at least annually and for a new operator	Per laboratory SOP	Re-determine when necessary	Assigned laboratory	Sensitivity	Low enough to support QLs
Method Blank	One per analytical batch of 20 or fewer samples	Per laboratory SOP	Investigate and correct	Assigned laboratory	Sensitivity	Less than QLs
The assigned laboratory must perform all the QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method Lloyd Kahn. If DESA laboratory is assigned, they will follow the QC requirements in the DESA method.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Metals (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Metals
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 6010B/6020 (Accutest EMA222-04 and EMA-217-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the PRDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicates	One per analytical batch of 20 or fewer samples	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Identify problem and correct	Assigned laboratory	Precision	RPD <20% for duplicate values greater than or equal to 5 times the QL

QC Samples Table for Metals (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Metals
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 6010B/6020 (Accutest EMA222-04 and EMA-217-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Calibration Check Standard	One per analytical batch of 20 or fewer samples	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Correct problem, recalibrate and reanalyze	Assigned laboratory	Accuracy/Bias	± 10 percent of the true value
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	Each matrix type and each sample delivery group (SDG)	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Investigate possible matrix effect. Record in case narrative.	Assigned laboratory	Accuracy/Bias	75-125% Recovery or per lab control charts

QC Samples Table for Metals (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Metals
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 6010B/6020 (Accutest EMA222-04 and EMA-217-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Control Sample (LCS)	Each group of samples digested	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Redigest and reanalyze	Assigned laboratory	Accuracy/Bias	± 10 percent of the true value
Method Detection Limits (MDLs)	At instrument setup and at least annually and for a new operator	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Re-determine when necessary	Assigned laboratory	Sensitivity	Low enough to support QLs

QC Samples Table for Metals (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Metals
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	SW846 Method 6010B/6020 (Accutest EMA222-04 and EMA-217-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Accutest Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per analytical batch of 20 or fewer samples	SW846 Method 6010B/ 6020 (Accutest SOP EMA222-04 and EMA217-08)	Investigate and correct	Assigned laboratory	Sensitivity	Less than QLs
The assigned laboratory must perform all the QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable SW846 methods. If DESA or CLP laboratories perform the analyses, they will follow their own SOP or Statement of Work.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Methylmercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1630 (Battelle SOP MSL-I-15-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicates	1 per 20 field samples	USEPA Method 1630 (Battelle MSL-I-15-08)	Reanalyze. Failure to meet criteria shall be reported in data summary. Failure of multiple replicates requires re-distillation and analysis of batch.	Assigned Laboratory	Precision	RPD <35% for values >5 times the MDL. No more than 35% of all relative standard deviations can be >35%

QC Samples Table for Methylmercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1630 (Battelle SOP MSL-I-15-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Certified Reference Material or On-going Precision and Recovery Samples	1 per batch of 20 or fewer	USEPA Method 1630 (Battelle MSL-I-15-08)	Correct per SOP and reanalyze. Report in data summary.	Assigned Laboratory	Accuracy	67-133% of certified value
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	Each batch of 20 or fewer	USEPA Method 1630 (Battelle MSL-I-15-08)	Investigate matrix effects, record in case narrative	Assigned laboratory	Accuracy and precision	Recovery 65-135%, RPD ≤35%

QC Samples Table for Methylmercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1630 (Battelle SOP MSL-I-15-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Reagent Blank	3 per batch of 20 or fewer	USEPA Method 1630 (Battelle MSL-I-15-08)	Reanalyze. If confirmed and all samples are >10 times the blank, no corrective action is required. If samples are <10 times the blank, the batch must be redistilled and reanalyzed.	Assigned laboratory	Sensitivity	<5 times the MDL
Initial and Continuing Calibration Verification	Every 10 samples	USEPA Method 1630 (Battelle MSL-I-15-08)	Correct problem, recalibrate and reanalyze.	Assigned laboratory	Accuracy	<20% of initial calibration

QC Samples Table for Methylmercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1630 (Battelle SOP MSL-I-15-08)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Detection Limit (MDL)	Annual	USEPA Method 1630 (Battelle MSL-I-15-08)	Determine before analyzing samples	Assigned laboratory	Sensitivity	Low enough to support QLs
The assigned laboratory must perform all the QC sample analyses and meet all measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1630.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Total Mercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Total Mercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1631 (Battelle SOP MSL-I-13-09)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicates	1 per 20 field samples	USEPA Method 1631 (Battelle MSL-I-13-09)	Reanalyze. Failure to meet criteria shall be reported in data summary. Failure of multiple replicates requires re-distillation and analysis of batch.	Assigned Laboratory	Precision	RPD <35% for values >5 times the MDL. No more than 35% of all relative standard deviations can be >35%

QC Samples Table for Total Mercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Total Mercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1631 (Battelle SOP MSL-I-13-09)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Certified Reference Material or On-going Precision and Recovery Samples	1 per batch of 20 or fewer	USEPA Method 1631 (Battelle MSL-I-13-09)	Correct per SOP and reanalyze. Report in data summary.	Assigned Laboratory	Accuracy	77-123% of certified value
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	Each batch of 20 or fewer	USEPA Method 1631 (Battelle MSL-I-13-09)	Investigate matrix effects, record in case narrative	Assigned laboratory	Accuracy and precision	Recovery 71-125%, RPD ≤24%

QC Samples Table for Total Mercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Total Mercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1631 (Battelle SOP MSL-I-13-09)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Reagent Blank	One per batch of 20 or fewer	USEPA Method 1631 (Battelle MSL-I-13-09)	Reanalyze. If confirmed and all samples are >10 times the blank, no corrective action is required. If samples are <10 times the blank, the batch must be redistilled and reanalyzed.	Assigned laboratory	Sensitivity	<5 times the MDL
Initial and Continuing Calibration Verification	Every 10 samples	USEPA Method 1631 (Battelle MSL-I-13-09)	Correct problem, recalibrate and reanalyze.	Assigned laboratory	Accuracy	<15% of initial calibration

QC Samples Table for Total Mercury (Worksheet 28)

Matrix	Sediment and Tissue
Analytical Group	Total Mercury
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	USEPA Method 1631 (Battelle SOP MSL-I-13-09)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Detection Limit (MDL)	Annual	USEPA Method 1631 (Battelle MSL-I-13-09)	Determine before analyzing samples	Assigned laboratory	Sensitivity	Low enough to support QLs
The assigned laboratory must perform all the QC sample analyses and meet all measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1631.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Inorganic Arsenic (Worksheet 28)

Matrix	Tissue
Analytical Group	Inorganic arsenic
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Battelle Marine Science Laboratory SOP MSL-I-037-01
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the PRDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
Laboratory Duplicate (or MS/MSD)	One per analytical batch of 20 or fewer samples	Battelle Marine Science Laboratory SOP MSL-I-037-01	Identify problem and correct	Assigned laboratory	Precision	RPD <20% for duplicate values greater than or equal to 5 times the QL
Calibration Check Verification	Initially and after every 20 samples	Battelle Marine Science Laboratory SOP MSL-I-037-01	Recalibrate and if necessary reanalyze samples affected	Assigned laboratory	Accuracy/Bias	Initial calibration <10%. Calibration Verification <15% of initial calibration

QC Samples Table for Inorganic Arsenic (Worksheet 28)

Matrix	Tissue
Analytical Group	Inorganic arsenic
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Battelle Marine Science Laboratory SOP MSL-I-037-01
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Control Sample	One per analytical batch of 20 or fewer samples	Battelle Marine Science Laboratory SOP MSL-I-037-01	Investigate – may require redigestion of all affected samples	Assigned laboratory	Accuracy/Bias	Within 15%
Matrix Spike and Matrix Spike Duplicate (MS and MSD)	Each matrix type and each sample delivery group (SDG)	Battelle Marine Science Laboratory SOP MSL-I-037-01	Investigate possible matrix effect. Record in case narrative.	Assigned laboratory	Accuracy/Bias	Recovery ±25% or per lab control charts, RPD <20%
Method Detection Limits (MDLs)	At instrument setup and at least annually and for a new operator	Battelle Marine Science Laboratory SOP MSL-I-037-01	Re-determine when necessary	Assigned laboratory	Sensitivity	Low enough to support QLs
Method Blank	One per analytical batch of 20 or fewer samples	Battelle Marine Science Laboratory SOP MSL-I-037-01	Investigate and correct	Assigned laboratory	Sensitivity	Less than QLs

QC Samples Table for Inorganic Arsenic (Worksheet 28)

Matrix	Tissue
Analytical Group	Inorganic arsenic
Concentration Level	Low
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Battelle Marine Science Laboratory SOP MSL-I-037-01
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Battelle Marine Laboratories
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
The assigned laboratory must perform all the QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in Battelle Marine Science Laboratory SOP MSL-I-037-01.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for Percent Lipid (Worksheet 28)

Matrix	Tissue
Analytical Group	Percent Lipid
Concentration Level	Unknown
Sampling SOP	Split of CPG homogenized sample
Analytical Method/ SOP Reference	Lab SOP (Accutest EGN273-01) based on SM method
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	Assigned Laboratory
No. of Sample Locations	Per Worksheet 18

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1 per 20 field samples	QAPP	If the RPDs exceed limits for the field replicate, this will be addressed by the Data Reviewer	Malcolm Pirnie assigned data reviewer	Precision	RPD <40% for duplicate values greater than or equal to 5 times the CRQL
MS/MSD	1 per 20 field samples	Laboratory SOP (Accutest EGN273-01)	If out of control investigate and flag the data	Assigned laboratory	Precision and Accuracy	Recovery 75-125%, RPD <20%
Balance Calibration	Prior to each analysis	Laboratory SOP (Accutest EGN273-01)	Correct before analyzing samples	Assigned laboratory	Accuracy	Per Laboratory SOP (Accutest EGN273-01)
The assigned laboratory must perform all the QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the laboratory SOP.						

QAPP Worksheet #28
(UFP-QAPP Manual Section 3.4)

QC Samples Table for *Chironomus dilutus* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Chironomus dilutus)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory negative control	1/test	Survival: ≥ 70% Average ash free dry weight: ≥ 0.48 mg per surviving individual	Notify client. Restart test.	Chris Nally (Laboratory Director)	Health of test organisms	Survival: ≥ 70% Average ash free dry weight: ≥ 0.48 mg per surviving individual

QC Samples Table for *Chironomus dilutus* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Chironomus dilutus)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory positive control (Reference toxicant)	1/test	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Notify client.	Chris Nally (Laboratory Director)	Health of test organisms	The LC50 for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.

QC Samples Table for *Chironomus dilutus* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Chironomus dilutus)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407)
Sampler's Name	Malcolm Pirnie Field Sampling Crew
Field Sampling Organization	Malcolm Pirnie Field Sampling Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Quality of overlying water	See Worksheet 12	Test conditions: Dissolved oxygen ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, hardness, and ammonia: should not vary by more than 50% during the test	Notify client and determine if restart is required. If not, adjust water quality to ensure values are brought into control.	Chris Nally (Laboratory Director)	Acceptability of test conditions	Dissolved oxygen ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, Hardness, and Ammonia: Should not vary by more than 50% during the test

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

QC Sample Table for *Hyalella azteca*(Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Hyalella azteca)*
Concentration Level	Low
Sampling SOP	Split of CPG Sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory negative control	1/test	Survival: ≥ 80% Average dry weight: ≥ 0.15 mg per surviving individual	Notify client. Restart test.	Chris Nally (Laboratory Director)	Health of test organisms	Survival: ≥ 80%

QC Sample Table for *Hyalella azteca*(Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Hyalella azteca)*
Concentration Level	Low
Sampling SOP	Split of CPG Sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory positive control (Reference toxicant)	1/test	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Notify client.	Chris Nally (Laboratory Director)	Health of test organisms	The LC50 for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.

QC Sample Table for *Hyalella azteca*(Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity (*Hyalella azteca)*
Concentration Level	Low
Sampling SOP	Split of CPG Sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Quality of overlying water	See Worksheet 12	Test conditions: Dissolved oxygen ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, Hardness, and Ammonia: Should not vary by more than 50% during the test.	Notify client and determine if restart is required. If not, adjust water quality to ensure values are brought into control.	Chris Nally (Laboratory Director)	Acceptability of test conditions	Dissolved oxygen: ≥ 2.5 mg/L Temperature (daily mean): 23ºC±1ºC Temperature (instantaneous): 23ºC±3ºC Alkalinity, Hardness, and Ammonia: Should not vary by more than 50% during the test.

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

QC Samples Table for *Ampelisca abdita* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity *(Ampelisca abdita)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory negative control	1/test	Average survival: ≥ 90% Individual replicate survival: ≥ 80%	Notify client. Restart test.	Chris Nally (Laboratory Director)	Health of test organisms	Average survival: ≥ 90% Individual replicate survival: ≥ 80%

QC Samples Table for *Ampelisca abdita* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity *(Ampelisca abdita)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory positive control (Reference toxicant)	1/test	The LC50[1] for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.	Notify client.	Chris Nally (Laboratory Director)	Health of test organisms	The LC50 for a positive control test should be within the mean LC50 ±2 standard deviations of the control chart.

QC Samples Table for *Ampelisca abdita* (Worksheet 28)

Matrix	Sediment
Analytical Group	Toxicity *(Ampelisca abdita)*
Concentration Level	Low
Sampling SOP	Split of CPG sample
Analytical Method/ SOP Reference	ASTM 2007; USEPA 2000 (Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426)
Sampler's Name	Malcolm Pirnie Field Crew
Field Sampling Organization	Malcolm Pirnie Field Crew
Analytical Organization	American Aquatic Testing, Inc.
No. of Sample Locations	Per Worksheet 18

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Quality of overlying water	See Worksheet 12	Test conditions: Dissolved oxygen ≥ 6.0 mg/L Temperature (daily mean): 15ºC±1ºC Salinity: 30±2 ppt	Notify client and determine if restart is required. If not, adjust water quality to ensure values are brought into control.	Chris Nally (Laboratory Director)	Acceptability of test conditions	Dissolved oxygen ≥ 6.0 mg/L Temperature (daily mean): 15ºC±1ºC Salinity: 30±2 ppt

1: LC50 (or Lethal Concentration 50) is the concentration of a chemical that kills 50 percent of a sample population.

QAPP Worksheet #29 (UFP-QAPP Manual Section 3.5.1)
Project Documents and Records Table

Identify the documents and records that will be generated for all aspects of the project including, but not limited to, sample collection and field measurement, on-site and off-site analysis, and data assessment.

Project Documents and Records Table

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Oversight forms and field notes	Oversight observations, split sample collection, and COC records	Copies of oversight forms and COC records will be made and stored in the project files	Field sampling audit check list	Not applicable
Air bills	Air bills	Copies of air bills will be kept in project files	Project Records	Not applicable
Analytical and sample data packages	Custody records	Copies of electronic data deliverables will be prepared by laboratory and saved in the project electronic-files directory. Instrument calibration records and laboratory data will be stored in electronic or hardcopy format.	Laboratory quality assurance checklist	Not applicable
Data validation reports for subcontract laboratory data	Custody records	Stored in project electonic-files directory	Quality assurance checklists	Not applicable
Oversight Report	Not applicable	Stored in project electronic-files directory	Malcolm Pirnie, Inc. Quality Assurance Checklist	Not applicable

ANSETS = Analytical Services Tracking System
CLP = Contract Laboratory Program
COC = Chain of Custody
DESA = Division of Environmental Science and Assessment
MEDD = Multimedia Electronic Data Deliverable
RCSS = Regional Sample Control Center (see text below)
SDG = Sample Delivery Group
USACE = United States Army Corps of Engineers
USEPA = United States Environmental Protection Agency

Project Document Control System

Project documents will be controlled by the Malcolm Pirnie, Inc. Project Manager, who will maintain and distribute hardcopies and electronic copies of the project documents and any amendments. Electronic copies of project information will be maintained in the project electronic-file directory and the project database.

Data Recording

Data for this project will be collected by handwritten entries onto oversight forms. Forms II Lite software will be the primary tool used to generate COC records and sample labels. Forms II Lite software has been designed to meet USEPA requirements. Computer-generated data associated with laboratory analyses will be generated by the assigned USEPA-CLP laboratory, DESA laboratory, or subcontract laboratory. Data will be provided in USEPA Region 2 MEDD format.

Data Quality Assurance Checks

The Malcolm Pirnie, Inc. Oversight Field Leader will monitor the progress of sample collection to verify that samples are collected as planned. The progress of sample collection and processing will be monitored through documentation of the samples collected each day.

The contracted laboratory (either CLP or non-CLP) will have a formal in-house Quality Assurance Plan to which it adheres and implements as part of daily operations. Data generation processes will be reviewed and modified to meet objectives, if necessary. A formalized data generation procedure will be utilized. Each analyst must have previously demonstrated, through the laboratory quality assurance program, their requisite skills.

Laboratory Data Transmittal

Laboratory data are managed by the laboratory's internal management system, beginning with sample check-in on the sample-receiving data terminal. For non-CLP laboratories, full laboratory data reports for each sample delivery group (SDG) will be delivered to Malcolm Pirnie, Inc. according to the specifications listed in Worksheet 30. In addition, USEPA requires that non-CLP laboratories adhere to the Analytical Services Tracking System (ANSETS) reporting requirements, which utilize the ANSETS Data Requirement form. Detailed instructions and procedures can be obtained by contacting the USEPA Region 2 RSCC, Ms. Jennifer Feranda, at 732-321-6687 or feranda.jennifer@epa.gov, or Mr. Adly Michael at 732-906-6161 or Michael.adly@epa.gov. For CLP laboratories, third-party validated laboratory results will be received by Malcolm Pirnie, Inc. through the USEPA RSCC, and will include MEDDs.

Data Storage and Retrieval

Paper copies of the oversight forms, electronic copy of files, and the photographic log will then be transmitted regularly to the Malcolm Pirnie, Inc. Project Manager. The completed forms will be stored in the custody of the Project Manager for the duration of the project. The full laboratory data reports submitted to Malcolm Pirnie, Inc. will be stored in the custody of the Site Quality Officer. Raw data and electronic media of all field samples, including quality control samples and blanks, will be archived from the date of generation and will be kept by the laboratory per the requirements of USEPA-CLP. Hard copies of project files will be archived off-site at a secure facility and retained until the end of the contract; project closeout will be conducted in accordance with USEPA Close-out Guidelines. Data will be transferred to the USACE and USEPA upon completion of the project. Retrieval of data by others will be at the discretion of the USACE and the USEPA. The length of time that records will be archived will be at the discretion of the USACE and USEPA. Each laboratory shall archive, electronically, the sample analyses and submit the electronic data files along with the data deliverable package. In addition, each laboratory must submit instrument manufacturer, method files and identification file information. Malcolm Pirnie, Inc. must receive this information in the event a laboratory on this project closes or updates hardware/software.

QAPP Worksheet #30 (UFP-QAPP Manual Section 3.5.2.3)
Analytical Services Table

Complete this worksheet for each matrix, analytical group, and concentration level. Identify all laboratories or organizations that will provide analytical services for the project, including on-site screening, on-site definitive, and off-site laboratory analytical work. If applicable, identify the subcontractor laboratories and backup laboratory or organization that will be used if the primary laboratory or organizations cannot be used.

Analytical Services Table (Worksheet 30)

Matrix [1]	Analytical Group	Concentration Level	Sample Location/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ (Name and Address, Contact Person and Telephone Number)
Sediment	Pesticides	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Sediment	PCB Congeners	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP: MSU-020 R06)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Sediment	PCDD/F Congeners	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP: MSU-018 R05)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Sediment	PAH	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	Laboratory SOP for HRMS/LRMS (Laboratoy SOP: MLA-021 R09)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.

Analytical Services Table (Worksheet 30)

Matrix [1]	Analytical Group	Concentration Level	Sample Location/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ (Name and Address, Contact Person and Telephone Number)
Sediment	TCL SVOC	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	SW846 Method 8270C (Laboratory SOP: EMS8270-15/EOPGPC -04)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Sediment	Metals	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	SW846 Method 6010B/6020 (Laboratory SOP: EMA217-08 and EMA222-04)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Sediment	Total Mercury and Methyl mercury	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1630/1631 (Laboratory SOP: MSL-I-013-09 and MSL-I-015-08)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382	A backup laboratory has not been assigned at this time.
Sediment	TOC and Percent Moisture	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method Lloyd Kahn and Gravimetric (Laboratory SOP: EGN233-07 and EGN0007-07)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Tissue	Pesticides	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1613B Modified for HRGC/HRMS (Laboratory SOP: MLA-028 R05)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Tissue	PCB Congeners	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1668A for HRGC/HRMS (Laboratory SOP: MSU-020 R06)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.

Analytical Services Table (Worksheet 30)

Matrix [1]	Analytical Group	Concentration Level	Sample Location/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ (Name and Address, Contact Person and Telephone Number)
Tissue	PCDD/F Congeners	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1613B for HRGC/HRMS (Laboratory SOP: MSU-018 R05)	65 days (35 days for laboratory analysis plus 30 days for data validation) [2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Tissue	PAH	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	Laboratory SOP for HRMS/LRMS (Laboratoy SOP: MLA-021 R09)	65 days (35 days for laboratory analysis plus 30 days for data validation)[2]	Axys Analytical Services 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone: 1-888-373-0881	A backup laboratory has not been assigned at this time.
Tissue	TCL SVOC	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	SW846 Method 8270C (Laboratory SOP: EMS8270-15/EOPGPC -04)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Tissue	Metals	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	SW846 Method 6010B/6020 (Laboratory SOP: EMA217-08 and EMA222-04)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Tissue	Inorganic arsenic	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	Battelle Marine Science Laboratory SOP MSL-I-037-01	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382	A backup laboratory has not been assigned at this time.
Tissue	Total Mercury and Methyl mercury	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	USEPA Method 1630/1631 (Laboratory SOP: MSL-I-013-09 and MSL-I-015-08)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Subcontractor: Battelle Marine Sciences Laboratory 1529 West Sequim Bay Road Sequim, WA 98382	A backup laboratory has not been assigned at this time.

Analytical Services Table (Worksheet 30)

Matrix [1]	Analytical Group	Concentration Level	Sample Location/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ (Name and Address, Contact Person and Telephone Number)
Tissue	Percent Lipid	Unknown	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	SM2540B or equivalent (Laboratory SOP: EGN273-01)	51 days (21 days for laboratory analysis plus 30 days for data validation)	Accutest Laboratories 2235 Route 130 Dayton, New Jersey 08810 Contact: Diane Komar Phone: 1-732- 329-0200	A backup laboratory has not been assigned at this time.
Sediment	Toxicity (*Chironomus dilutus)*	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED001.1 modified for test conditions outlined in CPG laboratory SOP QA-1407	90 days (60 days for toxicity test plus 30 days for data validation)[3]	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Contact: Chris Nally Phone: (610) 434-9015	A backup laboratory has not been assigned at this time.
Sediment	Toxicity (*Hyalella azteca)*	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED006.1 modified for test conditions outlined in CPG laboratory SOP QA-1467	90 days (60 days for toxicity test plus 30 days for data validation)[3]	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Contact: Chris Nally Phone: (610) 434-9015	A backup laboratory has not been assigned at this time.
Sediment	Toxicity *(Ampelisca abdita)*	Low	Split samples will be collected judgmentally by the oversight staff (refer to Worksheet 18)	ASTM 2007; USEPA 2000. Laboratory SOP: GENSED009.1 modified for test conditions outlined in CPG laboratory SOP QA-1426	90 days (60 days for toxicity test plus 30 days for data validation)[3]	Accutest Subcontractor: American Aquatic Testing, Inc. 890 North Graham Street Allentown, PA 18109 Contact: Chris Nally Phone: (610) 434-9015	A backup laboratory has not been assigned at this time.

1: Sediment matrix refers to sediment split sample analyzed for sediment chemical concentration, and sediment material used for toxicity testing.
Tissue matrix refers to fish tissue split sample and benthic tissue split sample from *in-situ* and laboratory bioaccumulation tests.
2: Subcontract laboratories will communicate with the Site Quality Control Officer on split sample status and potential analytical difficulties (if any arise). With the approval of

the Site Quality Control Officer and Project Manager, the turn-around-time for the laboratory data package deliverable can be adjusted to account for re-analysis or additional quality control as necessary.

3: Toxicity testing data will not require full data validation. Toxicity data will only be reviewed against the acceptance limits provided in Worksheets 12 and 28.

ASTM = American Society for Testing and Materials
PAH = Polycyclic aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDD/F = Polychlorodibenzodioxin/furan
SOP = Standard Operating Procedure
SVOC = Semivolatile organic compounds
TCL = Target Compound List
TOC = Total organic carbon
USEPA = United States Environmental Protection Agency

QAPP Worksheet #31 (UFP-QAPP Manual Section 4.1.1)
Planned Project Assessments Table

Identify the type, frequency, and responsible parties of planned assessment activities that will be preformed for the project.

Planned Project Assessments Table

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment	Person(s) Responsible for Responding to Assessment Findings	Person(s) Responsible for Identifying and Implementing Corrective Actions	Person(s) Responsible for Monitoring Effectiveness of Corrective Action
Quality control reports of any non-conformance	Daily as required	Internal	Malcolm Pirnie, Inc.	Oversight Field Crew	Malcolm Pirnie, Inc. Site Quality Control Officer	Malcolm Pirnie, Inc. Project Manager or designees	Malcolm Pirnie, Inc. Site Quality Control Officer
Field Health and Safety Audit	Within the first two weeks of oversight work	Internal	Malcolm Pirnie, Inc.	Malcolm Pirnie, Inc. Health and Safety Manager or designees	Malcolm Pirnie, Inc. Project Manager	Malcolm Pirnie, Inc. Project Manager or designees	Malcolm Pirnie, Inc. Project Safety Officer
Technical System Audit of split sample processing	Within the first two weeks of split sample collection	Internal	Malcolm Pirnie, Inc.	Malcolm Pirnie, Inc. Site Quality Control Officer	Malcolm Pirnie, Inc. Project Manager	Malcolm Pirnie, Inc. Project Manager or designees	Malcolm Pirnie, Inc. Site Quality Control Officer

1: SOP No. 2 “Procedure to Conduct a Technical Systems Audit” is provided in Attachment 2.

QAPP Worksheet #32 (UFP-QAPP Manual Section 4.1.2)
Assessment Findings and Corrective Action Responses

For each type of assessment describe procedures for handling QAPP and project deviations encountered during the planned project assessments.

Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response	Timeframe for Response
Non-Conformance	See below	Malcolm Pirnie, Inc. Site Quality Control Officer	As soon as possible	Complete non-conformance form	Malcolm Pirnie, Inc. Project Manager	As soon as possible
Technical System Audits	See Technical Systems Audit report SOP No. 2 in Attachment 2	Malcolm Pirnie, Inc. Site Quality Officer, Project Manager, or designees	Within week	See below section on Field Corrective Actions	Malcolm Pirnie, Inc. Field Oversight Leader and Project Manager	Within week
Internal Laboratory Audits	Per Laboratory Quality Manual	Laboroatory Management or designee	Annually	Per Laboratory Quality Manual	Laboraotory Personnel	Per Laboratory Quality Manual

Non-Conformance/QC Reporting

A non-conformance is defined as an identified or suspected deficiency or discrepancy with regard to an approved document (*e.g.*, improper sampling procedures, improper instrument calibration, calculation, computer program); or an item where the quality of the end product itself or subsequent activities using the document or item would be affected by the deficiency; or an activity that is not conducted in accordance with the established plans or procedures.

Any staff member engaged in project work that discovers or suspects a non-conformance is responsible for initiating a non-conformance report to the Site Quality Control Officer. The Site Quality Control Officer will evaluate each non-conformance report, and the Site Quality Control Officer will provide a disposition which describes the actions to be taken.

The Project Manager will verify that no further project work dependent on the nonconforming item or activity is performed until approval is obtained and the non-conformance is properly addressed. If the non-conformance is related to material, the Project Manager shall be responsible for making or identifying, with the non-conformance report number, the nonconforming item (if practical) and indicating that it is nonconforming and is not to be used. A copy of each

non-conformance report will be included in the project file. Copies of all non-conformances shall be maintained by the Site Quality Control Officer.

Assessment and Oversight

To monitor the capability and performance of the field oversight activities, a field health and safety audit and technical systems audit will be performed. Performance audits of laboratories are conducted to measure the accuracy of the measurement systems.

Technical System Audits

Field audits will be conducted on an ongoing basis during the project as field data are generated, reduced, and analyzed. Numerical manipulations, including manual calculations, will be documented. Records of numerical analyses will be legible, of reproduction-quality, and sufficiently complete to permit logical reconstruction by a qualified individual other than the originator. System audits of site activities will be accomplished by an inspection of field site activities. During this audit, the auditor(s) will compare current field practices with standard procedures. The following elements will be evaluated during a Technical Systems Audit:

- Whether procedures and analyses are conducted according to procedures outlined in the Oversight QAPP.
- Whether proper sample documentation is being recorded.
- The level of quality control conducted by the field team.
- Decontamination procedures, where applicable.
- Sample packaging and shipment.

Technical Systems Audits are conducted for each field team at the beginning of each field oversight task. As long as the field team(s) demonstrate proficiency in the oversight procedures being audited, a follow-up audit will not be required. However, if the audit indicates the need for corrective action, a second Technical Systems Audit will be required. Following the initial audit, Technical Systems Audits will be conducted on the following schedule:

- Whenever key personnel leave the project or new key personnel are added to the project.
- Whenever a significant amount of time (more than 6 months) has elapsed between Technical Systems Audits for a particular field task.

Any minor deficiencies that are noted during the Technical Systems Audit will be corrected in the field as they occur. If major deficiencies are noted (*i.e.*, those that cannot be immediately corrected in the field), a Stop-Work Order will be issued until appropriate measures can be taken to correct the problem. A Stop-Work Order

may be issued by the Site Quality Control Officer, following notification to the Project Manager. The conditions and the need for a Stop-Work Order will be documented in sufficient detail to permit evaluation of the deficiency and determination of proper corrective action(s). Pertinent communications with the Site Quality Control Officer, Field Oversight Leader, and Project Manager that pertain to an evaluation of the problem along with potential solutions and their implementation will be attached to the Stop-Work Order. In order for work to resume following a Stop-Work Order, the Project Manager and Site Quality Control Officer must rescind it in writing. The Site Quality Control Officer is responsible for tracking non-conforming conditions, evaluating the effectiveness of corrective measures, and assuring that the necessary steps have been taken to prevent recurrence of the original problem.

Regardless of whether major, minor, or no deficiencies were noted during the audit, a written report of the Technical Systems Audit will be prepared by the Site Quality Control Officer and submitted to Malcolm Pirnie, Inc., USEPA, and USACE, as well as the Field Oversight Leader and the oversight field crew. This report will identify any deficiencies found and will outline the corrective actions that were recommended/implemented to address them. A copy of SOP No. 2 on conducting a Technical Systems Audit is attached to the Oversight QAPP. Periodically during the audit, it may be determined that the Site program should be modified to increase data quality or efficiency. These modifications will be documented by the Project Manager or Site Quality Control Officer in a Field Modification Form (attached to the Oversight QAPP).

Field Corrective Actions

At the end of each sampling day, the sampling team is to report any problems requiring corrective action that were encountered during the day. Corrective action will be undertaken when a non-conforming condition is identified. A non-conforming condition occurs when QA objectives for precision, accuracy, completeness, representativeness, or comparability are not met, or when procedural practices or other conditions are not acceptable. A report is to be filed that documents the problems encountered and the corrective action implemented. A Stop-Work Order may be issued by the Site Quality Control Officer, following notification to the Project Manager, if corrective action does not adequately address a problem, or if no resolution can be reached.

Internal Laboratory Audits

As part of its quality assurance program, the Laboratory Quality Assurance Manager will conduct periodic checks and audits of the analytical systems to ensure that the systems are working properly and personnel are adhering to established procedures and documenting the required information. These checks and audits will also assist in determining or detecting where problems are occurring. In addition to conducting internal reviews and audits, as part of its established quality assurance

program, the laboratory is required to take part in regularly scheduled performance evaluation and laboratory audits from state and federal agencies for applicable tests. Each laboratory selected to support this program must maintain current state or federal certifications, as appropriate.

Laboratory Corrective Actions

If a particular laboratory analysis is deemed "out of control," corrective action will be taken by the laboratory to maintain continued data quality. Each laboratory must adhere to their in-house corrective action policy. The coordinator of the laboratory's analytical section will be responsible for initiating laboratory corrective action when necessary.

QAPP Worksheet #33 (UFP QAPP Manual Section 4.2)
QA Management Reports Table

Identify the frequency and type of planned QA Management Reports, the projected delivery date, the personnel responsible for report preparation, and the report recipients.

QA Management Reports Table				
Type of Report	**Frequency (daily, weekly monthly, quarterly, annually, etc.)**	**Projected Delivery Date(s)**	**Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)**	**Report Recipient(s) (Title and Organizational Affiliation)**
Field Health and Safety Audit	Within the first two weeks of field work	Month after field work begins	Health and Safety Manager or designee	USEPA and USACE
Technical System Audit	Within the first two weeks of field work and with follow up audits if significant deficiencies are found	Month after field work begins	Site Quality Control Officer	USEPA and USACE
Data Validation Report	After laboratory data are received	Within 45 days after receiving data	Data Validator	Site Quality Control Officer and Project Manager
Corrective Action Reports	When corrective action is required	When corrective action is implemented	Project Manager	Project Team and Project Manager

The USACE and USEPA will receive several types of management reports. These reports will include the results of any corrective action reports and data validation reports. Problems or issues that arise between regular reporting periods may be identified to program management at any time. Information included in these reports will include the following:

- Results of Technical System Audits conducted during the period.
- An assessment of any problems with the measurement data, including accuracy, precision, completeness, representativeness, and comparability.
- A listing of the non-conformance reports including Stop-Work Orders issued during the period, related corrective actions undertaken, and an assessment of the results of these actions.
- Identification of significant quality assurance problems and recommended solutions, as necessary.

QAPP Worksheet #34 (UFP-QAPP Manual Section 5.2.1)

Verification (Step I) Process Table

Describe the processes that will be followed to verify project data. Verification inputs include items such as those listed in Table 9 of the UFP-QAPP Manual (Section 5.1). Describe how each item will be verified, when the activity will occur, and what documentation is necessary, and identify the persons responsible. Internal or external is in relation to the data generator.

Verification (Step I) Process Table			
Verification Input	**Description**	**Internal/ External**	**Responsible for Verification (Name, Organization)**
COC	Form will be internally reviewed upon completion and verified against field logs and laboratory reports. Review will occur with the completion of each report	Internal	Malcolm Pirnie, Inc.
Oversight Report	Oversight reports will be verified with the oversight forms	Internal	Malcolm Pirnie, Inc.
Laboratory data packages	Laboratory data packages will be used to verify the report results in the project report and against Oversight QAPP criteria	Internal	Malcolm Pirnie, Inc.

COC = Chain of Custody
QAPP = Quality Assurance Project Plan

Data Verification

- The Field Oversight Leader or designee is required to review the oversight forms for errors or omissions. This information is transmitted to the Site Quality Control Officer or designee for correction.
- In addition, the Site Quality Control Officer or designee is responsible for reviewing field data for completeness and to verify that the field crew followed the requirements detailed in this Oversight QAPP. If any problems with the information are found, the Site Quality Control Officer or designee will document the problems.

QAPP Worksheet #35 (UFP-QAPP Manual Section 5.2.2)
Validation (Steps IIa and IIb) Process Table

Describe the processes that will be followed to validate project data. Validation inputs include items such as those listed in Table 9 of the UFP-QAPP Manual (Section 5.1). Describe how each item will be validated, when the activity will occur, and what documentation is necessary and identify the person responsible. Differentiate between steps IIa and IIb of validation.

Validation (Steps IIa and IIb) Process Table			
Step IIa/IIb	Validation Input	**Description**	**Responsible for Validation (Name, Organization)**
IIa	Methods	Records support implementation of SOP in Oversight QAPP.	Malcolm Pirnie, Inc.
IIa	COC	Examine traceability of data from sample collection to generation of project report.	Malcolm Pirnie, Inc.
IIb	Deviations from SOP and project documents.	Determine impacts of any deviation from method and the project plan.	Project Team

COC = Chain of Custody
QAPP = Quality Assurance Project Plan
SOP = Standard Operating Procedure

QAPP Worksheet #36 (UFP-QAPP Manual Section 5.2.2)
Validation (Steps IIa and IIb) Summary Table

Identify the matrices, analytical groups, and concentration levels that each entity performing validation will be responsible for, as well as criteria that will be used to validate those data.

Validation (Steps IIa and IIb) Summary Table					
Step IIa/IIb	**Matrix**	**Analytical Group**	Concentration Level	**Validation Criteria**	**Data Validator (title and organizational affiliation)[1]**
IIa/IIb	All matrices collected per the Oversight QAPP	All analytical parameters analyzed by USEPA CLP laboratory (Not required for non-chemical)	Low to high	USEPA Region 2 Validation Criteria	USEPA Data Validators
IIa/IIb	All matrices collected per the Oversight QAPP	All non-CLP and non-DESA laboratory data. Not required for non-chemical analyses. Toxicity testing data will not require full data validation. Toxicity data will only be reviewed against the acceptance limits provided in Worksheets 12 and 28.	Low to high	USEPA National Functional Guidelines	Malcolm Pirnie, Inc. validators

CLP = Contract Laboratory Program
DESA = Division of Environmental Science and Assessment
EDD = Electronic Data Deliverable (see text below)
MEDD = Multimedia Electronic Data Deliverable (see text below)
OSWER = Office of Solid Waste and Emergency Response (see text below)
QAPP = Quality Assurance Project Plan
QA/QC = Quality assurance/quality control (see text below)
RCSS = Regional Sample Control Center (see text below)
SDG = Sample Delivery Group (see text below)
SOW = Scope of Work (see text below)
SOP = Standard Operating Procedure (see text below)
TAL = Target Analyte List (see text below)
TCL = Target Compound List (see text below)
USEPA = United States Environmental Protection Agency

USEPA CLP Data

Validation of any USEPA CLP data will be accomplished by comparing the contents of the data packages and QA/QC results to the requirements contained in the applicable analytical methods (*e.g.*, SOW), laboratory SOPs, and validation guidelines. Any TAL/TCL data generated through the CLP will be validated by RSCC using the latest applicable USEPA Region 2 validation

procedures in accordance with the following USEPA guidance documents or their most recent revisions:

- USEPA CLP National Function Guidelines for Inorganic Data Review, OSWER 9240.1-45, USEPA 540-R-04-004, October 2004.
- USEPA CLP National Functional Guidelines for Superfund Organic Methods Data Review, OSWER 9240.1-46, USEPA-540-R-07-003, July 2007.
- USEPA CLP National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans Data Review, OSWER 9240.1-51, USEPA-540-R-05-001, September 2005.
- USEPA Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use, OSWER 9200.1-85, USEPA-540-R-08-005, January 2009.

The final deliverable will be an EDD, which is formatted according to the USEPA Region 2 MEDD guidelines.

USEPA DESA Laboratory Data

Any data generated by the USEPA Region 2 DESA laboratory in Edison, New Jersey are considered USEPA-validated and are useable as reported. No third party data validation will be performed on any DESA-generated data. The final deliverable will be an EDD, which is formatted according to the USEPA Region 2 MEDD guidelines.

Commercial Subcontractor Laboratory Data

The commercial subcontractor laboratory data will be validated by Malcolm Pirnie, Inc. or subcontractor against the Oversight QAPP and method criteria.

The Malcolm Pirnie, Inc. data validator will also conduct a validation review of the first SDG received for each analytical parameter. This means that the validator will review the raw data and log book sheets, and will recalculate at least 10 percent of the sample and QC sample results. If this validation indicates that the laboratory is producing acceptable data, the validation reviews may be scaled back and subsequent data packages will have a less rigorous review. The validation will

then be based on the reviewed data packages and EDD files provided by the laboratory.

Once data validation is completed, a data validation report will be generated. The report will contain information regarding the parameters that are qualified, the reason for the qualification, and the direction of the bias (only for parameters qualified as estimated), when possible. Based upon the quality assurance review of the analytical data, specific codes (data qualifiers or 'flags') will be placed next to results to provide an indication of the quantitative and qualitative reliability of the results. The data qualifier codes in the National Function Guidelines are proposed for this project. Qualifiers assigned by laboratories will be defined by each laboratory in their data package and will be superseded by the data validator's qualifiers. The final deliverable will be an EDD, which is formatted according to the USEPA Region 2 MEDD guidelines.

QAPP Worksheet #37 (UFP-QAPP Manual Section 5.2.3)
Usability Assessment

Describe the procedures/methods/activities that will be used to determine whether data are of the right type, quality, and quantity to support environmental decision-making for the project. Describe how data quality issues will be addressed and how limitations of the use of the data will be handled.

Usability Assessment
Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: The Malcolm Pirnie, Inc. data validator or subcontractor will validate the non-CLP chemical data in accordance with the protocols outlined on Worksheet 36. Toxicity testing data will not require full data validation. Toxicity data will only be reviewed against the acceptance limits provided in Worksheets 12 and 28.
Describe the evaluative procedures used to assess overall measurement error associated with the project: As part of the data validation process, the validator identifies any qualifications, the bias, if known, of the data, applies qualifiers and comments on the usability of the data. Once the validation package is received from the validator it is reviewed by the Site Quality Control Officer or a designee. Any QA/QC problems with the validation will be discussed with the validator and laboratories. Usability of toxicity data will be based on achieving sample holding times, acceptable water quality conditions during testing, and laboratory control treatment survival and growth criteria.
Identify the personnel responsible for performing the usability assessment: The usability of the data is the responsibility of the project team. The Project Manager will assign technical staff to perform the split sample comparison after the data has been validated and reviewed.

CLP = Contract Laboratory Program
QA/QC = Quality assurance/quality control
USEPA = United States Environmental Protection Agency

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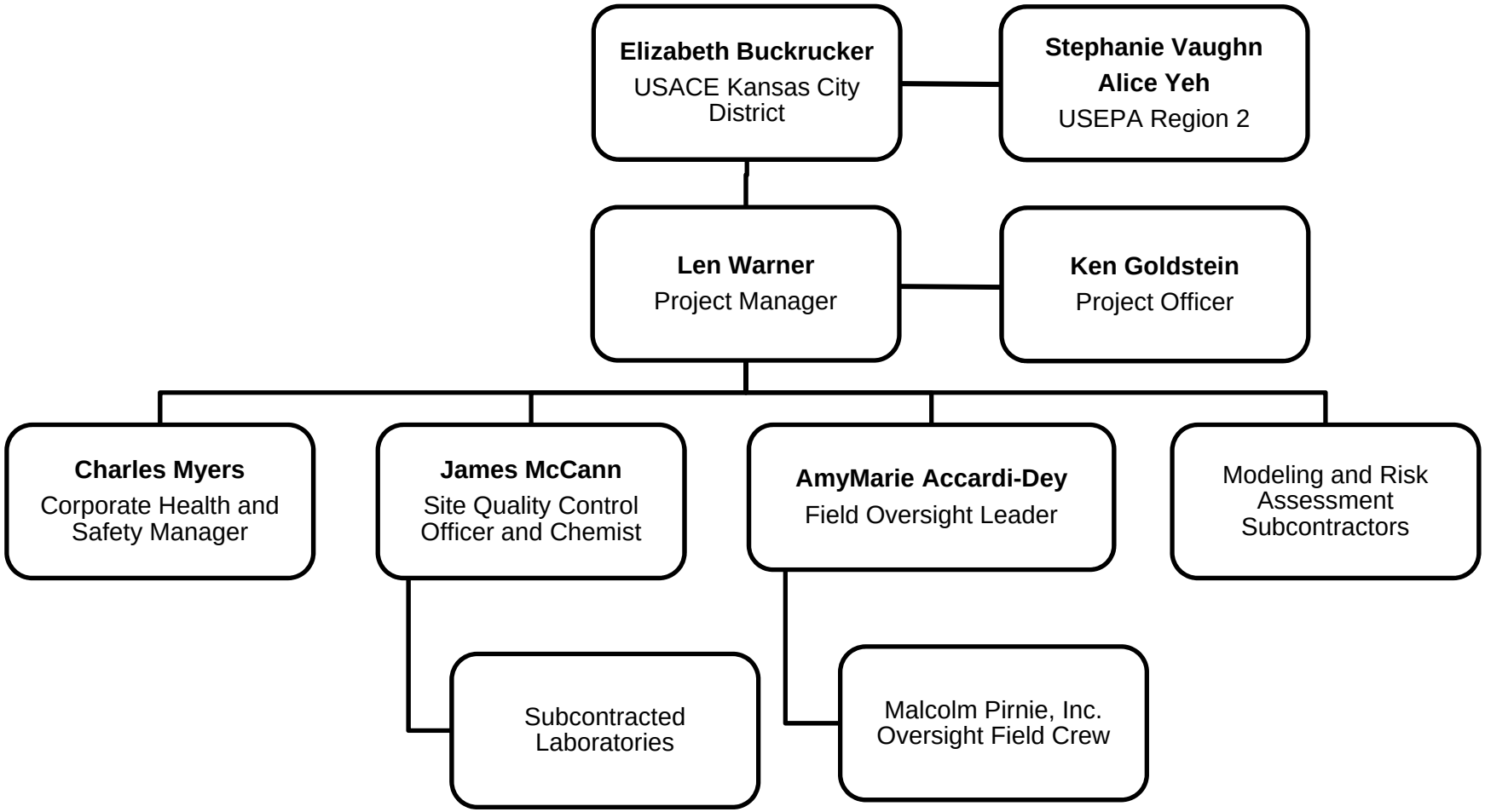
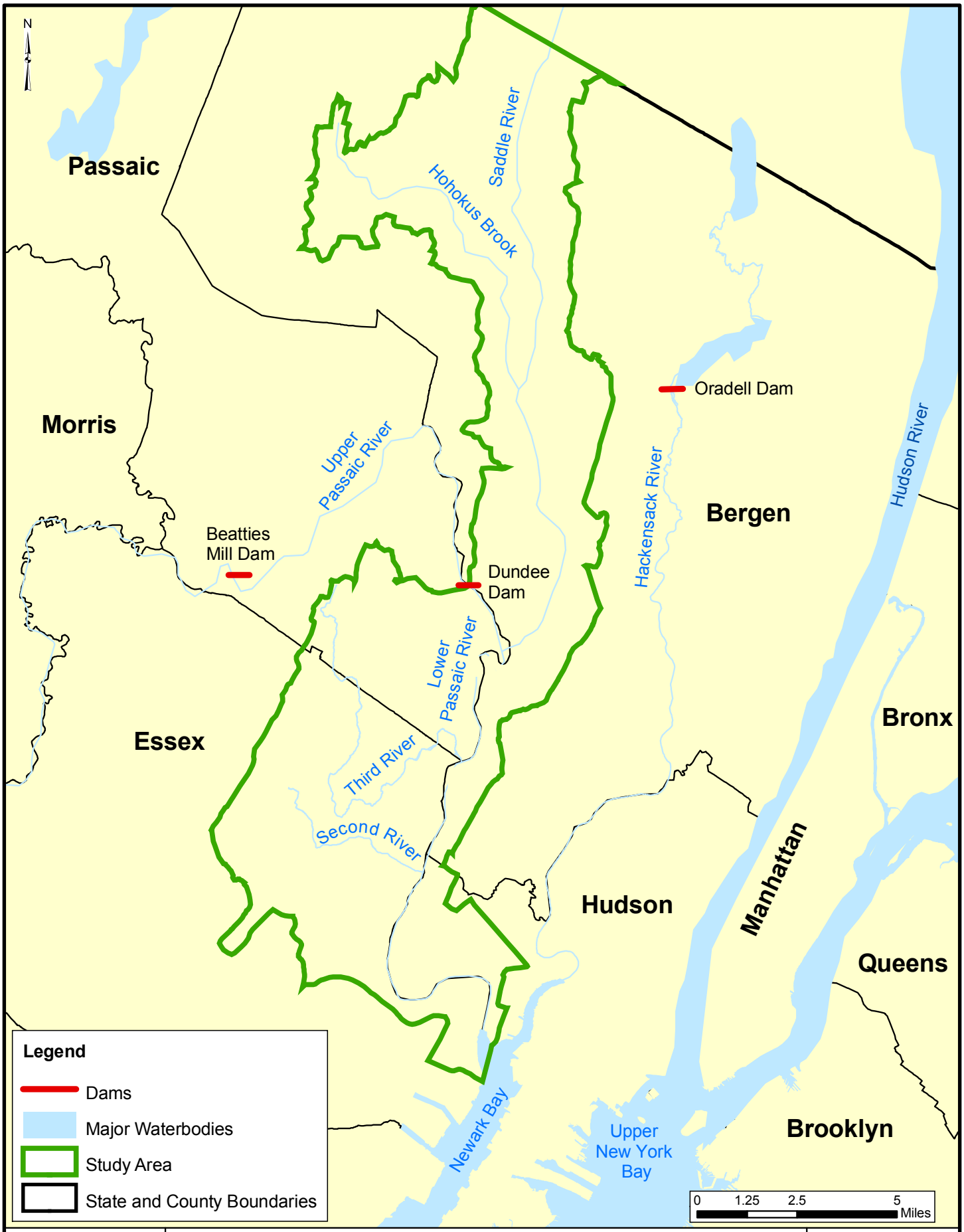


USEPA = United States Environmental Protection Agency
USACE = United States Army Corps of Engineers

	Project Organization Chart *Lower Passaic River Restoration Project*	Figure 1 August 2009



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Study Area Location Map

Lower Passaic River Restoration Project

Figure 2

August 2009

Attachment 1: SOP No. 1

Procedure to Conduct Sample Management for Contract Laboratory and Non-Contract Laboratory Program Samples

Procedure to Conduct Sample Management for Contract Laboratory Program and non-Contract Laboratory Program Samples

I. Introduction

This guideline is to provide reference information on sample management procedures.

II. Definitions

Contract Laboratory Program (CLP) – The United States Environmental Protection Agency (USEPA) CLP was developed to retain laboratory services that will ensure that all environmental samples collected under the Superfund Program will be analyzed in accordance with recognized USEPA laboratory methods and quality assurance/quality control (QA/QC) procedures. See http://www.epa.gov/superfund/programs/clp/ for detailed information on the CLP.

Target Compound List (TCL) – This is a list of organic compounds typically analyzed for by the CLP. The list is broken into three subdivisions: volatile organic compounds (VOC), semi-volatile organic compounds (SVOC), pesticides, and polychlorinated biphenyls (PCB).

Target Analyte List (TAL) – This is a list of inorganic parameters typically analyzed for by the CLP. Parameters on this list include heavy metals and cyanide.

Routine Analytical Services (RAS) – Laboratory analysis for parameters included on the TCL and/or the TAL in solid and aqueous samples.

Non-RAS – Laboratory analysis for substances or parameters not included on the TCL or the TAL. Also encompasses analysis of non-soil/sediment, non-aqueous matrices, and analysis of RAS compounds using non-RAS protocols.

Trip Blanks – Trip blanks are used to check for sample contamination originating from sample transport and shipping as well as from site conditions. Trip blanks are necessary when aqueous environmental samples are collected for VOC analysis.

Rinsate Blanks – Rinsate blanks, also known as field blanks, are used to check the efficacy of sampling equipment decontamination procedures. Rinsate blanks are collected for each type of non-dedicated sampling equipment used onsite. Demonstrated analyte-free water is poured over the equipment, collected in containers, and analyzed for the analytes of concern.

Field Duplicate – Field duplicates are two separate samples collected from the same sampling location. Field duplicates are used to evaluate field sampling precision and are collected at a set frequency for each analyte group. For solids, a sample aliquot is homogenized and split into two sampling containers.

Matrix Spike/Matrix Spike Duplicates (MS/MSD) – MS/MSD analysis is the process by

which standard mixes of various organic TCL compounds are added to field samples prior to extraction. The sample is then split into duplicates and analyzed. The analysis is used to evaluate the matrix effect of the sample upon the analytical methodology. Triple volume of aqueous samples for MS/MSD analysis is collected in the field, at a frequency of at least 5 percent per matrix/concentration. No extra volume is required for the soil samples.

III. Guidelines

The use of sample management procedures during sample collection is intended to ensure that samples required during the site investigation are accounted for when the project is completed. The sample management officer (SMO) is responsible for the implementation of sample management, and also for assuring that the proper QA/QC samples are collected. These goals can be achieved by adhering to the procedures and guidelines described in Sections IV, V, and VI below.

IV. Laboratory Coordination

Analysis of CLP Samples

For samples that will be analyzed through the CLP, a request must be made through the Regional Sample Control Center Coordinator (RSCC), prior to the initiation of sample collection activities, for assignment of a laboratory per USEPA Region 2 SOP No. HW-32: Standard Operating Procedure for Implementing the National Strategy for Procuring Analytical Services for All OSWER Programs, Revision 5, March 17, 2005. At this time, any requested modifications to the CLP SOWs must also be described [*e.g.*, lower detection limits, adding a parameter to the TCL or TAL list, requesting a quicker turnaround time (TAT)].

A description of how to request CLP services is included in the USEPA-issued CLP Guidance for Field Samplers, OSWER 9240.0-44, EPA 540-R-07-06, July 2007. This guidance document can be found online at the following URL:
http://www.epa.gov/superfund/programs/clp/guidance.htm.

A request for CLP services generally includes the following steps:

1. Contact the RSCC well before the sampling event to discuss the CLP sample submission requirements. For USEPA Region 2, the RSCC is Jennifer Feranda, who can be contacted at 732-321-6687.
2. Fill out the RSCC request forms.
3. RSCC will contact the originator of the request with the Case Number and assigned laboratories. At times, the USEPA Region 2 Division of Environmental Science and Assessment (DESA) Laboratory may choose to perform all or part of the analyses requested.
4. For a long-term project, weekly contact should be maintained with the RSCC.

For samples submitted to a CLP laboratory, Forms II Lite software must be used by the samplers

to record the sample information and to create CLP sample numbers and the required COC forms. Assistance with Forms II Lite can be obtained by calling the help desk at 703-818-4200 or by visiting the Forms II Lite web site at http://dyncsdao1.fedcsc.com/itg/forms2lite/.

Analysis of non-CLP Samples

Subcontractor laboratory(ies) will be procured for the project to conduct analysis of non-CLP parameters, as required. Weekly contact should be maintained with these laboratories to keep them informed of the status of the sampling program.

V. Preparation of Sample Containers

When CLP and/or DESA laboratory(ies) are used, Malcolm Pirnie, Inc. will purchase certified clean sample containers from an approved supplier. Copies of these certifications should be kept in the project files for future reference. When non-CLP laboratory(ies) are used, arrangements should be made with the subcontract laboratory to provide suitable, clean sample containers appropriate for each test.

It should be noted that non-CLP subcontract labs usually also provide coolers, but when samples are being sent to an assigned CLP lab or to the USEPA Region 2 DESA Laboratory, the samplers must make arrangements to obtain the coolers through the Malcolm Pirnie, Inc. Equipment Facility prior to the sampling event. The Malcolm Pirnie, Inc. Equipment Facility is located in the Tall Pines Industrial Park, 382 Route 59 Section 286, Monsey, NY 10952 (Contact Max Bateman at 845-357-0965).

VI. QA/QC Samples

Rinsate Blanks

Rinsate blanks (or Equipment Blanks) are collected for each type of equipment used to collect samples at the frequency specified in the Oversight Quality Assurance Project Plan (QAPP). It is recommended that rinsates be collected at a minimum frequency of one per week and at a maximum frequency of one rinsate per location per day. Decontaminated equipment must be properly stored in an area and in a manner that will prevent cross contamination. The analyte-free water required for equipment decontamination and rinsate blank collection will be purchased by Malcolm Pirnie, Inc. from an approved supplier.

Where possible, composite rinsates will be collected from all equipment associated with a particular matrix for analysis of non-volatile parameters.

Rinsate blanks are collected using the following procedure:

1. Pour demonstrated analyte-free water over clean equipment.
2. Collect the water into sample containers.
3. Preserve, package, and ship to the analytical laboratory for analysis.

Field Duplicates

Samples for duplicate analysis are collected in the field for each matrix sampled, at the frequency described in Oversight QAPP. Sufficient quantity of matrix must be collected from the same sample location to fill a duplicate set of sample containers. The duplicate volume is shipped to the laboratory under a separate, "blind" sample ID (or CLP sample number).

For soil/sediment samples, the VOC fraction is collected as co-located grab samples, while the non-VOC fraction is homogenized prior to collection. For dust and wipe samples, field duplicate samples should be collected from an adjacent area of equal size.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Matrix Spike/Matrix Duplicate (MS/MD)

MS/MSD analyses for organics are typically conducted for 1 in 20 environmental samples per concentration/matrix. Three times the total volume is necessary for collection of aqueous MS/MSD samples. No extra volume is required for the soil samples. MS/MSDs are noted as such on the chain of custody (COC).

VII. Sample Documentation, Packaging, and Shipping Procedures

One or more members of the field team should be designated as SMO. The SMO will bear the ultimate responsibility for the documentation, packaging, and shipping of the samples. These procedures are outlined in the sections below.

Pre-Field Activities

If samples are being submitted to non-CLP labs, no special arrangements are required prior to the initiation of fieldwork. If samples are being submitted to CLP-assigned labs, the USEPA RSCC must be contacted for information regarding the following items prior to going out into the field:

- CLP Sample Numbers.
- SMO-assigned Case Numbers.
- Traffic Report/COC (TR/COC) Records.
- Chain-of-custody seals.

Refer to the USEPA CLP Guidance for Field Samplers, Chapter 2 for detailed instructions regarding pre-field activities.

Documentation and Chain of Custody

For documentation purposes, the field team will enter information about each sample into the field logbook as they collect the sample. The information recorded should include but not be limited to the following:

- The Malcolm Pirnie, Inc. assigned sample number (sample ID).
- The CLP Number and Case Number (for CLP samples, only).
- Method of sample collection.
- Sample date.

- Time of collection.
- Preservative(s) used.
- Analyses required.
- Sample type.
- Associated rinsate(s).
- Sampler's initials.

The same information should be included on the sample bottle label(s).

Once all of the samples have been collected, they should be grouped for shipment by receiving laboratory and the COC filled out (depending whether samples are being shipped to a CLP and non-CLP laboratory):

- When samples are being shipped to a non-CLP laboratory, COC forms provided by the laboratory can be used.

- When samples are being shipped to a CLP-assigned laboratory, the COC and sample labels should be created and printed using the Forms II Lite software. The labels can be printed in the field using a laptop PC and printer. It is also possible to pre-print the labels using the Forms II Lite prior to going to the field. Refer to the Forms II Lite User's Guide for instructions on the use of Forms II Lite software. Forms II Lite can also be used to create COCs for non-CLP samples. If circumstances require that handwritten sample labels must be used for CLP samples, follow the requirements in checklist Appendix E-4 of the USEPA's CLP Guidance for Field Samplers.

Before placing a sample in a cooler, the sample label should be covered with clear tape. The sample labels should contain the following information:

- Malcolm Pirnie, Inc.-designated sample number.

- For CLP samples only, the assigned CLP Sample Number and CLP Case Number must be recorded on each sample taken during a sampling event.

- The month, day, and year the sample was collected.

- The type of analysis requested.

- The type of preservation performed in the field.

<u>CLP Documentation Requirements</u>

A full description of the CLP documentation requirements are found in Sections 1.4 and 3.2 of USEPA's CLP Guidance for Field Samplers. Samplers must:

- Record the CLP Number and Case Number on each sample bottle.

- Complete the TR/COC Record using the Forms II Lite software, making sure to indicate on the TR/COC Record if samples require the use of a Modified Analysis.

- Complete and attached sample labels.

- Complete and attach tags to meet Regional requirements.

- Complete and attach custody seals to meet Regional requirements.

- Complete field operations records, as necessary.

Contact the RSCC before the sampling event for information regarding the assigned CLP Sample Numbers, SMO-assigned Case Numbers, TR/COC Records, and COC seals for sampling events. Under no circumstances should the site name appear on any documentation that is sent to the laboratory when shipping CLP samples.

Packaging and Shipping Samples

Below are guidelines for packaging and shipping samples. A checklist for packing CLP samples for shipment can also be found in Appendix E-6 of the USEPA's CLP Guidance for Field Samplers.

1. Make sure the caps on the sample bottles are tightly sealed. Wipe down the outside of all of the sample bottles.
2. Preserve the samples according to requirements in the QAPP.
3. For CLP, apply one custody seal around the circumference of the container or over the cap and onto the sides of the container. The custody seal must applied to sample containers in such a manner as to reveal if the container was opened during transit.
4. Place sample label on container and cover label with clear plastic tape.
5. Place containers in its individual zip-lock bag. Eliminate extra air space from the bag before sealing.
6. For CLP samples, place the associated sample tag into the zip-lock bag with the sample.
7. Wrap a piece of bubble-wrap around the container/zip-lock bag to protect container.
8. Prepare the shipping container (usually a cooler) so that no leakage can occur during shipping. Securely seal all valves using duct tape on both the inside and the outside of the cooler, and line with plastic or a larger garbage bag. Only coolers that conform to the general design requirements in 49 CFR 173.410 should be used for shipment.
9. Put 1-2 inches of packing material in the bottom of the coolers, and then place the samples into the garbage bag in the cooler.
10. Surround the sample bottles with bags of ice (only the samples that need to be cooled – refer to the QAPP requirements for sample preservation. Prior to placement in the cooler, remove the ice from the original bag and re-pack into doubled zip lock bags. Use enough ice to ensure that the proper temperature (2-6°C) is maintained during

transport. Place a temperature blank (40-mL vial filled with DI water and labeled as "temperature blank") into the cooler.

11. Place packing material over and around the sample bottles. Sufficient packing material must be used so the bottles will not move or break during transport.
12. Once the samples are packed, close and securely tie or tape the plastic or garbage bag.
13. Fill in the "relinquished by" and "received by" sections of the COC prior to shipment. The SMO should fill in the name of the commercial shipper (courier) and add the airbill number, if applicable, as the courier generally will not sign the COC.
14. Make enough copies of the COC form(s) to allow for placement of one set in each cooler that is not the lead cooler. Seal the original COC form in a ziplock bag and tape to the inside of the lead cooler, and seal one copy of the COC form(s) in a ziplock bag and place in each of the other cooler(s).
15. For CLP samples, retain one copy of the COC form for the SMO and one copy for transmission to the RSCC (send within 1 day). For non-CLP samples, retain one copy of the COC form for the SMO.
16. Close the cooler and seal with strapping tape. If visibly dirty, wipe down the outside of the cooler. Apply two signed and dated custody seals to the cooler diagonally across from each other where the cooler lid meets the cooler. Apply the custody seals in such a manner as to reveal if the cooler was opened during transit.
17. Place an address label on the outside of each cooler and cover with clear tape. If more than one cooler is being sent to one destination, label each cooler appropriately, *e.g.*, 1 of X, 2 of X, etc. Attach the airbill to one of the coolers. Generally, the samples are sent via overnight carrier for next day delivery. This should be confirmed with the Field Team Leader.
18. Notify the laboratory of the shipment before 9:00 a.m. on the day after shipping. For CLP samples, fill out the Sample Shipping Call-In Form. Call or fax the shipping information to RSCC by 9:00 am the following morning. For non-CLP samples, follow the notification system agreed to in the subcontract.
19. Instructions for shipping and packaging CLP samples can be found in the CLP Guidance for Field Samplers. Appendix E of the guidance contains sampling checklist which should be followed.

Note: Some samples have very short holding times. In some limited instances, the samples may need to be either hand delivered to a laboratory or picked up by the laboratory's courier service.

VIII. References

USEPA 2007, Introduction to the Analytical Services Branch (ABS) Contract Laboratory Program, EPA 540-R-07-02, OSWER 9240.0-42, January 2007

USEPA 2007, Contract Laboratory Program Guidance for Field Samplers, OSWER 9240.0-44, EPA 540-R-07-06, July 2007

Forms II Lite, Version 5.1, User's Guide

Attachment 2: SOP No. 2

Procedure to Conduct a Technical Systems Audit

Title: Procedure to Conduct a Technical System Audit

I. Introduction

This guideline is to provide information on Technical Systems Audit to be conducted for the Lower Passaic River Oversight program.

II. Guidelines

The purpose of the TSA is to ensure that the sampling team adheres to the guidelines contained in the project documents. Prior to conducting the audit, a copy of the Final Oversight Quality Assurance Project Plan (QAPP) will be reviewed by the auditor. During the TSA the sampling team's adherence to these guidelines will be verified and any deficiencies from the guidelines will be documented. The effect of the deficiencies will be noted, and any necessary corrective actions will be instituted.

Prior to conducting the audit, the auditor will contact the Project Manager to discuss the audit. This contact will ensure that the sampling team is properly prepared for the sampling event.

A. Conducting the TSA

The following procedures will be used to conduct the TSA:

1) The auditor will bring the following equipment/documents into the field:

- Copy of the Oversight QAPP, and any relevant memos, correspondence or addenda
- Field laptop
- TSA audit checklist
- Digital camera

2) The following aspects of the sampling event will be audited:

- Quality Assurance/Quality Control (QA/QC) samples
- Sampling methodologies
- Field documentation, including photographs
- Sample management tasks
- Decontamination procedures

B. Corrective Action in the Field

Besides observing and reporting, the auditor is responsible for initiating steps for the start-up of corrective action procedures.

If the auditor witnesses discrepancies in the field between the Oversight QAPP and the performance of the sampling team, the auditor has several options available for corrective action. These options are dependent upon the type of deficiencies observed.

Deficiencies observed and the corrective action taken must be documented in the auditor's log book.

- Minor Deficiencies

  Minor deficiencies are problems where the impact, if any, to the data can be easily eliminated and the deficiency can be corrected or the procedure repeated to achieve the desired result. Minor deficiencies that are observed by the auditor will immediately be brought to the attention of the field team. The auditor and the field team will discuss the problem and agree upon what corrective action is necessary. This will allow for the deficiencies to be corrected immediately in the field.

- Major Deficiencies

  Major deficiencies are events or procedures that substantially deviate from approved work plans, will result in increased project costs not previously approved, or will significantly impact the quality of the data.

  Upon witnessing a major deficiency, the auditor will temporarily stop all related site work and will inform the field team of the problem. The auditor and field team will discuss the deficiency as well as what steps are necessary for corrective action. If the deficiency can be corrected in the field, the auditor may allow work to resume as long as all necessary corrective actions are taken. Information regarding the nature of the deficiency as well as the corrective action(s) taken will immediately be transmitted to the Malcolm Pirnie, Inc. Project Manager.

If the deficiency cannot be corrected in the field, a Stop-Work Order will be issued until appropriate measures can be taken to correct the problem. A written report of the major deficiencies will be prepared by the Site Quality Control Officer and submitted to the United States Army Corps of Engineers (USACE), United States Environmental Protection Agency, and the Malcolm Pirnie, Inc. Project Manager. The Stop-Work Order will remain in effect until the proper corrective action(s) can be implemented.

C. Preparation of a TSA Report

The TSA report provides a means of relaying the events of a sampling episode to key personnel. These events could possibly affect the sample integrity (QA/QC) and therefore, are important to the decisions made regarding analytical data. This report will identify any deficiencies found in the field and will outline the corrective actions that were recommended/implemented to address any minor deficiencies observed. The field audit report will also recommend appropriate corrective actions for any major deficiency noted. Follow-up reports describing completed corrective actions which addressed major deficiencies will be submitted by the Malcolm Pirnie Inc Project Manager to the USACE and USEPA.

A quality control field audit report will usually contain the following information:

- Date and location of field audit
- Sample matrices witnessed
- Name of personnel conducting the sampling
- Summary of sample methodology
- Description of any infractions that occurred and the corrective actions taken
- Conclusions
- Recommendations
- Quality control field audit checklist

Attachment 3

Example of Chain of Custody Form for Transfer of Split Samples

ATTACHMENT 3

EXAMPLE CHAIN OF CUSTODY FORM FOR TRANSFER OF SPLIT SAMPLES

Chain of Custody Record

Date of Tranfer:
Transfer From: **Lower Passaic River CPG**
Transfer To **Malcolm Pirnie Inc.**

Chain of Custody Record	
Relinquished by:	(Date/Time)
1.	
2.	
3.	
4.	
5.	

Sampler Signature:	
Received by:	(Date/Time)
1.	
2.	
3.	
4.	
5.	

CHAIN OF CUSTODY

Sample Number	Malcolm Pirnie, Inc. Split Sample Number	Matrix	Conc/Type	Preservative	Sampling Location	Collection Date/Time	PCB Congeners	PCDD/F Congeners	PAH	Pesticides	SVOC	Metals	Mercury (USEPA Method 1631)	Methylmercury (USEPA Method 1630)	Arsenic (USEPA Method 1632 modified)	TOC	Percent Moisture	Percent Lipid	Toxicity Test Hyalella azteca	Toxicity Test Chironomus dilutus	Toxicity Test Ampelisca abdita	Remark
e.g. SGXX-XXX	*e.g. SGXX-XXX-MPI*																					

Shipment for case complete (Y or N)?	Sample to be used for laboratory QC:	Additional Sampler Signature(s):	Cooler Temperature upon receipt: **NA**	Chain of Custody Seal Number:	
Concentration: L = low, M = low/medium, H = High		Type/Designate: C = Composite, G = Grab		Custody Seal Intact?	Shipment Iced?

Attachment 4

Example of Chain of Custody Form for Non-Contract Laboratory Program Samples

ATTACHMENT 4

EXAMPLE OF CHAIN OF CUSTODY FORM FOR NON-CONTRACT LABORATORY PROGRAM SAMPLES

Chain of Custody Record		TAT:	**Case No:**
			DAS No:
			SDG No:
Date Shipped:	**Chain of Custody Record**	Sampler Signature:	**For Lab Use Only**
Carrier Name:	Relinquished by: (Date/Time)	Received by: (Date/Time)	
Airbill:	1.	1.	Lab Contract No:
Shipped to:	2.	2.	Unit Price:
	3.	3.	Transfer to:
	4.	4.	
	5.	5.	

CHAIN OF CUSTODY

Sample Number	Malcolm Pirnie, Inc. Split Sample Number	Matrix	Conc/Type	Preservative	Sampling Location	Collection Date/Time	PCB Congeners	PCDD/F Congeners	PAH	Pesticides	SVOC	Metals	Mercury (USEPA Method 1631)	Methylmercury (USEPA Method 1630)	Arsenic (USEPA Method 1632 modified)	TOC	Percent Moisture	Percent Lipid	Toxicity Test Hyalella azteca	Toxicity Test Chironomus dilutus	Toxicity Test Ampelisca abdita	Remark (For Laboratory Use Only)
e.g. SGXX-XXX	*e.g. SGXX-XXX-MPI*																					

Shipment for case complete (Y or N)?	Sample to be used for laboratory QC:	Additional Sampler Signature(s):	Cooler Temperature upon receipt:	Chain of Custody Seal Number:	
Concentration: L = low, M = low/medium, H = High		Type/Designate: C = Composite, G = Grab		Custody Seal Intact?	Shipment Iced?

Attachment 5

Field Modification Form

FIELD MODIFICATION FORM
FOR
LOWER PASSAIC RIVER OVERSIGHT
MALCOLM PIRNIE, INC.

Date:

Document:

Activity:

Requested Modification:

Rationale:

Attachments:

Malcolm Pirnie Project Manager: _____

Malcolm Pirnie Project Quality Control Officer: _____

Attachment 6

Oversight Forms

CPG Sampling Location ID	River Mile	Description of Sampling Location	
Date of Deployment	Equipment Deployed	Comments on Sampling Location or Deployment	Corrective Action (as required)
Date of Retrieval	Community Survey and Fish Health	Comments on "Catch" or selected receptors	Corrective Action (as required)
Date	Print Oversight Staff Person Name	Signature of Oversight Staff Person	

CPG Sampling Location ID	CPG Sampling ID Number	Date of Processing	Description of Sample

Comment on Individual Fish Health	Corrective Action (as required)

Comments on Sample Processing	Corrective Action (as required)

Comment on Fish Stomach Content (as required)	Corrective Action (as required)

Was sufficient mass available to collect a split sample?	Requested Analyses		Date of split sample shipment to CPG lab
☐ Yes ☐ No *Minimum tissue mass for split sample is 85 grams.*	☐ PCDD/F ☐ PCB Congeners ☐ PAH ☐ Pesticides	☐ Metal (including mercury) ☐ Arsenic ☐ Methylmercury ☐ SVOC ☐ Percent Lipid	
Malcolm Pirnie, Inc. Assigned Sample ID Number			

Date	Print Oversight Staff Person Name	Signature of Oversight Staff Person

CPG Sampling Location ID	River Mile	Date of Sampling	Description of Sampling Location

Comment on Sampling Location or Deployment	Corrective Action (as required)

Comment on Benthic Community Survey	Corrective Action (as required)

If Applicable, Comment on In-situ Bioaccumulation Deployment	Corrective Action (as required)

Was split sample collected?	Requested Analyses	Date of Split Sample Shipment
☐ Yes ☐ No	☐ Toxicity - Hyalella ☐ Chemistry ☐ Toxicity - Ampelisca ☐ In-situ bioaccumulation ☐ Toxicity - Chironomus ☐ Laboratory bioaccumulation *For bioaccumulation split samples, notify Oversight Field Leader of potential split sample. Only toxicity and chemistry split samples will be collected in the field.*	
Malcolm Pirnie, Inc. Split Sample ID Number		

Date	Print Oversight Staff Person Name	Signature of Oversight Staff Person

Attachment 7

Laboratory Standard Operating Procedures (Battelle Marine Sciences Laboratory Standard Operating Procedures are available to the Partner Agencies upon request.)

Accutest Laboratories
Standard Operating Procedure

Lab Manager:_____

QA Manager:_____

Effective Date:_____

TITLE: PERCENT SOLIDS and TOTAL SOLIDS in SOIL/SOLID MATRICES

METHOD REFERENCES: SM18 2540G , ASTM Method D4643-00

Revised Sections*: Title, 1.1, 1.2, 1.3, Section 10 (all), Section 12(all), Section 13(all), 14.4*

1.0 SCOPE AND APPLICATION

1.1 This method is for the measurement of the percent solids or total solids in samples of soil, sludge, or other solid material. This method is based on a method SM18 2540G and on ASTM method 4643-93.

1.2 The oven drying techniques for percent solids as described in this SOP can be applied to any sample type where percent solids can be determined. The microwave drying technique for percent solids described in this SOP can only be applied to samples which do not fall into the categories listed: lower percent solids (<50%), sludges or any other sample with a high organic content, samples containing high amounts of hydrated materials or larger clumps or particles, and samples with high TDS in the pore water (i.e. marine deposits). In addition, samples designated for hexavalent chromium analysis or NYASPB reporting cannot be dried in the microwave.

1.3 Sludge samples for regulatory reporting must follow the sludge procedure outlined in this SOP.

2.0 SUMMARY OF METHOD

2.1 A homogeneous aliquot of sample is placed in a tared dish and weighed. The wet sample is then dried to constant weight. The difference between the initial and final weight indicates the amount of water in the sample. Percent solids are calculated using the dry weight of the sample divided by the total weight of the sample. Percent moisture is calculated using the weight of water in the sample divided by the total weight of the sample.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Not applicable.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as

a separate batch.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE (DUP): A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed.

5.0 HEALTH AND SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Chemical Hygiene Plan. Always wear a lab coat and glasses and the appropriate gloves when analyzing samples for percent solids.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 No specific holding time is in place for the calculation of percent solids. The samples should be stored at 0 to 4°C until the time of analysis.

7.0 APPARATUS AND MATERIALS

The items listed below are needed for the sample analysis.

7.1 Crucibles. Capable of heating to 105°C and capable of being heated in a microwave.

7.2 Two or three place balance. All balances must have their calibration verified with Class S weights daily before the analysis of each batch of samples. Note: A 3 place balance is required for CLP samples.

7.3 Stainless Steel or Teflon coated Spatulas

7.4 Drying oven capable of maintaining a constant temperature at 103 to 105°C.

7.5 Variable temperature microwave oven.

7.6 Dessicator with dessicant.

8.0 STANDARDS AND REAGENTS

8.1 No special standards or reagents are required for this method.

9.0 INTERFERENCES

9.1 When heated at 103 to 105°C, samples will lose moisture, but can also lose certain volatile components and ammonium carbonate. When heated in the microwave, there is a possibility that the soil is overheated if the microwave is not cycled properly. Microwave heating should not be used for any samples with high organic content (black or oily appearance), with low percent solids (50% or less), or on soils containing significant amounts of hydrated materials or soils in which the pore water contains high dissolved solids (for example, marine deposits).

10.0 SAMPLE CLASSIFICATION PROCEDURE.

10.1 Each sample must first be classifed as one of the following three types; a) a soil or solid that can be analyzed using the microwave method, b) a soil or solid that can be analyzed using the oven %solids method, or c) a sludge being analyzed for regulatory purposes that must use the sludge method. Classify the sample for analysis by microwave or oven. Certain sample types and certain protocols do not allow for the use of the microwave method. Samples which fall into any of the categories listed below should not be analyzed using the microwave.

10.1.1 Soils or solids to be analyzed by the microwave method must not be in any of the following categories.

10.1.1.1 Any NYASPB samples.

10.1.1.2 Any samples requiring analysis for hexavalent chromium (XCr).

10.1.1.3 Any samples with high organic content.

10.1.1.4 Any samples containing significant amounts of hydrated materials or with larger clumps or particles.

10.1.1.5 Any samples with low percent solids (< 50%).

10.1.1.6 Any samples in which the pore water contains high dissolved solids (for example marine deposits.)

10.1.1.7 Any sludge samples being reported for regulatory purposes.

10.1.2 Soils or solids to be analyzed by the oven %solids method can be any soils or solids that are not sludge samples being reported for regulatory purposes.

10.1.3 Sludges to be reported for regulatory purposes must be analyzed following the sludge %solids/total solids method.

11.0 MICROWAVE ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE

11.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour or for 20 minutes at 50 to 70 percent power in the microwave. Allow to cool in a dessicator.

11.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

11.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

11.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top

of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

11.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

11.5 Remove approximately a 5 to 20 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 20, set up a sample duplicate.

11.5.1 For any samples where it is difficult to obtain a representative sample aliquot, increase the sample aliquot size to 25 to 50 g.

11.5.2 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

11.5.3 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

11.6 Place a batch of 20 samples in the microwave and dry them for approximately 10 minutes at 50 to 70 percent power. Let the samples cool for 5 minutes and then dry them for an additional 10 minutes at 50 to 70 percent power.

11.6.1 Power levels and times will need to be adjusted for smaller batches of samples. Check with area supervisors for assistance.

11.7 Remove the samples and let cool for 5 minutes. If they are going to be out for longer than 10 minutes, place them in a dessicator before weighing.

11.8 Weigh the samples on the balance and record the final weights. This can be done manually or electronically. Take at least 2 samples and stir them with a spatula, making sure not to retain any sample particles on the spatula. The 2 samples used for this check should be the 2 that have the highest moisture content (lowest percent solids) in the batch. Any samples with < 50% solids must be submitted for redo using the oven drying method.

11.9 Place these 2 samples back in the microwave and microwave for 3 to 5 minutes at 50 percent power. Remove the samples and let cool for 5 minutes.

11.10 Weigh the samples on the balance and record the final weights. Again, this can be done either manually or electronically.

11.10.1 If the sample weights on the redry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then then the whole batch should be stirred and redried until all percent solids agree within this criteria.

12.0 OVEN ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE (NOT TO BE USED FOR SLUDGES).

12.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour. Allow to cool in a dessicator.

12.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

12.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

12.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

12.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

12.5 Remove approximately a 5 to 20 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 20, set up a sample duplicate.

12.5.1 For any samples where it is difficult to obtain a representative sample aliquot, increase the sample aliquot size to 25 to 50 g.

12.5.2 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

12.5.3 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

12.6 Place a batch of samples in the oven at 103 to 105°C. The samples must remain in the oven for a minimum of 1 hour and up to 24 hours. Drying times should not exceed 24 hours unless specific project instructions are being followed. .Record the drying time.

12.6.1 Samples with high organic content must stay in the oven for a minimum of 8 to 12 hours.

12.6.2 Remove the samples and let cool for 5 minutes. If they are going to be out for longer than 10 minutes, place them in a dessicator before weighing.

12.6.3 Weigh the samples on the balance and record the final weights. This can be done manually or electronically.

12.6.3.1 If the samples are in the oven less than 12 hours, then place all of the samples back in the oven for a minimum of 1 hour at 103 to 105°C.

12.6.3.2 If the sample weights on the redry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then then the whole batch must be stirred and redried until all percent solids agree within this criteria.

12.7 Percent solids are calculated using the equation shown below.

Percent moisure = 100 – percent solids.

$$\text{Percent solids} = 100 \times \frac{(\text{final dry weight} + \text{crucible}) - \text{crucible tare weight}}{(\text{wet weight} + \text{crucible}) - \text{crucible tare weight}}$$

13.0 ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE/TOTAL SOLIDS FOR SLUDGE MATRICES.

Below is a step-by-step procedure for the analysis of sludge samples for percent solids and percent moisture and total solids.

13.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour. Allow to cool in a dessicator.

13.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

13.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

13.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

13.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

13.5 Remove approximately a 25 to 50 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 10, set up a sample duplicate.

13.5.1 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

13.5.2 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

13.6 Place a batch of samples in the oven at 103 to 105°C. The samples must remain in the oven for a minimum of 8 hours and up to 24 hours. Drying times should not exceed 24 hours unless specific project instructions are being followed. .Record the drying time.

13.6.1 Remove the samples and place them in a dessicator to cool.

13.6.2 Once the samples are cool, weigh them on the balance and record the final weights. This can be done manually or electronically.

13.6.3 Then place all of the samples back in the oven for a minimum of 1 hour at 103 to 105°C. Repeat steps 13.6.1 and 13.6.2.

13.6.4 If the sample weights on the redry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then the affected sample(s) must be stirred and redried until all percent solids agree within this criteria.

13.7 Percent solids are calculated using the equation shown below.

Percent moisure = 100 – percent solids.

$$\text{Percent solids} = 100 \times \frac{\text{(final dry weight + crucible) - crucible tare weight}}{\text{(wet weight + crucible) – crucible tare weight}}$$

14.0 QC REQUIREMENTS

14.1 Each batch of 20 samples will include a duplicate sample. The exception is for sludge samples where a duplicate is required for one in 10 samples.

14.2 The limit for duplicate samples is 5 % RPD. If the RPD values are outside of this range, and all other method quality control is within limits, then sample non-homogeneity should be suspected. A description of the duplicate sample appearance should be provided for all batches where the 5% RPD is not met. In general, it is recommended that batches with samples with high RPD's be reanalyzed to confirm the original results.

The calculation for %RPD = $\frac{\text{100 x (Sample result – Duplicate result)}}{\text{(Sample result + Duplicate result)/2}}$

14.3 The balance calibration must be verified at a minimum of 2 levels bracketing the range of weights measured each day before use. The calibration must meet the specifications listed in the balance logbook. If they do not, the balance must be recalibrated and rechecked before any samples can be analyzed.

14.4 For samples dried in the microwave, a minimum of 2 redries is required for every 20 samples. For solid or soil samples dried in the oven, all samples must be redried if the original drying time is less than 12 hours. For sludge samples, all samples must be redried. Redries must match within 0.05 g or 4% of the original weight, whichever is less.

15.0 DOCUMENTATION REQUIREMENTS

15.1 All data regarding the analysis must be recorded on the data worksheet. Make sure that all sample information is included on these sheets. Any unusual characteristics of the samples should be noted in the comment section. This can be done electronically or manually. Make sure to double check crucible and sample ID's when they are recorded.

15.2 Initial balance calibrations must be recorded in the balance calibration check log for each balance.

16.0 DATA REVIEW AND REPORTING

16.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are

responsible for making sure that the raw data is fully documented.

16.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The supervisor is also responsible for making sure that the QC calculations are done correctly and responsible for reviewing the data entry into the LIMS. No LIMS entry review is necessary when the data is electronically transferred.

16.3 After the supervisor or designated reviewer completes their review, the data is released for client access in the LIMS. The raw data is submitted to the area manager. The manager will periodically review data for technical completeness. The raw data is then transferred to the report generation department.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in the waste management SOP.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager:_____

QA Manager:_____

Effective Date: _____

TITLE: TOTAL ORGANIC CARBON IN SOILS SAMPLES

METHOD REFERENCES: "Procedures for Handling and Chemical Analysis of Sediment and Water Samples" prepared for the US EPA Corps of Engineers, May 1981, modified, and SW846 Method 9060, September 1986, modified, and EPA Region 2 Lloyd Kahn Method, July 1988.

***Revised Sections*: 8.1, 10.2 (all), 4.0 Definition of MDL**

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine total organic carbon in any solid matrix. It may also be used for liquid matrices containing a high level of total organic carbon. Samples that are primarily aqueous may also be analyzed using this method, but sample sizes should be limited to $\leq$ 0.10 g.

1.2 The product code for total organic carbon is TOC for the Corp. of Engineers methods and for the modified SW846 9060 method. The product code is TOCLK for total organic carbon run by the Lloyd Kahn EPA Region 2 method.

2.0 SUMMARY OF METHOD

2.1 Total organic carbon is determined by combusting an acidified sample and quantitating the carbon dioxide released using infrared analysis. The quantitation is done by comparison to a linear calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 The normal reporting limit for TOC in soils is 1000 mg/kg. This is based on a 0.1 g sample size. A minimum reporting limit of 100 mg/kg can be obtained by using a 1.0 g sample size. A reporting limit of 100 mg/kg is required for samples being analyzed for Lloyd Kahn TOC. A low level calibration standard is run at the level of this reporting limit.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria. Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier or limits defined in the SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK SAMPLE. Digest and analyze a high and a low standard with each batch of samples. These standards must have a recovery of 90 to 110 %. If the spike blank is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

LAB CONTROL SAMPLE. A solid lab control sample from an external source may be distilled with a batch, depending on individual client requirements. The solid lab control is evaluated using manufacturer's limits. If the lab control is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMIT (MDL) The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The furnace operates at high temperature and the furnace should be allowed to cool down before doing any system maintenance or troubleshooting. If there are any signs of a system blockage, open the sample introduction port and turn off the furnace to prevent build up of back pressure.

5.3 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples should be kept under refrigeration at 4^0 C until they are analyzed.

6.2 No holding time is outlined in the Corp. of Engineers method for TOC. SW846 9060 specifies a holding time of 28 days for aqueous samples. Unless otherwise specified, this 28-day holding time will also be applied to solid samples analyzed using this SOP.

6.3 A 14 day holding time should be followed when analyzing TOC soils following the EPA Region II Lloyd Kahn method.

7.0 INTERFERENCES

7.1 High results may be obtained if the inorganic carbon is not completely removed from the sample before analysis. To ensure that all of the inorganic carbon is removed, heat an acidified sample at least 10 minutes at 75°C before starting the analysis. Some volatile organics may be lost in this heating step, resulting in a low bias in the TOC result.

8.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

8.1 Shimadzu 5000 TOC analyzer or TOC-V analyzer with soil analysis module or equivalent.

8.1.1 Each day of analysis, the humidifier should be checked to ensure that the water level is within 1 inch of the top of the humidifier.

8.1.2 Each day of analysis, the baseline should be checked to make sure that it is stable and near zero.

8.1.3 Whenever calibration check recoveries or blanks are out of compliance, the flow and the condition of the catalyst should be checked. If the catalyst appears bad (contains many small fines), it should be cleaned and replaced. Refer to the instrument manuals for additional information on system maintenance.

8.2 Syringes, 0.100 ml size.

8.3 Analytical balance, capable or weighing to 0.1 mg. The calibration of the analytical balance should be verified each day before use.

8.4 Volumetric glassware, class A, for standards preparation.

8.5 Ceramic boats.

8.6 Drying oven, capable of being set to 75°C

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water taken from the DI tap with the carbon filter should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent logbook.

9.1 Sucrose Stock Solution, 200000 mgC/l (20% C from sucrose): Dry sucrose in dissector. Weigh out 47.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock should be replaced whenever crystallization of the sucrose is apparent. It can be held for a maximum of 3 months. Refrigeration is not required.

9.2 Sucrose Standard Solutions: Dilute the above stock solution (200000 mC/l) as shown below to make the suggested calibration standards. Add concentrated hydrochloric acid to bring the pH to less than 2 before diluting each standard to the final volume.

9.2.1 Different standards may be used, but a minimum of 5 standards and a blank are required for the initial calibration. The top standards shown below are close to the top of the linear range of the instrument and sometimes will not work at these levels.

9.2.2 Two suggested curve levels are shown below. These standards must be held for no longer than one month.

9.2.3 High curve. Either the 50000 mgC/l or the 40000 mgC/l may be used as the highest standard. Both are not required.

Standard Level	ml of stock	Final volume (ml)
50000 mgC/l	25.0	100
40000 mgC/l	20.0	100
25000 mgC/l	12.5	100
10000 mgC/l	10.0	200
5000 mgC/l	5.00	200

1000 mgC/l	1.00	200
Blank	0.000	100

9.2.4 Lower curve.

Standard Level	ml of stock	Final volume (ml)
25000 mgC/l	12.5	100
20000 mgC/l	10.0	100
10000 mgC/l	10.0	200
5000 mgC/l	5.00	200
1000 mgC/l	1.00	200
Blank	0.000	100

9.3 Glucose Stock solution, 50000 mgC/l (5% C from glucose): Dry glucose in dessicator. Weigh out 12.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock should be replaced whenever crystallization of the glucose is apparent. It can be held for a maximum of 1 month. Refrigeration is not required.

9.4 Glucose Check Solution, 25000 mgC/l (2.5% C from glucose): Dilute 50.00 ml of the glucose stock solution (50000 mC/l) to approximately 80 ml with DI water. Add concentrated hydrochloric acid to bring the pH to less than 2 and then dilute to a final volume of 100 ml with DI water. This solution should be made up monthly.

9.4.1 A different concentration of this check solution will be needed if a lower curve is run.

9.4.2 This is from a separate source than the calibration curve and can be used as the ICV check.

9.5 Nitric Acid, reagent grade. Used for acidifying samples to remove inorganic carbon.

9.5.1 Dohrman Instruments recommends that phosphoric acid not be used for this purpose. Dohrman found that the phosphoric acid tended to coat both the boat and the catalyst in the furnace with a layer of polyphosphoric acid and that, possibly as a consequence of this, the release of inorganic carbon as carbon dioxide was slower than with nitric acid and possibly incomplete.

9.6 Oxygen Gas, high purity.

9.7 Pre-baked cat litter or silica sand.

10.0 PROCEDURE

10.1 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC soil analyzer. For the procedure with the newer Shimadzu TOC-V soil analyzer, refer to step 10.2. (More details for use of the software can be found in the TOC-V CPH/CPN users manual.)

10.1.1 Turn on the oxygen. The pressure in the soil module should be set at 2 and the carrier gas should be set as marked on the dial (0.5 l/min). The oxygen pressure at the tank must be at least 60 psi to maintain sufficient pressure at the instrument. Check to make sure that the humidifier contains sufficient water. It should be filled to within approximately 1 inch of the top of the humidifier. (The humidifier is located under the magnetic plate on the right side of the instrument.)

10.1.2 If the power is off, then turn on the power at the side of the soil and water modules and for the computer.

10.1.3 Go into the TOC software on the TOC. Select measure and then connect. Wait for the software to connect with the TOC analyzer. Proceed to options and then instrument conditions. Under TOC, there should be no check next to Furnace on. Under ASI, there should be no check next to ASI used. Under SSM, the TOC furnace should be turned on.

10.1.4 Go to view and click on the background monitor. A graph will appear on screen showing the position of the baseline and the status of the furnace temperature. Wait for the baseline to stabilize and for the furnace temperature to indicate that it is OK. Make sure that the hatch on the boat sampler is tightly closed and that there are no leaks in the system. If the baseline is not within $\pm$ 10 of zero, then the zero of the instrument may need to be adjusted. Check with the lab supervisor or manager for further instructions.

10.1.5 If the instrument has not been calibrated within the last month, then it is recommended that it be calibrated at this point. (A new calibration is required at least once per quarter.)

10.1.5.1 Select a new file and insert standards. A minimum of 2 injections must be used for each standard. Five standards and a blank are required for the calibration. The lowest standard should be at 1000 mgC/l or lower. A 100 ul injection size should be used for all standards.

10.1.5.2 After the standard file is created and inserted into the run file, then save the run file using the save as command. The file should be named with the instrument ID (A or B), the last digit of the year, the month, the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on instrument A from 3/28/01 would be named A10328s1.

10.1.5.3 Press start in the software and follow the prompts. Place a clean boat filled with a small tuft of glass wool in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch and push the boat all the way forward. Enter OK at the software.

10.1.5.4 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.1.5.5 Select the option to repeat the injection and repeat the steps outlined above.

10.1.5.6 When all of the standards have been completed, then review the curve using the view, calibration option.

10.1.5.6.1 If a correlation coefficient of greater than 0.995 is obtained, then save the curve using the file, save option. Check to make sure that the intercept, calculated using a weight of 1.0 g for Lloyd Kahn or using a weight of 0.1 g for other TOC analyses, is less than the reporting limit for each method (100 mg/kg for Lloyd Kahn or 1000 mg/kg for other TOC soils.)

10.1.5.6.2 If either the correlation coefficient or the intercept does not meet the above criteria, than recalibrate before proceeding with the samples.

10.1.5.7 If a previous calibration is being used, then it must be verified with a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC. Make sure to use duplicate injections for all analyses. Note: The method blank may be used as the calibration blank check.

10.2 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC-V soil analyzer.

10.2.1 Turn on the oxygen. The pressure in the water module should be set at 200 Kpa and the carrier gas should be set as marked on the dial (150 ml/min). The oxygen pressure at the tank must be at least 60 psi to maintain sufficient pressure at the instrument. Check to make sure that the humidifier contains sufficient water. It should be filled to within the two white lines on the side of the humidifier. (The humidifier is located inside the water analyzer at the right side of the instrument.)

10.2.2 If the power is off, then turn on the power at the side of the soil modules and at the bottom right of the front panel of the water moldule and for the computer.

10.2.3 Go into the TOC software on the TOC. In the TOC-Control V main window, double click on the sample table editor and click OK on the user name box.

10.2.4 Before starting the run, open the background monitor to make sure that the baseline is stable and the furnace is up to temperature. If there are problems at this point, check with the lab supervisor or manager for further instructions.

10.2.5 Click File, New, and choose Calibration Curve and click OK. Follow the directions on each screen. For the system, pick TOC-V with SSM. Click on the calibration points. Then enter the file name. The file should be named with the instrument identifier (A or B or C), year (1 digit), the month (2 digits), the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on

instrument C from 3/12/07 would be named A70312s1. Enter the file name and then go to the volume. Enter the concentration and number of points. Edit the points to correct the concentrations. Enter next until the last screen is reached and then click on finish.

10.2.5.1 If using a previously generated calibration, then this step can be omitted. A new calibration is required at least once per quarter, but it is recommended that this be run once per month.

10.2.6 Go back to the TOC-Control V main window and double click the sample table editor. Click File and New to open the sample run icon. Click the system tab and select the TOC-SSM system. Click on the new file and follow the prompts on the screen. Name the file using the convention as described above.

10.2.7 Connect to the instrument using the connect toolbar button or from the instrument menu. Insert the calibration file created above into the sample table. You must load the new curve into the method before running the samples.

10.2.8 To start running the calibration, press start in the software and follow the prompts. Place a clean boat filled with a small tuft of glass wool in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch. Enter 100 ul into the volume prompt and then hit start. Wait for the prompt and then push the boat forward.

10.2.9 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.2.10 When all of the standards have been completed, then review the curve using the view, calibration option. If a correlation coefficient of greater than 0.995 is obtained and the intercept is less than the RDL, then save the curve and put it into the method(s) that you are running. Then you can proceed to add samples.

10.6 After the calibration or calibration checks are completed, then analyze the external check standard made from glucose. This standard must agree within 10 percent of the true value. If it is not within this range, determine the source of the problem before proceeding. Note: The spike blank may be used as the external calibration check, but then the results must be within 10 percent of the true value.

10.7 After every 10 samples, a continuing calibration check (CCV) sample must be analyzed. The continuing calibration check should be a standard near the mid-range of the curve. The continuing calibration check should agree within 10 percent of the true value. If the CCV is not within 10% of the true value, then no samples can be reported in the area bracketed by this CCV unless the CCV is biased high (110 to 150%) and the sample results to be reported are less than the reporting limit.

10.8 For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it should be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is

not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the samples results to be reported are less than the reporting limit.

10.9 Begin analyzing the samples following the procedure outlined below.

10.10.1 Weigh out from 100 to 1000 mg of sample (wet weight) into a ceramic boat using a 4-place analytical balance. For samples that contain high levels of TOC smaller sample sizes may be needed. For unknown samples, start with a sample size of 100 mg. (All method blanks and spike blanks should be calculated assuming a 100 mg sample size and should be set up using silica sand or pre-baked cat litter.) Samples that contain non-homogeneous particulates should be homogenized with a mortar and pestle before weighing out the sample aliquot.

10.10.1.1 If a client is requiring a detection limit lower than 1000 mg/kg, then larger sample sizes are required. A detection limit of 100 mg/kg requires a weight of 1 gram. A smaller sample size may be used only to bring the sample to within the range of the calibration curve.

10.10.1.2 If less than 50 mg is used for a sample to bring it within linear range, then 4 replicates must be analyzed at that weight.

10.10.2 Add nitric acid dropwise to the sample until no additional effervescence is observed and the surface of the sample is covered with the acid. Heat the acidified sample in an oven at 75°C for a minimum of 10 minutes.

10.10.3 If the duplicate sample injections have a coefficient of variation (CV) of greater than15 percent or an RPD of greater than 20%, then repeat the analysis with 2 additional duplicate injections. If, on the repeated analysis, a high CV or RPD is still obtained, then the sample results should be reported with a flag due to possible sample non-homogeneity. This 15% CV or 20% RPD criteria does not apply if the sample results are low and the results are within plus or minus the reporting limit of each other.

$$CV = (\text{Std Dev}_{n-1} / \text{mean}) \times 100$$

$$RPD = (\text{Result1} - \text{Result 2})) \times 100/\text{mean}$$

10.10.4 With each batch of 20 samples or less, a matrix spike and a duplicate should be analyzed. On each analysis day, a method blank and spike blank must be analyzed. All of these quality control points must be analyzed in duplicate.

10.10.4.1 Prepare the method blank by treating a small amount (approximately 100 mg) of pre-baked cat litter or silica sand with nitric acid and heating at 75 ° C for a minimum of 10 minutes.

10.10.4.2 Prepare the spike blank in the same manner as the method blank, but spike it with 100 ul of a 20000 mgC/l standard or external solution before adding the acid. Note: The spike blank can be used in place of the external check, but then must be prepared from the external source and must meet the 10 % check criterion.

10.10.4.3 Prepare the duplicate in the same manner as a sample.

10.10.4.4 Prepare the matrix spike by adding 100 ul of a 20000 mgC/l standard or external solution to a sample aliquot before adding the acid and heating the sample.

10.10.5 At the end of the analysis, a continuing calibration check must be analyzed. If the calibration check is not within 10 percent of the true value then all samples bracketed by the out of compliance CCV must be reanalyzed. (If the CCV is within 110 to 150%, then samples with results <RDL may be reported.)

10.10.6 If required, a CCB should be analyzed after the final CCV check of the analysis. Refer to Section 10.9.

10.11 The final sample results are calculated using the equation shown below. The calculation is done automatically in the Shimadzu TOC software except for the percent solids correction. The percent solids correction is added when the data is transferred in the LIMS system. See area supervisor or manager for further details.

Organic Carbon, Total (mg/kg) =

$$\frac{\text{Conc. from curve (ug)}}{\text{sample weight in g} \times \text{\%sol}/100}$$

11.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.1 Method Detection Limits (MDLs). MDLs should be established using a blank sample spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year.

11.2 Calibration Curve. The instrument must be calibrated a minimum of once per quarter. It is recommended that the instrument be calibrated at least once per month. The calibration curve must have a correlation coefficient of at least 0.995 and the intercept must be less than the reporting limit. If the instrument is not calibrated on a given day, then the curve must be verified using a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC.

11.3 Method Blank. The laboratory must prepare and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that

limit, the samples must reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.4 Spike Blank. The laboratory must prepare and analyze a spike blank with each set of 20 or less samples. For a running batch, a new spike blank is required for each different analysis day. The laboratory should assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. (If the spike blank is used in place of the external, then it must be within recovery limits of 90 to 110 percent.) If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. In all other situations, all samples associated with a spike blank outside of recovery limits must be reanalyzed.

11.5 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. (Note: For Florida samples, spikes should be prepared for 1 in 10 samples.)

11.5.1 The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.5.2 The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.6 Matrix Duplicate. The laboratory must prepare and analyze a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. Matrix spike duplicates may be used in place of matrix duplicates. The duplicate rpd is calculated as shown below.

11.6.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.6.2 This duplicate fills the requirement for quadruplicate injections for one sample in 20 for the TOCLK method.

11.6.3 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \text{\% RPD}$$

11.7 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV)). A standard from a separate source than the calibration should be run at the beginning of

each run. This ICV should be within 10 percent of the true value. If it is not, the problem must be resolved before any samples can be analyzed. Note: The spike blank may be used in place of the ICV as long as a separate source standard is used and the 10 percent criterion is met.

11.8 Continuing Calibration Verification (CCV). Analyze the continuing calibration verification solution after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high (111 to 150%) and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

11.9 Continuing Calibration Blank (CCB). For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it should be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the sample results to be reported are less than the reporting limit.

12.0 DOCUMENTATION REQUIREMENTS

12.1 Each analyst should review all data and assemble a data package consisting of the following information. This data package should be turned into the supervisor for review after the analysts complete their LIMS review (see 12.3 below).

- Results report, showing dilutions, replicate injection results, and CV or RPD results.
- Preparation/run log showing weights taken at the balance for each injection.
- Standards prep sheet.
- Reagent information sheet.
- QC Summary sheet with calculations

12.2 In addition, all reagent information such as lot numbers should also be recorded in the reagent log book. Any unusual characteristics of the samples should be noted on the raw data or on the preparation log. Make sure that all sample ID's and dilutions are labeled on the data.

12.3 An ASCI format file should be generated and copied over to the LIMS. The analyst is responsible for reviewing the data in the LIMS and adding appropriate spike amounts and true values before sending the data for supervisor approval.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This

document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES

14.1 Shimadzu Instrument Manual

ACCUTEST LABORATORIES
Standard Operating Procedure

Lab Manager_____

QA Manager_____

Effective Date:_____

TITLE: PERCENT LIPIDS BY GRAVIMETRIC ANALYSIS

METHOD REFERENCES: IN HOUSE METHOD

***Revised Sections*: NA – new SOP**

1.0 SCOPE AND APPLICATION

1.1 This method is for the measurement of percent lipids in biota samples.

2.0 SUMMARY OF METHOD

2.1 The sample is homogenized in a blender. An aliquot of the homogenized sample is extracted with methylene chloride. The extract is dried over sodium sulfate. The solvent is evaporated from the extract and the residue (% lipids) is dried to constant weight.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method has been established at 0.1%.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH. A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For this method, a batch can contain a maximum of 10 samples.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 10 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control

recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX. The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE. A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATE. A matrix spike duplicate may be prepared in place of a laboratory duplicate, depending on specific client requirements. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike should be assessed as outlined under the sample duplicate definition and the matrix spike recovery should be assessed as outlined under the matrix spike definition.

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). MDLs should be established for all appropriate methods, using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an

indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

5.0 HEALTH & SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.

5.3 Methylene chloride is known to cause cancer in laboratory animals. Always handle with the appropriate protective gloves. Do all work where solvent is present in a hood.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Biota samples should be stored in a freezer until needed in the lab.

6.2 There is no established holding time for this method. It is recommended that all analyses be started within 28 days.

7.0 APPARATUS AND MATERIALS

The items listed below are needed for the sample preparation steps.

7.1 Four decimal place analytical balance. All balances must have their calibration verified with Class S weights before and after each batch of samples.

7.2 Whatman PS filter paper or equivalent.

7.3 Glass VOA vials with Teflon lined caps.

7.4 125 ml round bottom flasks.

7.5 Water bath, capable of heating to a temperature of 70 to 75 degrees C.

7.6 Glass funnels

7.7 Glass beakers or Erlenmeyer flasks

7.8 Magnetic stirrers with PTFE-coated stirring bars.

7.9 Graduated cylinders

7.10 Glass boiling beads

7.11 Class A volumetric pipets.

8.0 STANDARDS AND REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required.

8.1 Methylene Chloride, reagent grade or better.

8.2 Sodium Sulfate, anhydrous crystal

8.3 Fish oil spiking lab control and spiking solution. Cut apart fish oil gel tablets and pour out the oil. Using an analytical balance weigh out approximately 3.0 g of fish oil into a 100ml volumetric flask. Record the weight used. Fill to the mark with methylene chloride. Store in a capped vial.

9.0 INTERFERENCES

9.1 The definition of lipids is based on the procedure used. This procedure will measure all lipids and other materials which are soluble in methylene chloride and which do not volatilize below 70 to 75°C.

10.0 EXTRACTION AND ANALYSIS PROCEDURE FOR PERCENT LIPIDS.

Below is a step-by-step procedure for the extraction and analysis of biota samples for percent lipids.

10.1 Dry clean, label round bottom flasks and clean glass boiling beads at 105 °C for a minimum of 1 hour. Store in a desiccator. Throughout this procedure, the flasks must be handled only with clean metals tongs or tweezers.

10.2 Add 2 to 3 glass beads to each round bottom flask and weigh to constant weight on an analytical balance. Record the final weight under the tare weight column on the data sheet.

10.3 For the method blank, add 25 ml of methylene chloride to a labeled VOA vial and cap tightly. For the blank spike, add 25 ml of methylene chloride and 1.0 ml of the fish oil spiking solution and cap tightly.

10.4 For each sample, weigh out 3.0 g of homogenized biota sample into a labeled VOA vial and cap. For the duplicate weight out a second 3.0 g aliquot. For the matrix spike weight out a third 3.0 g aliquot and spike with 1.0 ml of the fish oil spiking solution. Then add 25 ml of methylene chloride to each sample, matrix spike, and duplicate.

10.5 Vortex each sample and QC for 1 minute and let settle.

10.6 Filter the extract through the filter paper containing approximately 3 g of sodium sulfate into a round-bottom flask that has been tared to constant weight. Rinse the vial and the filter paper with methylene chloride. Add the rinses to the boiling flask.

10.7 Place the flask on a water bath at 70 °C and let the methylene chloride evaporate off. Do not let the temperature exceed 75°C. When the flask appears almost dry remove the flask, wipe the moisture off the outside of the flasks and blow out the flask for 15 sec. with nitrogen to remove the solvent vapor.

10.8 Transfer the flasks to a desiccator. Cool the flask in the desiccator for a minimum of 30 minutes. (Normally samples are desiccated from 4 hours to overnight, but shorter times are acceptable as long as constant weights are obtained.) Weigh the flasks on an analytical balance. Continue to desiccate and weigh the flasks until constant weight is obtained. Constant weight is defined as a weight change of less than 0.0005 g.

10.9 Calculate the weight percentage of lipids present using the calculation shown below.

$$(100 \times (A - B))/W = \%\ \text{lipids}$$

where

A = weight of the flask + the sample in g.
B = tare weight of the flask in g.
W = the weight of the sample in g

11.0 QC REQUIREMENTS

11.1 A method detection limit study must be done approximately once per year. The MDL study is done following the procedure outlined in the Accutest laboratory MDL SOP. A minimum of seven replicates spiked at 3 to 5 times the MDL should be taken through the procedure.

11.2 A precision and accuracy study must be completed before any samples are analyzed by this method and whenever any method modifications are made. The precision and accuracy study consists of extracting and evaporating 4 samples of a standard spiked with 1.0 ml of the fish oil spiking solution. The recovery of each spike must be within the range of 80 to 120% recovery and all of the values for the study must be in the range of plus or minus 3 times the standard deviation. New analysts must also show demonstration of capability by performing this precision and accuracy study.

11.3 Each batch of samples will include, at a minimum, a spike blank, a method blank, a matrix spike and a duplicate or matrix spike duplicate. A batch is defined as 20 or less samples extracted at the same time. In some cases, a matrix spike duplicate may be required in place of a duplicate.

11.3.1 Method Blank. The laboratory must prepare and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that limit, the samples must reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.3.2 Spike Blank. The laboratory must prepare and analyze a spike blank with each set of 20 or less samples. For a running batch, a new spike blank is required for each different analysis day. The laboratory should assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. (If the spike blank is used in place of the external, then it must be within recovery limits of 90 to 110 percent.) If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. In all other situations, all samples associated with a spike blank outside of recovery limits must be reanalyzed.

11.3.3 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.3.3.1 The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.3.4 Matrix Duplicate. The laboratory must prepare and analyze a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. Matrix spike duplicates may be used in place of matrix duplicates. The duplicate rpd is calculated as shown below.

11.3.4.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

11.3.4.2 The duplicate RPD should be calculated as shown below.

$$\frac{(\text{Sample Result - Duplicate Result}) \times 100}{(\text{Sample Result + Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

11.4 The balance calibration must be verified at 2 levels before and after each set of 14 or fewer measurements. The calibration verification is done with 2 mg and 1000 mg class S weights. The calibration must be within 10% for the 2 mg weight and within 0.5% for the 1000 mg weight. If the calibration is not verified after the measurements are completed, then the balance must be recalibrated and the batch reweighed.

12.0 DOCUMENTATION REQUIREMENTS

12.1 All reagents must be recorded in a reagent logbook with manufacturers, lot numbers, and expiration dates. All reagent information must be cross referenced on the sample worksheet.

12.2 All data regarding the analysis must be recorded on the data worksheet. Make sure that all sample information is included on these sheets. Any unusual characteristics of the samples should be noted in the comment section. Make sure that all sample ID's and flask numbers are clearly labeled on the data.

12.3 All initial balance calibrations must be recorded in the balance calibration check log provided next to each balance. Continuing calibration checks should be provided on the worksheets for constant weight.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, ESM003. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES

14.1 No additional references are required.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager_____

QA Manager_____

Effective Date: _____

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES

REFERENCES: SW846 7471A and SW846 7471A M

Revised Sections: ***removed 8.2.3, revised 7.2, 7.3, 7.4 (all), 7.5, 8.1.3, 8.1.4, 8.1.5, 8.2.1.1, 8.2.2.1, 10.0 (title), 10.4, 10.6, 13.4, 14.1, 14.2, and 14.3.*** ***Change to Revision 14:*** ***revised 12.2.***

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury in soils, sediments, bottom deposits, and sludge type materials. The reporting limit for mercury soil samples, based on a 0.6 g sample size, is 0.033 mg/kg.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of

approximately 10 percent. Recovery requirements vary by method. For this method a recovery from 80 to 120% is required. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{} = \text{MSD RPD}$$

(MS Result + MSD Result)/2

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All solid samples should be stored at 4 $\pm$ 2ºC until the time of digestion.

6.2 All samples should be analyzed within 28 days of the date of sampling.

7.0 APPARATUS

7.1 Two Leeman instruments are available for analysis. One is a Leeman PS200II automated analyzer and the other is a Leeman Hydra AA automated analyzer. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

7.1.1 Change the sample tubing as needed.

7.1.2 Change the drying tubing as needed.

7.1.3 Clean the exterior of the instrument as needed.

7.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

7.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

7.2 Graphite heating block. Capable of heating at 95 °C for 2 hours.

7.3 Digestion Bottles . Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

7.4 Calibrated glass tubes with verified 60.0 ml and 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume. (The 60.0 ml calibration is only required for water digestions).

7.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottle calibration log following the procedure outlined below.

7.4.2 Carefully measure 60.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

7.4.3 If the bottom of the meniscus is on the calibration line, then the bottle passes calibration and can be used.

7.4.4 If the bottom of the meniscus is not on the line, then the bottle should be removed from service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

7.4.4.1 Two different lines for the same volume (i.e. 60 ml) cannot be etched on the same bottle as that may lead to confusion in the measurement of the final volume.

7.4.5 Repeat the steps in 7.4.2 through 7.4.4 using a 100 ml final volume instead of the 60 ml final volume.

7.5 Class A , to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

7.6 Analytical Balance, 4 place. Calibration must be verified daily before use with NIST traceable weights.

7.7 Automatic pipetter bottles.

7.8 Volumetric pipets, class A.

8.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed. Different reagents are required for the different heating techniques.

8.1 Water Bath and Digestion Block Reagents.

8.1.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated nitric.

8.1.1.1 Make sure to only prepare the amount of acid that will be needed for the prep and analysis.

8.1.1.2 This preparation must be done in a hood.

8.1.2 Dilution Acid: To approximately 800 ml of DI water, add 37.5 ml of concentrated HCl and 12.5 ml of concentrated nitric acid. Dilute to 1000 ml with DI water and mix well. This dilution acid is used for making dilutions of digested samples from the water bath and digestion block digestion procedures.

8.1.3 Potassium permanganate, 5% solution: Dissolve 50 g of potassium permanganate in 1000 ml of DI water. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

8.1.4 Stannous chloride. Add 7.5 ml of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride and dissolve. Make sure that this solution is dissolved while in use.

8.1.4.1 Stannous sulfate may be used in place of stannous chloride.

8.1.5 Sodium chloride-Hydroxylamine hydrochloride or Sodium chloride-Hydroxylamine hydrosulfate. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

8.2 Mercury standard solutions.

8.2.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

8.2.1.1 The 10 ppm external source should be made up following the directions in 8.2.1.

8.2.2 100 ppb Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.2.1 The 100 ppb external source should be made up following the directions in 8.2.2.

8.2.3 10 ppb Hg solution. Using a 10.0 ml volumetric pipette, add 10.0 ml of 100 ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.0 INTERFERENCES

9.1 Potassium permanganate is added to eliminate possible sulfide interferences. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. High copper concentrations (> 10 mg/kg) may also interfere with mercury recoveries.

9.2 Samples that are high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and analyzed. This may be accomplished by using an excess of the hydroxylamine hydrosulfate.

9.3 Certain volatile organics may also absorb at this wavelength and can interfere.

10.0 GRAPHITE DIGESTION BLOCK PROCEDURE FOR SOIL DIGESTION

10.1 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each digestion tube. Calibration standards must be prepared fresh each day. Add 5 ml of DI water to each standard before digestion. The final concentration of Hg is calculated in the final digestate.

Ml of 10 ppb Hg solution	ml of 100 ppb Hg solution	Total ug of Hg	ug/L of Hg
0.000	0.000	0.000	0.000
2.00	0.000	0.020	0.20
5.00	0.000	0.050	0.50
0.00	1.00	0.100	1.00
0.00	2.50	0.250	2.50
0.00	5.00	0.500	5.00

10.2 Samples. For each sample, homogenize the sample well and weigh out three representative 0.2 g aliquots of the sample into one labeled digestion tube. *The individual 0.2 g weights do not need to be recorded, but the total weight (approximately 0.6 g) of the three aliquots must be recorded.* A solid lab control should be prepared in the same manner. Note: a smaller sample size may be used for the solid lab control if the true value will be over the range of the curve with three 0.2 g aliquots.

10.3 Make up additional quality control samples as shown below. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the method.) Make sure to clearly label each digestion tube. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve and at a different level than the CCV or the calibration standards. A low check standard is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 100 ppb Hg solution	ml of DIwater	µg/l of Hg
CCV Check(s)	2.5	7.5	2.5
MB	0.0	10.0	0.0
MS	2.0	0.0	2.0
MSD	2.0	0.0	2.0
Duplicate*	0.0	0.0	0.0
ICV	3.0	7.0	3.0

*Per project specification.

10.4 To all samples, QC, and standards add 5 ml of DI water and 5 ml of aqua regia and then heat for 2 minutes in a digestion block at 95ºC.

10.5 Cool the samples and then add 25 ml of DI water and 15 ml of potassium permanganate solution to each sample and mix thoroughly. Allow the samples to standard for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

10.5.1 For samples containing a mixture of solvent and water, take a sample aliquot of approximately 20 g (lower for higher solvent samples) of sample and add the reagents listed above. Pour the sample in a beaker and heat on a hot plate at 95 ° C (± 5° C) until no solvent layer is visible. Then transfer the digestate to a digestion tube and proceed as outlined below. A method blank and spike blank must also be taken through this entire procedure.

10.6 Cap the samples and place them in the graphite digestion block for 30 minutes at 95° C. Record the temperature and time for each digestion batch on the analysis sheet. Remove and cool.

10.7 Enter the prep data into the LIMS system, double checking all weights and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculation.

11.0 MERCURY ANALYSIS PROCEDURE

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 For the Leeman PS200II, go to the main menu on the Leeman software and make sure that it is in the analyze mode. (Use the jump to analyze command if it is not.) Note: you can always get back to the main menu by pushing the F1 key. Then proceed to taskmaster in the program and go to the wake up system command. The pump should turn on at 7 ml/min and the mercury lamp should turn on. Make sure to allow a minimum of 20 minutes for the lamp to warm up. If the Hg lamp needs to be optimized, it can be done from this menu.

11.1.3.2 For the Hydra AA, go to the Runner section and select the control tab. Click on the Hg lamp and the pump. The gas will turn on automatically when the pump is turned off. If can also be turned on separately if necessary. The pump rates and gas pressure are set in the protocol. Refer to the instrument maintenance manual for more information on setting up a new protocol. If the Hg lamp needs to be optimized, it can be done using the lab adjust on this page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.4.1 For the Leeman PS200II, the pressures can be checked using Utilities, Diagnostics and test gas. The output should be 7 psi and the input should be between 60 to 90 psi. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.4.2 For the Leeman Hydra AA, go to the Utility tab and pick the gas control test option. The output should be approximately 7 psi and the input should be between 60 to 90 psi. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Pick the proper protocol to run for the instrument. For the PS200II, go to Protocol, Get Protocol. Pick the proper protocol and enter. For the Hydra AA, go to the main screen in runner and select the proper protocol in the upper right hand corner.

11.1.5.1 Check with the area supervisor or manager for the proper protocol to use for each instrument.

11.1.6 Start a batch to save your data. This is referred to as a Folder in the PS200II software and a batch in the Hydra AA software.

11.1.6.1 For the PS200II, this is done as follows. Go to Open Folder and enter in the folder you will be using. The folder should normally be named H1 followed by the month and date, followed by the matrix designation for the batch, followed by the run number. For example, the first soil batch on 3/14/03 would be named H10314S1.

11.1.6.2 For the Hydra AA, go to the sample runner tab and click on start new batch. The batch name is limited to 8 characters. The batch should normally be named H2 followed by the month and date, followed by the matrix designation for the batch, following by the run number. For example, the first soil batch on 3/24/03 would be named H20324S1. The realtime print option can also be turned on from this tab.

11.1.7 Set up autosampler racks containing the samples that are going to be run.

11.1.7.1 For the PS200II, go to Autosampler and Rack Entry and Edit and enter your folder name. Enter your samples and the appropriate QC. CCV and CCB checks can be entered in the Macro column. A CP at the end of the macro line indicates that the check standards will be run before the sample on that line.

11.1.7.2 For the Hydra AA, go to main tab and click on the rack editor button. Enter your samples and the appropriate QC. CCV and CCB checks can be entered in the macro column. This tab may also be reached by clicking on the autosampler icon at the top of the page.

11.1.8 Enter or verify the standard values.

11.1.8.1 For the PS200II, from the main menu, go to Calibration and Standards and enter the standard values. Go to Check standards and put in the check standard

values. (This does not have to be done on each run.) Then go to Reset and reset all of the options.

11.1.8.2 For the Hydra AA, from the runner menu click on the standard tab. Click the buttons to the left of the standards that are to be run. Also click on the number of replicates to be run for each standard. Normally one replicate is run per standard. The standard concentrations are defined under the database menu under the line info tab. The check standard concentrations and acceptance ranges are also defined under this line info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Finish the preparation of the samples and standards as outlined below.

11.2.1 For samples that were digested In the water bath or the graphite digestion block, add 6 ml of hydoxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 For the PS200II, turn on the print options so that a real time report will be generated. Start the calibration by pushing the F6 option. Enter the numbers of the standards to be run (normally 1 to 6) and the number of replicates to be run (normally 1). The calibration curve will be run by the autosampler. When the curve is complete, check to make sure that all acceptance criteria are met and then accept the curve. See section 13.3 for calibration curve criteria. Make sure that the curve is printed as soon as it is accepted.

11.4.2 For the Hydra AA, turn on the real time report by checking the real time printing option on the runner menu either under main or under sample. Then go to the runner menu and the standard tab. Push the standard auto button. The calibration curve will be run by the autosampler. When the curve is complete, go to the database menu and click the calibration curve tab. Check to make sure that all acceptance criteria are met and then accept the curve. See section 13.3 for calibration curve criteria. Make sure that the curve is printed as soon as it is accepted.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 For the PS200II, go to Setup and enter the rack name(s) and the number of cups to be analyzed. Push F8 to run the samples. The stannous chloride solution is added automatically to each sample by the autosampler and the absorbance results are recorded electronically by the software.

11.5.2 For the Hydra AA, go to the runner menu and the sample tab. Pick the autosampler rack that is to be run and type in the start cup and the end cup. Then push the button for run auto.

11.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.2.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

11.7.1 For the PS200II software, use the printer,report, generate option. For electronic reports, use the file, prn, generate option.

11.7.2 For the Hydra AA software, go to the data base menu and pick the report tab. Make sure that the correct report specification has been chosen (normally Accutest). Pick the batch that is to be printed and then push the generate report button. Generate both the electronic reports (prn file) and printed reports (report) from this menu.

11.8 The calculations are done in the LIMS as described below. . For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 To shut down the instrument, move the stannous chloride line from the stannous chloride bottle to the rinse container. Let the system rinse with 10% nitric for several minutes. Then switch the bath to DI water and let rinse for several more minutes. Then empty the rinse bath and let the pump and gas run until the lines are completely dry. Go to Taskmaster and select the standby mode option. Release the tension on all of the pump clamps.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly for each instrument for CLP analyses. IDL's must be done a minimum of yearly for non-CLP analyses. If an instrument is not to be used for CLP analysis, the IDL can be generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be digested using the same procedure as the samples. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met.

12.3.1 A linear calibration using the equation y = mx + b is applied where m is the slope and b is the intercept. The calibration is not forced through zero.

12.3.2 The correlation coefficient is calculated using the following equation:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

where x is the measured absorbance and y is the standard concentration.

12.3.3 If the calibration curve does not meet criteria, and is redigestion, then any samples digested along with that calibration curve must also be redigested.

12.4 Initial Calibration Verification Standard (ICV)). During each analysis, a standard from a different source than the calibration standard should be analyzed. Normally this is analyzed at the beginning of the run. For this method, the ICV should be within 10 percent of the true value. When the measurements exceed these control limits, the analysis shall be terminated, and the problem corrected before proceeding. All reported results must be bracketed by compliant QC. The exception is, if the ICV is biased high (110 to 150 % recovery) and no mercury is found in the samples, then the sample results may be reported for mercury.

12.5 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.)

12.6 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.7 CRA (Low) Check. For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. An in-house criterion of 50 to 150% recovery is normally applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

12.7.1 A number of clients have specific program requirements for frequency and recovery ranges on CRA checks. Check with the metals supervisor for additional information on these programs.

12.7.2 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.8 Method Blank. The laboratory must digest and analyze a method blank with each batch of 20 samples. A minimum of one method blank is required for every 20 samples. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required every 20 samples. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.9 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control or spike blank is required for every 20 samples. Note: For soils, if a lab control is not available, a spike blank can be used. For a running batch, a new lab control sample is required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120%. In house lab control limits may also be generated to support these default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

12.10 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The laboratory should assess the matrix spike recovery against control limits of 75 to 125. (In house control limits are generated annually for information purposes only.). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the

matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

12.11 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the original sample should be assessed. The rpds are calculated as shown below and should be assessed against a limit of 20% RPD. .(In house control limits are generated annually for information purposes only.). If a matrix spike duplicate or a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{(\text{Sample Result - Duplicate Result}) \times 100}{(\text{Sample Result + Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|\text{MS Result - MSD Result}|) \times 100}{(\text{MS Result + MSD Result})/2} = \text{MSD RPD}$$

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg soil samples must show all digestion information including the sample ID's, sample weights, bottle numbers, type of heating used, start times, end times, and pressure or temperature, as appropriate for all digestions. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the comments sections. Make sure also that all dilutions are clearly documented.

13.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent log book. All standards should be recorded on the digestion log with the samples.

13.3 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

13.4 Annual bottle calibration verfications must be documented in the Mercury Bottle calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for

making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman PS200II instrument manual.

16.2 Leeman Hydra AA instrument manual.

Accutest Labs
Standard Operating Procedure

Lab Manager_____

QA Manager_____

Effective Date: _____

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)

METHOD REFERENCE: SW846 6020, Revision 0, September 1994.

Revised Sections: ***9.15.1, 9.15.2, 11.7.2***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of total and dissolved metals in water samples and in waste extracts or in solid or aqueous digests.

2.0 SUMMARY

2.1 Samples are prepared for analysis by digestion. The prepared samples are introduced into a radiofrequency plasma by pneumatic nebulization. There the energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass to charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information is processed by a data handling system.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. Current reporting limits for this method have been established at the levels listed in Table 1. The reporting limits are dependent upon the metal being analyzed and are in all cases greater than the IDL and the MDL for each element. Note: Many clients require special reporting limits. Refer to the scheduling sheets and check with the metals supervisor for additional information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH. A group of 20 samples or less that behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit within a 24 hour period. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of 10

percent or every 2 hours during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. It must be run after each calibration. The external check standard criteria is ± 10% of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits should also be generated once sufficient data is available to support the default limits. If the lab control or spike blank is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against method limits. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against default limits of 75 to 125 % recovery. In house limits should be generated once sufficient data is available. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If no digestion

step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD ADDITION. The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C until digestion.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP-MS. These interferences are discussed below.

7.2 Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. If isobaric interferences are present in the ion being analyzed, then the data must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the element of interest.

7.3 Abundance sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent masses and is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured next to a large one. Spectrometer resolution should be adjusted to minimize these interferences.

7.4 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-0to charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. Refer to method 200.8 and 6020 for lists of common interferences and correction equations to be applied. If these interferences cannot be avoided by the use of different isotopes, then correction equations should be applied to the data.

7.5 Physical interferences can occur during the transfer of the solution to the nebulizer (viscosity effects).

7.6 Memory interferences can be caused by build up on the sampler and skimmer cones, and from buildup of sample material in the torch and spray chamber. Some elements, such as mercury, can suffer from severe memory effects. In that case, gold is added to the rise solution to decrease the Hg rinse out time.

8.0 APPARATUS

8.1 Currently there is one ICP-MS available for use in the lab. It is a Thermo Elemental X5 with XI interface. This instrument has been designed to handle environmental matrices. It is interfaced with a Cetec autosampler.

8.2 Class A volumetric glassware as needed and instrument autosampler tubes.

8.2.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

8.3 Polypropylene bottles for standard storage. These bottles must also be cleaned as outlined above.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. Note: All reagents can be scaled up or down proportionately if different final volumes are required.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric acid, trace metals grade. Note – ultra trace grade may be required if lower detection limits than normal are needed.

9.4 Standard stock solutions available from Inorganic Ventures, Ultra Scientific, MV Laboratories or equivalent. Note: All standards must be ICP-MS quality standards or must be demonstrated to be free of interferences at the levels of use. Standards should come labeled with an expiration date and certificate of concentrations from the manufacturer. If both of these items are not received, then the manufacturer should be contacted before use of the standard.

9.5 Calibration Standards: These can be made up by diluting the stock solutions to the appropriate concentrations. Fresh calibration standards should be prepared a minimum of every two weeks. They must be monitored weekly for stability.

9.5.1 Standards should be made in a low acid matrix. Concentrations of 1 to 2 percent nitric acid and 0 to 0.8 percent hydrochloric acid are suggested, although any acid concentration that provides good analytical results may be used. High chloride concentrations may cause interferences so chloride concentrations should be limited. HCl may be omitted if silver and antimony are not elements of interest.

9.5.2 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP-MS. Suggested standard levels are shown in Table 2. Calibrations must consist of a minimum of a blank and a high standard. The calibration must be verified with a low check at or near the reporting limit at the time of analysis for a number of states including New Jersey, Florida, North Carolina and for a number of clients as specified in the client program requirements.

9.5.3 All standards should be stored in acid washed FEP fluorocarbon bottles.

9.6 Mass Calibration Standard. This standard must contain a spread of elements across the full mass range, and must include Li and U. All elements must be at a concentration to be measured in pulse counting mode. A 20 ppb solution is recommended. An acid matrix of 1% nitric and 0 to 0.8% HCl is recommended.

9.7 Detector Plateau Standard. This standard is used to optimize the voltage range for analysis and it is recommended that 3 different masses in the low and mid mass range be included, with concentrations to be measured in the pulse counting mode. A solution containing Be (9), Co (59), and In (115) at approximately 20 ppb should generally work for this application. An acid matrix of 1% nitric and 0 to 0.8% HCl is recommended.

9.8 Cross Calibration Standard. This standard is used to make sure that the counts between the pulse and analog modes are properly aligned. It must contain elements over the range of the masses and must include Li and U. All elements must be at a concentration to be measured both in pulse and analog mode. Lower concentrations are recommended for the high masses and higher concentrations are recommended for the low masses. One suggested solution for cross calibration contains 500 ppb of most elements plus 100 ppb of U, Ce, and Li.

9.9 Tuning Standard. This solution is used to verify mass calibration and thermal stability and must contain a mix of elements representing all of the mass regions of interest. Recommended elements include 200.8 tuning elements (Be, Mg, Co, In, and Pb) at 10 ppb in a 1% nitric solution plus 10 ppb of Li, Tl, U, and Ce.

9.10 Internal Standards. Internal standards are added to all calibration standards, quality control, and samples during analysis, normally using a second channel of the peristalic pump and a mixing manifold. At a minimum, the internal standard solution must contain Sc, Y, In, Tb, and Bi. A solution containing 50 ppb of 6Li, Sc, Y, Rh, In, Tb, Ho, and Bi in 1% nitric acid is recommended. If Hg is being analyzed, then 200 ppb of Au must also be added to the standard. Refer to Table 3.

9.11 Calibration /Rinse Blank. The calibration and rinse blanks are prepared by diluting acids to the same concentrations found in the standards. The calibration blank is used to establish the analytical calibration curve and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

9.12 Continuing Calibration Verification Check (CCV). This solution is prepared by adding either mixed or single element metals solutions to a solution containing the same acid matrix as the calibration standards. The metals should be at concentrations near the middle of the calibration curve. (Note: This check is run after the calibration, after every 10 samples or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.) Refer to Table 2 for suggested concentrations for the CCV.

9.12.1 Method 6020 does not specify the source of the CCV check. However, it is recommended that these be prepared from the same source as the calibration as it required in method 200.8

9.13 Matrix Spike and Spike Blank Solution. Suggested levels for the final concentrations of the spike are shown in Table 4. This solution is prepared by adding either mixed or single

element metals solutions to a solution containing 1 percent nitric acid and 0 to 0.8 % HCl and diluting to a fixed final volume with this acid mixture. 0.5 ml of this stock solution should be added to spike blank and the matrix spike before they are digested and brought to a final volume of 50 ml.

9.14 Lab Control Solution. This solution is prepared by adding either mixed or single element metal solutions to a solution containing 1 percent nitric acid and 0 to 0.8 % HCl and diluting to a fixed final volume with this acid mixture. 50 ml of this solution is digested and brought to a final volume of 50 ml. The lab control and spike blank can be used interchangeably for aqueous matrices for this method.

9.15 Interference Element Check Solutions. The purpose of the ICSA and ICSAB solutions is to demonstrate the magnitude of interferences and provide an adequate test of any corrections. It is recommended that the following solutions be purchased commercially.

9.15.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. The ICSA solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L

9.15.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. The ICSAB solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L
As	0.020 mg/l
Cd	0.020 mg/l
Cr	0.020 mg/l
Co	0.020 mg/l
Cu	0.020 mg/l
Mn	0.020 mg/l
Ni	0.020 mg/l
Ag	0.020 mg/l
Zn	0.020 mg/l

9.16 Initial Calibration Verification (ICV) or Quality Control Sample (QCS). The metals in this solution should be at final concentrations that are at the mid-point of the calibration curve. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 1 percent nitric acid and 0 to 0.8 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. Note: The ICV sample must be from a separate source from the calibration standards. This solution should be stored in a FEP fluorocarbon or previously unused polyethylene bottle.

9.17 CRI Standards. The CRI standards contain the elements of interest at the reporting limit for each element. Note: This QC check is optional for this method but is required for work in New Jersey, North Carolina, Florida, and for many clients with special requirements. This should be prepared by diluting calibration standard(s) to the reporting limit level for each element. They should be made in the same matrix as the calibration standards.

9.18 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary.

10.0 INITIAL INSTRUMENT SET-UP PROCEDURE

10.1 A general procedure on how to operate the Thermo X5 ICP-MS is given below. Refer to the X5 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, and that there are no leaks in the torch area. Make sure that the Faraday cage is in the forward position and that the cage door is closed.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) Make sure that sufficient internal standard solution is present.

10.6 Turn on the instrument by clicking on the ON button. The instrument will automatically go through the start-up cycle which lasts approximately 90 to 120 seconds and let the instrument warm up for at least 30 minutes. Go to the instrument icon and the configuration page and make sure that the proper configurations and accessories are selected.

10.7 Every one to two days or as needed, tune the instrument. Tuning must always be done after moving the position of the torch or the cones. Tuning can be done either manually or by following autotune procedures. It is recommended that autotune procedures be followed initially and then manual tuning be done as a second step. The purpose of tuning is to optimize the instrument for the highest sensitivity while obtaining low levels of oxides and doubly charged species. In general, the high masses have good sensitivity while the lower masses have less sensitivity, so it is recommended that the instrument be tuned with more emphasis on the sensitivity of low to mid-range masses. After the tune is complete, make sure to save the optimized parameters.

10.7.1 The major parameters are the parameters that have the greatest effect on signal stability and sensitivity. If tuning manually, start with D1, then extraction, Lens1, focus, and pole bias. Monitor how the signal changes with each adjustment and adjust for the maximum signal and minimum oxide ratio.

10.7.2 The minor parameters are the parameters that are used to make smaller changes in the tune. Normally the horizontal and vertical positions are the minor parameters that need adjustment.

10.7.3 Click RTD (real time display) to monitor the signal as the tuning is done.

10.7.4 Monitor the tuning solution to make sure that masses are being properly assigned. If the mass calibration has shifted by more than 0.1 amu from unit mass, then update the mass calibration as described in 10.8.

10.8 Approximately once every 6 months or as needed, update the mass calibration. (The mass calibration must be adjusted if it has shifted by more than 0.1 amu from the unit mass.) Set up an experiment with the sample label of mass calibration and the type instrument set-up. Then go to the advance properties and click the update mass calibration option. Aspirate the mass calibration solution (see section 9.6) and queue the experiment. After the calibration is complete, then go to the instrument icon and click on the mass calibration that has just been performed. Look for peak widths of approximately 0.75 amu at 5% peak

height with an error of < 0.2 amu for optimal performance. If it is not within this range, check with the area supervisor before proceeding.

10.9 Approximately once per month, or more often if the detector is getting old, perform a detector plateau calibration. Set up an experiment with the sample label of detector plateau and the type instrument set-up. Go to the advance properties and check the Plateau detector box. Set the masses for the elements in the Detector plateau solution (see section 9.7) and enter start and end voltages approximately 400 volts below and above the current pulse counting HT voltage. The voltage step should be set at 20. Aspirate the detector plateau solution and queue the experiment. After the experiment is complete, go to the instrument icon and click on the detector plateau that has just been performed. Determine the value at approximately 90 percent on the plateau and enter the PC voltage on the tune page under global.

10.10 On a daily basis, perform an instrument cross calibration. The purpose of the cross calibration is to set the appropriate factor for aligning the pulse and analog counts. Set up an experiment with the sample label of cross calibration and the type instrument set-up. Go to the advanced properties and check the detector calibrate box and set the offset mass to 220. It is recommended to also set up a second sample with a survey run after the initial cross calibration. Aspirate the cross calibration check solution (see section 9.8) and queue the experiment. When the experiment is complete, go to the instrument icon and click on the detector cross calibration that was just performed. Check that the factors are < 40000. Go to the experiment and make sure that the analog and pulse counts are lining up well over the mass range.

10.11 Before calibrating, run and print out a performance test. This must include the following items.

10.11.1 Demonstrate instrument stability by running the tuning solution a minimum of five times. Relative standard deviations of the absolute signals must be less than 5 percent for all elements in the tuning solution. If this criteria is not met, correct the problem and then repeat the stability test. Print the results of this test and store with the raw data for the run.

10.11.2 Verify acceptable mass calibration by running the tuning solution and monitoring the peak width measured at 5% of peak maximum for 7Li, 24Mg, 25Mg, 26Mg, 115In, 206Pb, 207Pb, 208Pb, and 238U. If the peak widths are outside of the range of 0.65 to 0.85 and the masses are off more than 0.1 amu, then redo the mass calibration as outlined in 10.8 before proceeding.

10.12 Calibrate the instrument using a minimum of a calibration blank and a standard for each element. (Note: The calibration standards may be included in the autosampler program or they may be run separately.) If more than two standards are used, a correlation coefficient of 0.995 or better must be obtained using a first order (linear) curve fit. A minimum of three replicate integrations are required for all data acquisitions.

10.12.1 In between each analysis of a separate standard or sample, a rinse blank must be run through the lines of the sample introduction system. Each sample or standard should be aspirated for a minimum of 30 seconds prior to the acquisition of data to allow equilibrium to be established.

10.13 After the instrument is properly calibrated, begin by analyzing the ICV and ICB solutions. The ICV must be run after each calibration. For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The ICB results should be less than three times the IDL. If the ICB is greater than 3 times the IDL, but less than the reporting limit, and all samples bracketed by this QC are also less than the reporting limit, then the results are acceptable. The results are also acceptable if the ICB is less than 1/10 of the reporting limit. If either the ICV or the ICB are outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard(s) and showing that they meet QC criteria.

10.13.1 For elements that are not listed for method 6020 (see Table 1) and are present at background levels in the lab (for example Ca, Mg, Na, K), the ICB results must be < one half of the RL.

10.14 Run the CRI solution right after the ICB, (or any other place at the beginning of the run after the ICV, ICB and before any real samples are analyzed) unless otherwise instructed by the metals supervisor or manager. This check is not required by the method, but it is required by some states (New Jersey, North Carolina and Florida) and by some clients. For the CRI, all elements of interest must be within 50% of the true value or within client specified limits. Check with the metals supervisor for more information.

10.15 Then analyze the CCV and CCB check standards. For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. For the CCB, all elements to be reported must normally be less than three times the IDL. If the CCB is greater than 3 times the IDL, but less than the reporting limit, and all samples bracketed by this QC are also less than the reporting limit, then the results are acceptable. The results are also acceptable if the CCB is less than 1/10 of the reporting limit or less than three times the MDL.

10.15.1 For elements that are not listed for method 6020 (see Table 1) and are present at background levels in the lab (for example Ca, Mg, Na, K), the CCB results must be < one half of the RL.

10.15.2 The internal standard levels in the CCV and CCB must also be within 20% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.16 After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not list specific criteria for the ICSA and ICSAB, but in house criteria will be applied. For all the spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the correction factors are optimized and the ICSA and ICSAB are within specifications.

10.16.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

10.17 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Depending on the type of digestion and the sample matrix, samples and the associated QC should normally be diluted by a factor of from 2 to 5 before analysis. This dilution factor should be indicated in the sample ID file on the instrument.

10.17.1 Each sample analysis must be a minimum of 3 integrations. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element should be footnoted that there are possible analytical problems indicated by a high RSD between replicates. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.17.2 The internal standard levels must be monitored for all samples and quality control. If the internal standard is outside of the range of 30 to 120% of the original response in the calibration blank, then the sample must be diluted by a factor of 5 to bring the internal standard to within the correct range. If the internal standard is still outside of the range after the initial 1:5 dilution, then additional dilutions must be done until the internal standard is within the appropriate range. Y is sometimes seen in real samples. If the Y recoveries are high relative to the other internal standards, then do not use the Y internal standard.

10.17.3 For any readings that exceed the 90% of the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample.

10.17.4 Indicate dilution factors for samples using df followed by the dilution factor after the sample ID. There should be a space between the sample number and the df.

10.18 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 30 seconds or for the required period of time to ensure that analyte memory effects are not occurring. (60 seconds is recommended for normal methods excluding Hg and B. Longer times may be needed when Hg and B are being analyzed.)

10.19 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.

10.19.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element.

10.19.2 For the CCB, all elements to be reported must be less than three times the IDL. If the CCB is greater than 3 times the IDL, but less than the reporting limit, and all samples bracketed by this QC are also less than the reporting limit, then the results are acceptable. The results are also acceptable if the CCB is less than 1/10 of the reporting limit or less than three times the MDL. For elements that are not listed for method 6020 (see Table 1) and are present at background levels in the lab (for example Ca, Mg, Na, K), the CCB results must be < one half of the RL.

10.19.3 The internal standard levels in the CCV and CCB must also be within 20% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.20 After the run is completed, convert the data file to a CSV format using the option on the results screen. First save the file on the local drive using the file naming system described below. Update the run in the LIMS and enter the run name into the workgroup using lower case characters. Then copy the data from the local drive to the LIMS drive.

10.20.1 The file should be named as followed- initial instrument indicator (X), date (MMDD), year, run type (soil, water, or mixed), and sequential run number for that day. For example, the first water run from 12/17/02 would be designated X121702w1.csv.

10.21 Calculations are done in the LIMS using the calculations shown below.

10.21.1 Calculation for aqueous samples.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (}\mu\text{g/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.21.2 Calculation for solid samples.

original sample concentration of metal (mg/kg) =

$$\frac{\text{(conc. in the digestate (}\mu\text{g/l)) x (final digestate volume (ml))}}{\text{(Initial sample weight (g)) x (\%sol/100)}}$$

10.22 At the end of the analysis day the ICP-MS must be brought down using the following sequence.

- Rinse the tip in a solution of 4 percent nitric acid and 2 percent hydrochloric acid for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
- Turn off the plasma using off button.
- Release the tension on the pump tubing.
- Turn off the cool flow and the printer.
- Turn off the monitor.

11.0 QC REQUIREMENTS

11.1 This section outlines the QA/QC requirements necessary to meet the method 6020.

11.2 Instrument Detection Limits (IDLs). IDLs must be established for all analytes a minimum of once per quarter. They are calculated by taking the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day.

11.3 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 2 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response. In general, if the amount spiked for the MDL is greater than 10 times the actual MDL, then the MDL should be redone with a lower spike level.

11.4 Linear Calibration ranges. The upper limit of the linear calibration ranges should be established for each analyte by determining the signal responses from at least three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined whenever there is a significant change in instrument response. It is recommended that they be done at least every six months. For any readings that exceed the 90% of the linear range for a given element, a dilution is required. Normal linear range values by element are shown in Table 2.

11.5 Initial Calibration Verification (ICV) or Quality Control Sample (QCS) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV should be followed by the analysis of the ICB.

11.5.1 For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be at the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

11.5.2 For the ICB, all elements to be reported must be less than three times the IDL. If the ICB is greater than 3 times the IDL, but less than the reporting limit, and all samples bracketed by this QC are also less than the reporting limit, then the results are acceptable. The results are also acceptable if the ICB is less than 1/10 of the reporting limit. If the ICB is outside of criteria and does come under the exceptions stated above, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

11.5.2.1 For elements that are not listed for method 6020 (see Table 1) and are present at background levels in the lab (for example Ca, Mg, Na, K), the ICB results must be < one half of the RL.

11.6 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.

11.6.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. For this method (6020), the CCV may be from the same or a separate source than the calibration standards. It is recommended that the same source be used as outlined in method 200.8.

11.6.2 For the CCB, all elements to be reported must be less than three times the IDL. If the CCB is greater than 3 times the IDL, but less than the reporting limit, and all samples bracketed by this QC are also less than the reporting limit, then the results are acceptable. The results are also acceptable if the CCB is less than 1/10 of the reporting limit or less than three times the MDL.

11.6.2.1 For elements that are not listed for method 6020 (see Table 1) and are present at background levels in the lab (for example Ca, Mg, Na, K), the CCB results must be < one half of the RL.

11.6.3 The internal standard levels in the CCV and CCB must also be within 20% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

11.7 Interference Check Standards. After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not give specific criteria for the ICSA and ICSAB, but in house criteria should be applied. For all the spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the correction factors are optimized and the ICSA and ICSAB are within specifications.

11.7.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

11.7.2 Both the ICSA and ICSAB solutions must be made fresh weekly.

11.8 Low Level Calibration Check. The CRI standard containing the elements of interest at the reporting level for each element. This check is normally run at the beginning of the run, but depending on client requirements, may also need to be run periodically throughout the run. If no limits are specified, then in house acceptance criteria of 50 to 150 percent will be applied. If an analyte is outside of the specified range, check with the area supervisor or manager for further instruction.

11.9 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. The method blank must contain elements at levels of less that the reporting limit for each element. If the method blank contains levels over the reporting limits, the samples must be redigested and reanalyzed for the failing elements. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.10 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory should assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 percent. In house lab control and spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

11.10.1 If solid lab controls are used, then the manufacturer's limits should be applied.

11.11 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. . The laboratory should assess laboratory performance of the matrix spike against in house limits. Until in house limits can be generated, then default recovery limits of 75 to 125 percent should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote and a post-digest spike must be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

11.11.1 If a post-digest spike is required, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 75 to 125 percent are normally applied. If the spike recovery is outside of these limits, then the sample must be diluted and reanalyzed on dilution to compensate for the matrix effect. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report.

11.12 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample should be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

11.12.1 If a MSD or duplicate is out of control, then the MSD or duplicate should be reanalyzed to confirm that the high rpd for a given element is not a result of an analytical problem. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement, then the associated batch should be reanalyzed for that element.

11.12.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate should be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate should be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch should be digested and reanalyzed.

11.12.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) should be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

11.12.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

11.13 Serial dilution. A serial dilution is required on a frequency of one in 20 samples. It is normally done on the same sample as is used for the matrix spike. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally a factor of at least 100 times greater than the concentration in the reagent blank), then an analysis of a fivefold (1+4) dilution must agree to within $\pm$ 10% of the original determination. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below. Results of less than the IDL are treated as 0.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

11.13.1 The concentration in the reagent blank is normally < 3 times the IDL, so the factor of 100 times the concentration in the reagent blank (listed above) so the limits should be applied to sample concentrations of greater than 300 times the IDL.

12.0 DOCUMENTATION REQUIREMENTS

12.1 If samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data should be exported to the LIMS system.

12.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

12.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

12.4 The correction factors from each method must be printed out and stored in a notebook in the lab. Each time the correction factors are modified, a new printout must be obtained.

12.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.6 Supervisory (or peer) personnel must routinely review (approximately once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

13.0 INSTRUMENT MAINTENANCE

13.1 Recommended periodic maintenance includes the items outlined below.

13.2 Change the pump tubing weekly or as needed.

13.3 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

13.4 Change the sampler tip as needed (every one to two months).

13.5 Clean the recirculating pump lines as needed.

13.6 Clean the slides on the autosampler once per day.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES

15.1 Refer to other SOP's for ICP-MS analysis (EPA 200.8).

TABLE 1: ELEMENTS, MASSES, AND REPORTING LIMITS

Mass and Element	Listed for analysis in 6020	Additional lines to monitor	Normal Digested Aqueous Sample Reporting Limit (Dilution Factor of 2) in ug/l.	Normal Digested Solid Sample Reporting Limit (Dilution Factor of 2) in mg/kg.	Comments
7Li			2	0.2	
9Be	**		2	2.2	
11B		10B	10	1	
23Na			500	50	
25Mg		26Mg	500	50	24Mg has possible interferences from C-C
27Al	**		100	10	
39K			500	50	
43Ca		44Ca	500	50	44Ca has possible interferences from CO2
47Ti			2	0.2	
51V			10	1	
52Cr	**	53Cr	10	1	
55Mn	**		2	0.2	
56Fe		57Fe	100	10	
59Co	**		2	0.2	
60Ni	**	62Ni	10	1	
65Cu	**	63Cu	10	1	63 is the method recommended line, but 65 is used instead. 63Cu has possible interferences from ArNa
66Zn	**	67Zn, 68Zn	10	1	
75As	**		4	0.4	
82Se	**	77Se, 78Se	10	1	78Se used for correction only.
88Sr			2	0.2	
95Mo		97Mo, 98Mo	2	0.2	98Mo is the method recommended line, but 95 is used instead. 98Mo has possible interferences from ruthenium.
107Ag	**	109Ag	10	1	
111Cd	**	106Cd, 108Cd, 114 Cd	2	0.2	
118Sn			10	1	
121Sb	**	123Sb	4	0.4	123Sb is the method recommended line, but 121Sb is used instead. Xe is a possible interference for 123Sb and is sometimes found as a contaminant in argon.
137Ba	**		2	0.2	
205Tl	**	203Tl	1	0.1	
208Pb	**	206Pb,207Pb, and 208Pb summed and reported under 208Pb	1	0.1	
238U			2	0.2	
13C, 53ClO, 77ArCl and 153BaO also included in method to monitor and correct for interferences.					

TABLE 2: RECOMMENDED STANDARDS AND ICV AND CCV LEVELS AND NORMAL LINEAR RANGES

Mass and Element	BLANK	STDA	STDB	STDC	STDD		NORMAL LINEAR RANGE		ICV	CCV
7Li	0	5	50	250			500		125	125
9Be	0	5	50	250			250		125	125
11B	0	5	50	250			250		125	125
23Na	0	5	50	250	10000		100000		5000	5012
25Mg	0	5	50	250	10000		100000		5000	5012
27Al	0	5	50	250	10000		100000		5000	5012
39K	0	5	50	250	10000		100000		5000	5012
43Ca	0	5	50	250	10000		100000		5000	5012
47Ti	0	5	50	250			500		125	125
51V	0	5	50	250			500		125	125
52Cr	0	5	50	250			500		125	125
55Mn	0	5	50	250			500		125	125
56Fe	0	5	50	250	10000		100000		5000	5012
59Co	0	5	50	250			500		125	125
60Ni	0	5	50	250			500		125	125
65Cu	0	5	50	250			500		125	125
66Zn	0	5	50	250			500		125	125
75As	0	5	50	250			500		125	125
82Se	0	5	50	250			500		125	125
88Sr	0	5	50	250			500		125	125
95Mo	0	5	50	250			500		125	125
107Ag	0	5	50	250			500		125	125
111Cd	0	5	50	250			500		125	125
118Sn	0	5	50	250			500		125	125
121Sb	0	5	50	250			500		125	125
137Ba	0	5	50	250			500		125	125
205Tl	0	5	50	250			500		125	125
208Pb	0	5	50	250			500		125	125
238U	0	5	50	250			500		125	125

TABLE 3: INTERNAL STANDARD MASSES AND ELEMENTS

Mass and Element	Comments
6Li	
45Sc	
89Y	Sometimes found in soil matrices. Monitor recoveries with other internal standards
103Rh	
115In	
159Tb	
165Ho	
209Bi	

TABLE 4: MS AND BLANK SPIKE CONCENTRATIONS

Element	Soils Final Concentration in mg/kg	Mid -level Aqueous Final Concentration in µg/l	Low-level Aqueous Final Concentration in µg/l
Ag	10	50	100
Al	5400	2000	100
As	400	2000	100
B	100	2000	100
Ba	400	2000	100
Be	10	50	100
Ca	1250	25000	100
Cd	10	50	100
Co	100	500	100
Cr	40	200	100
Cu	50	250	100
Fe	5200	1000	100
K	1250	25000	100
Mg	1250	25000	100
Mn	100	500	100
Mo	100	2000	100
Na	1250	25000	100
Ni	100	500	100
Pb	100	500	100
Sb	100	500	100
Se	400	2000	200
Tl	400	2000	100
V	100	500	100
Zn	100	500	100
Sn	100	2000	100
Sr	100	2000	100
Ti	100	2000	100
Pd	100	2000	100

Accutest Laboratories
Standard Operating Procedure

Lab Manager_____

QA Manager_____

Effective Date: _____

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) USING SOLID STATE ICP.

METHOD REF: SW846 6010B

Revised Sections: ***3.1, 9.7.4, 10.8.8.2, 10.8.8.3, 12.13 (all), Table 1***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include, but are not limited to, Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, Pd, V, and Zn.

2.0 SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes operation of the ICAP 6500 Spectrometer following method SW846 6010B.

2.2.1 This inductively coupled argon plasma optical emission spectrometers (ICP-OES) uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based iTEVA software.

2.2.2 In the instrument, samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored the solid state detector.

2.2.3 Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as

possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Interferences which cannot be addressed with background correction, must be corrected using the appropriate interelement correction factors.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition, the reporting limits must always be greater than the MDL. Refer to the scheduling sheets and check with the metals supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent or every 2 hours during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses. It is recommended that this check be analyzed at the start of each run. For this method, the external check standard criteria is ± 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits should also be generated once sufficient data (usually a minimum of 20 to 30 analyses) is available to support the default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control or spike blank is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike should be assessed. A duplicate may be used in place of the matrix spike duplicate on client request. The matrix spike duplicate RPD is calculated as shown below. The control limit for the duplicate is 20% rpd. If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix SpikeDuplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the default limits of 75 to 125 percent. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

7.2 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are two solid state ICPs available for use in the lab. Both are Thermo 6500 ICP units. These units have been optimized to obtain low detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

8.2 Instrument autosamplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. They must then be rinsed at least 3 times with deionized water.

8.5 Autopipeters with tips. These must be calibrated and checked as outlined in the autopipeter SOP, EQA004.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For

acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, MV Laboratories, Ultra Scientific or equivalent. Note: All standards must be ICP quality standards.

9.5 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations. Since calibration standards are made fresh daily, they can be stored in volumetric glassware. (Any stocks or other check samples should be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.)

9.5.1 Standards should be approximately matrix matched to the samples. For most samples, a 5 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards should be modified or the samples should be diluted so that they are in a similar matrix to the curve.

9.5.2 Standards should be prepared so that there is minimal spectral interference between analytes.

9.5.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. Levels for the standards are shown in Table 3. The calibration curve should consist of a minimum of a blank and a standard.

9.6 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 50 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.7 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 5 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. All of these solutions should be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element should be within the range of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution. The metals concentrations for this standard should be at approximately the mid-point of the calibration curve for each element. This standard should be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions should be used on a periodic basis to check the interfering element corrections on the instruments. Note: If

interferences from different elements than those listed below are a problem, the interfering element solutions may be modified. Two acceptable solutions are outlined below.

9.7.3.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.7.3.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. . If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	Pd	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L
Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L

9.7.4 CRI Standards. The CRI standards contain the elements of interest at the lowest level that elements are to be reported. Note: This QC check is required for NELAC.

9.8 Matrix Spike and Spike Blank Solution (For soil samples). The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. The spiking solution is prepared by adding either mixed or single element metals solutions to a solution containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. Two mls of this stock solution should be added to the spike blank and the matrix spike before they are digested and brought to a final volume of 100 ml.

9.9 Matrix Spike and Lab Control Solution (For aqueous samples and TCLP leachates).

9.9.1 The final concentrations suggested for the matrix spike are shown in Table 5. Two spiking solutions, which are used for aqueous samples and TCLP leachates respectively, are prepared by adding either mixed or single element metals solution to solutions containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. 0.5 ml of the resulting stock solution is added to the matrix spike sample before they are digested.

9.9.2 A lab control sample should be digested and analyzed for every batch of 20 samples or less. The LCS is prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the lab control should be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml. In situations where any odd elements, such as B, Si, Sr, Sn, and Pd, is of interest for a specific project, besides a lab control, a spike blank is also digested.

9.10 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.11 Internal Standard Solution (with matrix modifier).). To a 1 liter flask containing approximately 800 ml of DI water, add 10.0 ml of 10,000 mg/l Lithium solution and 0.500 ml of 10000 mg/l yttrium. Add 30 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid and bring to a final volume of 1000 ml and mix well. This solution is added to all samples and standards as the instrument is running using a split line on the peristallic pump

10.0 PROCEDURE

10.1 General procedure on how to operate the SS Trace1 is described below. Refer to the Thermo 6500 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Set up the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Start up the instrument following the sequence shown below.

10.6.1 Double click the **iTEVA Control Center** Icon on desktop. Type ***admin*** in User Name field, and then click OK.

10.6.2 Once the iTEVA Control Center window is opened, click on **Plasma** Icon at status bar area. Then click on **Instrument Status** to check the interlock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust should be in green; drain flow and busy should be in gray) and the Optics Temperature. (It should be around 38°C.) Click on the Close box.

10.6.3 Click **Plasma On**. When the plasma is on, click close. Let the instrument warm up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize .

10.7 Torch Alignment and Auto Peak

10.7.1 If the torch has been cleaned, then it has to be realligned after it is replaced

10.7.1.1 Open the method and then click on **Sequence** tab, then click on List View Icon until you reach rack display.

10.7.1.2 Go to S-6 position (you can assign any position in the rack for torch alignment), then right click to select Go to empty sample S:6. (Now, the autosampler tip moves from Rinse to this position)

10.7.1.3 Click on **Analysis** tab, then select **Torch Alignment** from **Instrument** drop down menu. There will be a pop up dialog box present. Click RUN. Then there will be another dialog box pop up (This is a reminder for Torch Alignment Solution (2 ppm Zn)), click Ok. Now, the instrument is initiating an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

10.7.1.4 After Torch Alignment is done, click Close. Click on **Sequence** tab, then follow by **List View** Icon.

10.7.1.5 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for 2 minutes.

10.7.2 Perform Auto Peak.

10.7.2.1 It is recommended that the Auto Peak Adjust procedure be performed monthly or whenever the peak shape has shifted for any element. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustment. (CCV solution is used for this process.)

10.7.2.2 Click **Sequence** tab, then click on **List View** Icon till the rack is displayed.

10.7.2.3 Go to S-5 position (you can assign any position in the rack for auto peak adjust), then right click to select Go to empty sample S:5. (Now, the autosampler tip moves from Rinse to this position). Click on **Analysis** tab. All elements' result is showed in the display area. From **Instrument** drop down menu, select **Perform Auto Peak**. There will be a pop up dialog box present. Highlight _All Elements_, then click RUN. Then there will be another dialog box pop up (This is a reminder for Perform Auto Peak Solution), click Ok. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green " √" in front of All Elements, which indicates Auto Peak is completed.

10.8 Open the method and start up the run.

10.8.1 Click on **Analyst** Icon at the workspace. Go the Method and choose Open from the drop down menu. Select the method with a Revision (usually select the last revision used).

10.8.2 Go to **Method** tab at the bottom of left-hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the data display area (i.e.: SA073107M1: starts with SA, then follow by MM-DD, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs).

10.8.3 Click on **Sequence** tab at the bottom of left-hand corner. From **Auto-Session** drop down menu bar, click on **New Autosampler** to create a sequence. This will pop up a dialog box , then click on **New** and fill number of samples (i.e.: 100) in the Number of Samples field and the sample ID (usually leave this field empty) in Sample Name field. Type a sequence name (i.e.: SEQ073107M1: starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click OK, then put in "0" on Settle Time Between Sequences box, click OK.

10.8.4 Right click on **Untitled** (CETAC ASX-520 Enviro 5 Named Rack is the rack that currently using) at the workspace area, click on **Auto-Locate ALL** to locate all samples.

10.8.5 Double click on **Untitled** again, then click on the sequence name (i.e.: SEQ073107M1), on the data display area, type the sequence in Samplename column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

10.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as **Save As**. There will be a Save a Method dialog box present, go to Save Option to check on "Overwrite Method and bump revision number" box, then click OK.

10.8.7 Go to **Sequence** tab, click on **List View** Icon from tool bar, then click on **Connect Autosampler to PC and Initialize** Icon. (Now, the autosampler tip is up and sits on the top of the rinse cup.)

10.8.8 The sequence includes the calibration and run quality control.

10.8.8.1 Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately. If more than two standards are used, a correlation coefficient of 0.995 or better must be obtained using a first order curve fit. Second and third order curve fits are not acceptable.

10.8.8.2 Run the CRI solution after the calibration is completed and before any samples are analyzed. In a combined protocol with method EPA 200.7, the CRI is normally run right after the high standard.

10.8.8.2.1 For all samples, the CRI check solution must be at the reporting limit for each element. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

10.8.8.2.2 In house limits of 50 to 150% are applied to the CRI standard, but tighter criteria may be needed in some client or project specific situations.

10.8.8.2.3 For work following the Army Corp of Engineers Shell document, an acceptance criteria of 80 to 120 percent should be applied to this standard unless a project specific waiver is obtained,

10.8.8.3 Then continue by analyzing the ICV and ICB check standards. Include ICV, ICCV, ICCV, CCV, CCB, CRI, ICSA, ICSAB, ICV, ICB and any other appropriate quality control points in the run. For samples and quality control, insert the list pointer after a space after the sample. Check with the metals supervisors for additional information on the use of listpointers. In general, listpointer 2 refers to the SW846 6010 method and listpointer 1 refers to EPA 200.7 method.

10.8.8.3.1 For the ICV, all elements to be reported must be within 10 percent of the true values. After the ICV and ICB and before any actual samples are analyzed, the CCV and CCB should be analyzed. For the CCV, all elements to be reported must be within 10 percent of the true values. For both ICV and CCV, all replicates exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. Both ICB and CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest. (ICB and CCB values should be less than the reporting limits for the elements).

10.8.8.4 Before analyzing any real samples, an interference check solution must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions should contain less than two times the absolute value of the reporting limit for each element.

10.8.8.5 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outlined in Section 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.8.8.6 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Each sample analysis should be a minimum of 2 readings using at least a 5 second integration time. It is recommended that 3 readings be used for each sample analysis. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations

for the replicates should be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element should be footnoted that there are possible analytical problems indicated by a high RSD between replicates. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.8.8.7 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 60 seconds or for the required period of time to ensure that analyte memory effects are not occurring. A time of 120 seconds is recommended for most analyses.

10.8.8.8 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.

10.8.8.9 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates should be less than 5 percent.

10.8.8.10 The CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest and less than the reporting limit. If the CCB does not meet this criterion and is less than the reporting limit, it can be reanalyzed two more times. The average of the three readings must be within 3 standard deviations of the background mean. If these criteria are not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element. The exception is that samples that are less than the reporting limit may be reported if the CCB is biased high, but is still less than the reporting limit.

10.8.8.11 If the initial CCB is above the reporting limit, then all samples should be submitted for reanalysis. Do not rerun the CCB if the initial reading is above the reporting limit.

10.8.8.12 If reanalysis of the CCB is required, reanalyze a new pair of CCV, CCB before proceeding with the analysis of any additional samples.

10.8.8.13 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample is greater than 50 times of the instrument detection limit for that element.

10.8.8.14 Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike should be performed.

10.8.8.15 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.8.8.16 For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough to affect the element of interest even at a lower concentration, sample dilution with reagent blank and reanalysis is required. In these circumstance analyte detection limits are raised. Check with metals supervisor for more information.

10.8.8.17 Anytime that the interference is large relative to the sample, dilution may be required. Check with the metals supervisor for more information.

10.8.8.18 For any readings where the internal standard is outside of the range of 60 to 125% of the internal standard level in the calibration blank, then the sample should be diluted until the internal standard is within that range.

10.8.8.19 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run the ICSA and ICSAB solutions every 8 hours unless otherwise instructed by the metals lab supervisor or manager.

10.8.9 After the instrument is optimized, click **Run Auto-Session** Icon to start the run.

10.8.10 If you need to add or delete samples once the run is started, follow the steps shown below.

10.8.10.1 Adding Samples.

10.8.10.1.1 Click on **Sequence** tab, then click on **List View** Icon at the tool bar. There is the sequence table on the data display area.

10.8.10.1.2 Click on **Add Samples** Icon. This will pop up the dialog box, then fill number of samples that need to add in field. Click OK. By doing this, samples will be added at the end of sequence without a location the rack.

10.8.10.1.3 Go to the added samples, on the to position ID column, assign a number for each sample. This number will be the position in the rack. On the Samplename column, type in sample IDs, fill in Corr Fact (if needed) and Check Table.

10.8.10.1.4 The added samples will be analyzed at the end of the original sequence run order unless you assign them to run under different order.

10.8.10.2 Deleting Samples.

10.8.10.2.1 Click on **Sequence** tab, then click on **List View** Icon under the sequence display area.

10.8.10.2.2 To the sample that need to be deleted, on the to position ID column, change the number to "0". By doing this, that sample will be unlocated in the rack and the autosampler tip will go to the next sample.

10.9 When the analysis is completed export the data to LIMS following the procedure outlined below.

10.9.1 Double click on **ePrint** Icon on desktop. There will be a LEADTOOLS ePRINT dialog box pop up, then click **Finish Jobs** and **OK** boxes.

10.9.2 Double click the **PDF** Icon on desktop, the PDF file will present as Document_#. Right click on that file, select **Rename** to change the file name to an assigned analytical run ID. (i.e.: MA8324). This is the raw data for MA8324.

10.9.3 Drop the raw data to Lims.

10.9.4 By completing above steps, the raw data (i.e: MA8324) can be pulled up in the Raw Data Search function.

10.10 The data must be reviewed in the LIMS as outlined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (}\mu\text{g/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.11 Aft the end of the analysis day, the ICP must be brought down using the following sequence:

10.11.1 Place the autosampler tip in rinse cup and rinse in a mixed solution of 5% nitric acid and 5% hydrochloric acid for 10 minutes and in DI water for 20 minutes. **Note**: A stronger acid may be needed depending on the matrix of the samples that were analyzed.

10.11.2 Turn off the plasma by click on the **Plasma** Icon and click on **Plasma Off**.

10.11.3 Close all iTEVA programs/ windows.

10.11.4 Release the tension on the sample pump platen.

10.11.5 Switch off recirculating chiller.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

11.2 Calculate the IEC correction factors and enter them into the method. Verify that the recalculated sample results are within QC limits. Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$\text{IEC} = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

11.3 Analyze the ICSA/ICSAB solutions and/or SIE solutions and verify that the combined standards are within QC limits. If they are not, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

11.4 Save and update the method.

11.5 Interfering element correction factors saved as raw data along with the run printouts on a daily basis so that the IEC's for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010B.

12.2 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Detection Limits (IDLs). Instrument Dection Limits (IDLs). Although no frequency is given, it is required that IDL's be completed a minimum of once per year for all analytes or whenever instrument conditions have significantly changed. The Instrument Detection Limits (in ug/L) are determined by multiplying three times the standard deviation of 10 reading of a calibration blank. Each measurement shall be performed as though it were a separate analytical sample (i.e., each measurement shall be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration ranges. The upper limit of the linear calibration ranges should be established for each analyte by determining the signal responses from a minimum of three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit.

12.4.1 For work following the Army Corp of Engineers Shell document, the linear range cannot exceed the level of the high standard on that run. All elements to be reported that exceed the high standard must be reanalyzed on dilution and the results reported from the dilution.

12.5 Initial Calibration Verification Standard (ICV). After each calibration, a standard from a different source than the calibration standard should be analyzed with an initial calibration blank (ICB). For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates exceed 5 times the reporting limit should have a relative standard deviation of < 5%. The ICB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest. (All ICB values should be less than the reporting limits for the elements).

12.6 Interference Check Standard. An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions should contain less than the absolute value of two times the reporting limit for each element. If this criteria is not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents. This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required due to meet other method and/or client requirements. Run the ICSA and ICSAB solutions every 8 hours unless otherwise instructed by the metals lab supervisor or manager.

12.7 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain elements at less than the reporting limit for each element. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.8 Lab Control Sample/Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control or spike blank against recovery limits of 80 to 120 percent. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.9 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The control limits for the matrix spike recovery are from 75 to 125 percent recovery. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

12.9.1 Some clients may require a post-digest spike if the matrix spike is outside of the control limits. Spiking levels should be set as per client requirements. Either CLP type spike levels or SW846 spike levels may be used, depending on client needs. Check with the metals supervisor for more information.

12.9.1.1 For CLP type post-digest spikes, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 75 to 125 percent are normally applied, unless a client specifies a different limit. No action is necessary if the post-digest spike is outside of this limit, unless a preparation problem is suspected with the spike, in which case the post-digest spike should be remade and reanalyzed. The post-digest spike recovery should be footnoted on the matrix spike recovery for the element of interest.

12.9.1.2 Method 6010B specifies that the post-digest spike be in the range of 10 to 100 times the detection limit. Limits of 75 to 125 percent are normally applied, unless a client specifies a different limit. No action is necessary if the post-digest spike is outside of this limit, unless a preparation problem is suspected with the spike, in which case the post-digest spike should be remade and reanalyzed. The post-digest spike recovery should be footnoted on the matrix spike recovery for the element of interest.

12.10 Matrix Spike Duplicate. The laboratory must digest a matrix spike duplicate sample for a minimum of 1 in 20 samples. A duplicate may be used in place of a matrix spike duplicate on client request. The relative percent difference (rpd) between the matrix spike and the matrix spike duplicate should be assessed. The matrix spike duplicate or duplicate rpd is calculated as shown below. The control limit for the duplicate is 20% rpd. If a matrix spike duplicate or duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix Spike Duplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

12.11 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample or every two hours during an analysis run, whichever is more frequent, and at the end of the sample run. If the CCV

solution is not within 10 percent of the true value and the relative standard deviation for the replicates greater than 5 times the reporting limit is not < 5%, then no samples can be reported in the area bracketed by the failing CCV. An exception is that if the recovery of the CCV is in the range of 111% to 125% and the sample results are less than the report limits. (Note: If a CCV fails due to a calibration shift, rather than a one time problem, then the instrument should be recalibrated and the QC rechecked before any additional samples are analyzed.)

12.11.1 If the CCV recovery is within specification and the relative standard deviation is high, then the CCV can be reanalyzed as long as the 10% frequency is met. If the reanalysis is within specifications, then the bracketed samples can be reported.

12.12 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run. The CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest and less than the reporting limit. If the CCB does not meet this criterion and is less than the reporting limit, it can be reanalyzed two more times. The average of the three readings must be within 3 standard deviations of the background mean. If these criteria are not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element. The exception is that samples that are less than the reporting limit may be reported if the CCB is biased high, but is still less than the reporting limit. If the initial CCB is above the reporting limit, then all samples should be submitted for reanalysis. Do not rerun the CCB if the initial reading is above the reporting limit. If reanalysis of the CCB is required, reanalyze a new pair of CCV, CCB before proceeding with the analysis of any additional samples.

12.13 Low Level Calibration Check (CRI). The CRI is initially run after the calibration is completed and before any samples are analyzed. The CRI is normally run right after the high standard in combined 200.7/6010 run. Normal in house limits of 50 to 150 are applied to the CRI standard, but tighter criteria may be needed in some client or project specific situations.

12.13.1 For all samples the CRI check solutions must be at the reporting limit for each element. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

12.13.2 For MDL reporting, the low checks are not required at the MDL, but the sample results must be flagged with the appropriate concentration qualifiers to indicate that the reported values are below the reporting limits, but above the MDL.

12.13.3 For work following the Army Corp of Engineers Shell document, an acceptance criteria of 80 to 120 percent should be applied to this standard unless a project specific waiver is obtained.

12.14 Serial Dilution Analysis. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, it is recommended that a serial dilution be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample and the dilution result are greater than 50 times the IDL. If the dilution does not

agree, then remake and reanalyze the serial dilution. If the reanalysis is again not within the limit, the failing elements should be reported with a footnote indicating that there were possible matrix interferences. Alternatively, a serial dilution can be done with larger dilutions, and the sample can be reported from the dilutions. For example, a sample that failed the serial dilution criteria using the straight sample and a 1:5 dilution may pass the serial dilution criteria using a 1:2 dilution and a 1:10 dilution. In that case, the sample would be reported from the 1:2 dilution and the results would be footnoted that a dilution was required due to matrix interference. The calculation to be used for serial dilutions is shown below.

((Sample Result - Serial Dil. Result)/Sample Result) x 100 = Serial Dilution RPD

12.15 Post Digestion Spike Addition. Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike should be performed. Recovery limits of 75 to 125 percent should be used to assess post-digest spikes.

12.16 IEC Correction Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly.

13.0 CALCULATIONS

13.1 For water samples, the following calculations should be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (µg/l) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

13.2 For soil samples, the following calculations should be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data should be exported to the LIMS system and a copy of the run log should be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports should also be kept in the log. In addition to the maintenance, the maintenance log should also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.1.1 Change the pump tubing weekly or as needed.

15.1.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.1.3 Clean the radial view quartz surface weekly or more often if needed.

15.1.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.1.5 Change the sampler tip as needed (every one to two months).

15.1.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.1.7 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with Teflon spray a minimum of once per day.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis (CLP, and EPA 200.7 for both DW and WW).

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT			
Analyte	**Water & Wipe Reporting Limit (µg/l)**	**Soil Reporting Limit (mg/kg)**	**TCLP Reporting Limit (mg/l)**
Aluminum	200	20	
Antimony	6	2	
Arsenic	3	2	0.50
Barium	200	20	1.0
Beryllium	1	0.5	
Cadmium	3	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	10	2.5	
Iron	100	10	
Lead	3	2	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	10	4.0	
Potassium	10000	1000	
Selenium	10	2	0.50
Silver	10	1	0.010
Sodium	10000	1000	
Thallium	2	1	
Vanadium	50	5	
Zinc	20	2	
Boron	100	10	
Molybdenum	10	1	
Palladium	50	5.0	
Silicon	200	20	
Strontium	10	1	
Tin	10	5	
Titanium	10	1	

TABLE 2: ANALYTICAL LINES ON THE SSTRACE1 AND SSTRACE2	
Element	**Wavelength**
Al	396.1
As	189.0
Ca	317.9
Fe	259.9
Mg	279.0
Mn	257.610
Pb	220.3
Se	196.0
Tl	190.8
V	292.4
Ag	328.0
Ba	455.4
Be	313.0
Cd	228.8
Co	228.6
Cr	267.7
Cu	324.7
K	766.4
Na	589.5
Ni	231.6
Sb	206.8
Zn	206.2
B	208.9
Mo	202.0
Pd	340.4
Sr	407.7
Sn	189.9
Ti	334.9
Si	212.4

TABLE 3: CALIBRATION STANDARD LEVELS in ug/L						
Element	**STD A (Blank)**	**STD B**	**STD C**	**STD D**	**STD E**	**STD F**
Ba	0	4000	NA	NA	NA	NA
Be	0	4000	NA	NA	NA	NA
Cd	0	4000	NA	NA	NA	NA
Cr	0	4000	NA	NA	NA	NA
As	0	4000	NA	NA	NA	NA
Se	0	4000	NA	NA	NA	NA
Pb	0	4000	NA	NA	NA	NA
Tl	0	4000	NA	NA	NA	NA
Mn	0	4000	NA	NA	NA	NA
Co	0	4000	NA	NA	NA	NA
Zn	0	4000	NA	NA	NA	NA
Cu	0	4000	NA	NA	NA	NA
Ni	0	4000	NA	NA	NA	NA
Sb	0	4000	NA	NA	NA	NA
Mo	0	4000	NA	NA	NA	NA
B	0	4000	NA	NA	NA	NA
Sn	0	4000	NA	NA	NA	NA
Ti	0	4000	NA	NA	NA	NA
Ag	0	500	NA	NA	NA	NA
V	0	4000	NA	NA	NA	NA
Sr	0	4000	NA	NA	NA	NA
Si	0	10000	NA	NA	NA	NA
Pd	0	4000	NA	NA	NA	NA
Al	0	(5000)	(20000)	(40000)	(60000)	80000
Ca	0	(5000)	(20000)	(40000)	(60000)	80000
Fe	0	(5000)	(20000)	(40000)	(60000)	80000
Mg	0	(5000)	(20000)	(40000)	(60000)	80000
K	0	(5000)	(20000)	(40000)	(60000)	80000
Na	0	(5000)	(20000)	(40000)	(60000)	80000

Note: Values in ( ) are optional, but may be included in the curve to provide a better linear fit. All fits must be first order.

TABLE 4: HIGH STANDARD, ICV, and CCV LEVELS			
Element	**High Standard Suggested Level in ug/l**	**ICV Suggested Level in ug/l**	**CCV Suggested Level in ug/l**
Al	80000	5000	40000
As	4000	1000	2000
Ca	80000	5000	40000
Fe	80000	5000	40000
Mg	80000	5000	40000
Mn	4000	1000	2000
Pb	4000	1000	2000
Se	4000	1000	2000
Tl	4000	1000	2000
V	4000	1000	2000
Ag	500	500	250
Ba	4000	1000	2000
Be	4000	1000	2000
Cd	4000	1000	2000
Co	4000	1000	2000
Cr	4000	1000	2000
Cu	4000	1000	2000
K	80000	10000	40000
Na	80000	10000	40000
Ni	4000	1000	2000
Sb	4000	1000	2000
Zn	4000	1000	2000
B	4000	1000	2000
Mo	4000	1000	2000
Pd	4000	1000	2000
Sr	4000	1000	2000
Sn	4000	1000	2000
Ti	4000	1000	2000
Si	10000	1000	5000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE AND SPIKE BLANK			
Element	**Soils Final Concentration in mg/kg**	**Aqueous Final Concentration in μg/l**	**TCLP Leachates Final Concentration in mg/l**
Ag	10	50	0.05
Al	5400	2000	
As	400	2000	2.0
B	100	2000	
Ba	400	2000	10.0
Be	10	50	
Ca	1250	25000	
Cd	10	50	0.05
Co	100	500	
Cr	40	200	0.20
Cu	50	250	
Fe	5200	1000	
K	1250	25000	
Mg	1250	25000	
Mn	100	500	
Mo	100	2000	
Na	1250	25000	
Ni	100	500	
Pb	100	500	2.0
Sb	100	500	
Se	400	2000	2.0
Tl	400	2000	
V	100	500	
Zn	100	500	
Sn	100	2000	
Sr	100	2000	
Ti	100	2000	
Si	200	4000	
Pd	100	2000	

ACCUTEST LABORATORIES
Standard Operating Procedure

Lab Manager_____

QA Manager_____

Effective Date:_____

TEST NAME: METHOD 8270C, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

REFERENCE: SW846 8270C (Revision 3, December 1996)

Revised Sections: ***8.3.2, 10.1.1, 11.4, 11.8, 11.11.6, 15.4, 16.2***
Added Section: ***11.10.5 , 11.10.6*** ***Deleted Sections:*** ***15.5, 17***

SCOPE AND APPLICATION

1.1 The following method describes the analytical procedure that is utilized by Accutest to analyze semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water samples. Options are incorporated for the analysis of sixteen (16) polyaromatic hydrocarbons (PAH) and other compounds listed in table 8A by selected ion monitoring GC/MS (GC/MS-SIM).

1.2 Table 1 lists the neutral, acidic, and basic organic compounds that can be determined by this method. The applicable concentration range of this method is compound and instrument dependent. Some compounds may require special treatment due to the limitations caused by sample preparation and/or chromatographic problems.

2.0 SUMMARY OF METHOD

2.1 This method is performed in accordance with the following extraction methodologies in SW846, 3rd Edition: 3510, 3520, 3540, 3550 and 3580.

2.2 The resultant methylene chloride extract is injected into a tuned and calibrated GC/MS system equipped with a fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.4 Once identified, the compound is quantitated by internal standard techniques with an average response factor generated from the calibration curve.

2.5 Additional unknown peaks with a response greater than 10 % of the closest internal standard may be processed through a library search with comparison to a NIST98 database. An estimated concentration is quantitated by assuming a response factor of 1.

2.6 This method includes analytical options for PAHs and other selected compounds by GC/MS-SIM. The extract is fortified with an additional SIM specific internal standard mix and analyzed using selected ions that are characteristic of the compounds of interest following the analysis of lower concentration calibration standards analyzed under the same MS scan conditions. Qualitative and quantitative identification is conducted using the procedures employed for full scan analysis.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at either method detection limit or the lowest concentration standard in the calibration curve, depending on the requirements of different regulatory programs. Detected concentrations below this concentration cannot be reported without qualification. See table 9.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as “J”, estimated value. Program or project specifications may dictate that “J” qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH - a group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

CONTINUING CALIBRATION - a mid-range calibration check standard run every 12 hours to verify the initial calibration of the system.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations which cover the working range of the instrument; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds and must be analytes that are not sample components.

MATRIX - the predominant material of which the sample to be analyzed is composed.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards, is carried throughout the entire preparatory and analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which no interferant is observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESOLUTION - also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

INITIAL CALIBRATUION VERIFICATION (SECOND SOURCE CALIBRATION STANDARD) - a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run whenever an initial calibration is performed.

SURROGATES - pure analytes added to every blank, sample, matrix spike, matrix spike duplicate, and standard in known amounts before extraction or other processing; used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and 4,4'-DDT. Prepare primary standards of these toxic compounds in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

6.4 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

7.0 SAMPLE COLLECTION, PRESERVATION, & HOLDING TIMES

7.1 Water samples may be collected in 1-liter glass bottles with Teflon insert in caps. Soil samples may be collected in 250-ml widemouth amber glass bottles.

7.1.1 Sample should be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus avoiding possible phthalate contamination.

7.2 Test all aqueous samples for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample.

7.3 The samples must be protected from light and refrigerated at 4° C from the time of receipt until extraction and analysis.

7.4 Store the sample extracts at -10 °C in amber vials (protected from light), in sealed vials equipped with unpierced PTFE-lined septa.

7.5 HOLDING TIME

7.5.1 Aqueous samples must be extracted within 7 days of sampling.

7.5.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

7.5.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS & MATERIALS

8.1 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.1.1 Gas Chromatograph. HP-5890, HP-6890, or Agilent 6890-N which includes an analytical system that is complete with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases.

8.1.1.1 The injection port is designed for splitless injection with capillary columns.

8.1.1.2 The capillary column is directly coupled to the source.

8.1.2 Column.

8.1.2.1 30 m x 0.25 mm fused silica (0.25 μm film thickness) DB-5MS or equivalent capillary column. Condition the column as per manufacture's directions.

8.1.3 Mass Spectrometer (HP-5972, HP-5973 or Agilent 5975).

8.1.3.1 Full Scan Mode -Capable of scanning from 35-500 amu every 1 second or less utilizing 70 volt (nominal) electron energy in the electron impact ionization mode.

8.1.3.2 SIM Mode- Capable of selective ion grouping at specified retention times for increased compound sensitivity (table 2a).

8.1.3.3 Capable of producing a mass spectrum which meets all the EPA performance criteria in Table 3 when injecting 50 ng of Decafluorotriphenyl phosphine (DFTPP).

8.2 DATA SYSTEM

8.2.1 Acquisition and Instrument Control: HP Chemstation. A computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.2.2 Data Processing: HP Enviroquant. The software accommodates searching of GC/MS data files for analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the NIST98 spectra library for qualitative searches of non-target compounds present in the chromatogram. It flags all data files that have been edited manually by laboratory personnel.

8.2.3 Offline Magnetic Tape Storage Device (Lagato Networker) - the magnetic tape storage device copies data for long term, offline storage.

8.3 SYRINGE

8.3.1 10 µl graduated, auto sampler (Hamilton or equiv.).

8.3.2 Micro liter syringes, various sizes

9.0 REAGENTS AND STANDARDS

9.1 Solvents - Ultra pure, chromatography grade methylene chloride and acetone.

9.2 Stock Standard Solutions.

9.2.1 Certified, commercially prepared standards, from two separate sources are used.

9.2.1.1 <u>Base Neutrals</u>.

- Base/Neutrals Mix #1 (Absolute: Semivolatile Organics Standard Mix # 1).
- Base/Neutrals Mix #2 (Absolute: Semivolatile Organics Standard Mix # 2).
- PAH Mix (Absolute: Semivolatile Organics Standard Mix # 7).
- PAH Mixture #2 (Ultra).
- PAH Selected Ion Monitoring Mixture
- Benzidines Mix (Absolute: Semivolatile Organics Standard Mix # 6).
- Toxic Substances #2 (Absolute: Semivolatile Organics Standard Mix # 5).
- Pyridines Mixture (Ultra).
- Additonal requested compound(s) mix (Absolute).
- Base Neutral Mixture (2nd Source).

Acids.

- Phenols Mix (Absolute: Semivolatile Organics Standard Mix # 8).
- Toxic Substances #1(Absolute: Semivolatile Organics Standard Mix # 4).
- Acid Mixture (2nd Source).Internal Standard Mixtures.

9.2.2 Internal Standard Mixtures

9.2.2.1 Ultra (or equivalent) at a concentration of 4,000 μg/ml for each of the following compounds.

Full Scan

- 1,4-Dichlorobenzene-d4
- Naphthalene-d8
- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12
- Perylene-d12

SIM

- 1,2-Dichlorobenzene-d4
- 1-Methylnaphthalene-d10
- Fluorene-d10
- Fluoranthene-d10
- Benzo(a)pyrene-d12

9.2.2.2 The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0.8 - 1.20 relative to one of the internal standards.

9.2.2.3 Each 1 ml sample extract, and standard undergoing analysis should be spiked with 10 μl of the internal standard mixtures, resulting in a concentration of 40 μg/ml of each internal standard for full scan analysis and 4 ug/ml for SIM analysis.

9.2.3 Surrogate Standard Mixture

9.2.3.1 B/N Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 5,000 µg/ml each surrogate compound.

- Nitrobenzene-d5.
- 2-Fluorobiphenyl.
- p-Terphenyl-d14.

9.2.3.2 Acid Surrogate Standard Mix: RESTEK (or equivalent) at a concentration of 7,500 µg/ml each surrogate compound.

- Phenol-d5.
- 2-Fluorophenol.
- 2,4,6-Tribromophenol.

9.2.4 DFTPP Tune Stock.

9.2.4.1 Protocol (or equivalent) at a concentration of 2,500 µg/ml for the following compounds.

- Decafluorotriphenylphosphine.
- 4,4'-DDT.
- Benzidine.
- Pentachlorophenol.

9.2.4. Store at -10 ^{o}C or less when not in use or according to the manufacturer's documented holding time and storage temperature recommendations. Stock standard solutions must be replaced after 1 year or sooner if manufacture's expiration date comes first or comparison with quality control check samples indicates degradation.

9.3 Surrogate Spiking Solutions.

9.3.1 Two surrogate spiking solutions, base/neutral surrogate solution and acid surrogate solution, at a concentration of 100 µg/ml are prepared in Extraction. Spike each sample, and blank with 0.5 ml of each solution, prior to extraction, for a final concentration of 50 µg/l of each surrogate compound in the extract.

9.3.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.3.3 Store at -10 °C or less or according to the manufacturer's documented storage temperature recommendations. Prepare fresh surrogate spiking solutions every year, or sooner, if the manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.4 Intermediate Calibration Standard Solution.

9.4.1 The calibration stock solution is prepared by adding an appropriate amount of each stock and surrogate compounds into a 10 ml volumetric flask. Dilute the solution to the volume with methylene chloride and mix thoroughly. Refer to Table 7A for details.

9.5 Calibration Standards.

9.5.1 Initial Calibration Standards.

9.5.1.1 Calibration standards containing the surrogate compounds should be made by quantitative dilutions of the above intermediate solution. The calibration standards are prepared at a minimum of five concentrations to cover the range of 2 - 100 µg/ml for full scan and 0.02 – 5ug/ml for SIM, depending upon project specific requirements. Suggested levels and preparations are shown in Table 7A and 7B.

9.5.2 Continuing Calibration Verification.

9.5.2.1 The concentration of the mid range standard used for continuing calibration verification is alternated between 25 and 50 µg/ml for full scan and 2.5 and 1.0 for SIM.

9.5.3 Store the calibration standards in a refrigerator at 4 °C and prepare every 6 months or before the manufacturer's expiration date, whichever is sooner. Standards must be replaced immediately if the analysis of check standards indicates degradation.

9.6 Initial Calibration verification (ICV) -Second source calibration check standard.

9.6.1 The ICV standard is prepared per Table 7E, using the intermediate solutions prepared in Extraction.

9.6.2 The ICV is analyzed after each initial calibration.

9.7 Daily GC/MS Performance Checks.

9.7.1 The solution is prepared at 50 µg/ml by making a 1:50 dilution of DFTPP stock solution (Section 9.2.4) in methylene chloride.

9.8 Matrix Spike Solutions.

9.9.1 The matrix spike solutions for both Base/Neutral and Acid are prepared in Acetone at a concentration of 100 µg/ml for each compound. Prepare the matrix spike, matrix spike

duplicate and blank spike by spiking the selected sample and the blank with 0.5 ml of these solutions for a final concentration of 50 μg/l of each compound.

9.10 All organic new standard solutions are analyzed prior to use to verify the accuracy of the prepared concentration.

9.10.1 The prepared standard solution is analyzed using the determinative (instrumental) technique for the method.

9.10.2 The solution is analyzed following the completion of instrument calibration or a calibration check.

9.10.3 The concentration of the standard solution is determined using the software routines used in determining the acceptability of calibration verification.

9.10.4 The data is evaluated and the percent difference determined. The standard solution is approved for use if all designated compounds are present in the solution and the percent difference is less than the established criteria (±20%).

10.0 CALIBRATION

10.1 Initial Calibration.

10.1.1 The calibration range covered for routine analysis under RCRA employs standards of 1, 2, 5, 10, , 25, 50, 80, 100 μg/ml for full scan and 0.02, 0.05, 0.10, 0.20, 1.0, 2.5 ug/ml for SIM. A minimum of five standards must be run sequentially. The reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of surrogate spiking solutions to the calibration solution to define a range similar to the target compounds.

10.1.3 Aliquot 1 ml of each calibration standard into a 2 ml crimp top vial.

10.1.4 Prior to analysis, add 10 μl of the applicable (Full acan and/or SIM) internal standard solution (Section 9.2.2) to each standard. This results in a concentration of 40 μg/ml (Full scan) and 4ug/ml (SIM) for each internal standard.

10.1.5 Analyze the standard solutions using the conditions established in Section 11.0. Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 6.

10.1.6 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte, using minimum of five RF values calculated from the initial calibration curve.

10.1.7 For the initial calibration to be valid, the following criteria must be met.

10.1.7.1 The System Performance Check Compounds (SPCCs) (Table 5) must be checked for a minimum average response factor. The minimum mean response factor for these compounds is 0.05. If the initial calibration criteria for SPCCs are not achieved, perform corrective action before completing the calibration.

10.1.7.2 The % RSD for each individual Calibration Check Compound (CCC) (Table 5) must be less than 30 %. This check is used to identify gross instrument operating problems. If the initial calibration criteria for CCCs are not achieved, perform corrective action before completing the calibration.

10.1.7.3 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than 15 %.

10.1.7.4 If the %RSD of any individual (non CCC) compound is >15%, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.1.7.4.1 If a linear regression is employed, select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.1.7.4.2 The correlation coefficient (r value) must be $\geq$0.99 for each compound to be acceptable.

10.1.7.4.3 Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.1.7.5 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.1.7.6 The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.2 Initial Calibration Verification (ICV) - Source Calibration Check Standard.

10.2.1 The calibration is verified with a calibration check standard at 50 μg/ml (Full scan) or 1ug/ml (SIM) from an external source (Section 9.6). It must be analyzed immediately following the initial calibration.

10.2.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 20% for all the target compounds.

10.2.2.1 If % D is greater than 20%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification Standard - CCV

10.3.1 A calibration verification standard at close mid-level concentration of the initial calibration range at alternating 25 and 50ug/ml for full scan and 2.5ug/ml and 1ug/ml for SIM must be acquired every 12 hrs.

10.3.1.1 Vary the concentration of calibration verification standard on alternate verifications (i.e. every other calibration verification) using an alternative concentration standard. The standard selected must be lower than the midpoint calibration standard.

10.3.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.3.2.1 The minimum RF for SPCC compounds must be 0.05. Each SPCC compound in the calibration verification standard must meet its minimum response factor. The percent difference (% D) for CCC compounds must be less than 20%.

10.3.2.1.1 If the CCCs are not part of the target list, then all targeted analytes must meet the 20% D criteria. All non-CCC compounds should also meet the 20% D criteria.

10.3.3 If the first continuing calibration verification does not meet criteria, a second standard may be injected after notifing the team leader/manager and checking the system for defects.

10.3.3.1 A continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.4 If the verification criteria cannot be achieved, a new initial calibration must be performed.

10.3.5 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.3.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.3.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

11.0 PROCEDURE

11.1 Instrument Conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification should be approved by team leader/manger.

11.2 Daily GC/MS Performance Checks.

11.2.1 Mass Spectrometer Tuning. Every 12-hour, inject 1 µl of 50 ng/µl or 2 µl of 25 ng/µl DFTPP solution directly on to the column.

11.2.2 The GC/MS system must be checked to verify that acceptable performance criteria are achieved (see Table 3).

11.2.3 This performance test must be passed before any sample extracts, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.2.3.1 Select the scans at the peak apex and one to each side of the apex.

11.2.3.2 Calculate an average of the mass abundances from the three scans.

11.2.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.2.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.2.4.1 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.2.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.2.6 In order to assess GC column performance and injection port inertness, the DFTPP tune standard also contains appropriate amount of 4,4'-DDT, benzidine and pentachlorophenol.

11.2.6.1 Injection Port Inertness Check.

11.2.6.1.1 The injection port inertness of the GC portion of the GC/MS is evaluated by the percent breakdown of 4,4'-DDT. DDT is easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated by high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a GC/MS tune standard containing 4,4'-DDT every 12 hour, regardless of whether DDT is a target analyte. The degradation of DDT to DDE and DDD should not exceed 20%, in order to proceed with calibration procedures. Refer to Section 13.7 for calculation. Print the check and keep it on file.

11.2.6.2 Column Performance Check.

11.2.6.2.1 The condition of the GC column is evaluated by the tailing of benzidine and pentachlorophenol every 12 hour. Benzidine and pentachlorophenol should be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factors. The tailing factor criteria for benzidine (base-neutral fraction) must be < 3 and for pentachlorophenol (acid fraction) must be < 5. Print the check daily and keep on file.

11.2.6.3 If degradation is excessive and/or poor chromatography is observed, the injector port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

11.3 Initial Calibration

11.3.1 Refer to Section 10.1.

11.4 Initial calibration Verification (ICV) - Second Source Calibration Check

11.4.1 This standard must at least be analyzed when initial calibration provided. Refer to Section 10.2.

11.5 Continuing Calibration Checks

11.5.1 Refer to Section 10.3.

11.6 Sample Analysis.

11.6.1 Allow the sample extract to warm to room temperature. Spike 10 µl of the appropriate internal standard mix (4,000 µg/ml for full scan and 400ug/ml for SIM) into 1 ml sample extract, just prior to analysis. This is equivalent to a concentration of 40 µg/ml (full scan) and 4ug/ml (SIM) of each internal standard.

11.6.2 Inject 1 µl aliquot of the sample extract into the GC/MS system. A splitless injection technology is used.

11.6.3 If the response for any ion of interest exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

11.6.4 When the extracts are not being used for the analyses, store them at -10°C, protected from light, in sealed vials equipped with unpierced PTFE-lined septa.

11.7 Sample Dilution

11.7.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

11.7.2 If no lower dilution has been reported, the dilution factor chosen should keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

11.7.3 Preparing Dilutions.

11.7.3.1 Prepare sample dilutions quantitatively. Dilute the sample extract with methylene chloride using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc. Large dilutions may require serial dilutions or the use of a Class A 10 ml volumetric flask.

11.7.3.2 Syringe dilutions. – Calibrated syringes are used to prepare dilutions. Add the appropriate amount of methylene chloride to a clean autosampler vial. Add the proper amount of sample using a calibrated syringe of the appropriate volume for the dilution. Add sufficient internal standard to maintain a concentration of 40ug/ml. Cap the vial and gently shake to disperse the sample through the solvent.

11.7.3.3 Volumetric Flask Dilutions – Large dilutions may require the use of a 10 ml Class A Volumetric flask.

11.8 Establishing Search Criteria for target compounds. Search criteria for each compound listed in the method must be entered into the method quantitation/identification file in the Enviroquant software package. This activity must be performed before attempting qualitative and quantitative analysis on any acquired data file. The search criteria are based on compound retention time and the

characteristic ions from the reference mass spectrum. Characteristic ions are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The number of secondary ions displayed for each compound search varies between compounds.

11.8.1 Select the primary ion for the target compound from the characteristic ions in Table 6. If multiple characteristic ions are listed, the first ion is the major (primary) ion. Enter this ion as the search ion. Enter the relative abundance of this ion (100% for base peak ions) and set the relative abundance window at ± 30%.

11.8.1.2 Alternate primary ions may be selected when interferences exist from ion abundance contribution from close eluting compounds.

11.8.2 Enter the remaining ions as secondary ions. Secondary ions are not be used to locate peaks within the search window, but are be used to support the qualitative identification of selected peaks. The number of secondary ions displayed for each compound search varies between compounds depending on the number of ions in the spectra >30% relative abundance.

11.8.3 Set the relative abundance windows for the secondary ions at ± 30%.

11.8.4 Establish the relative retention window for each compound. Because it is a relative retention window the same width window applies to all compounds on the quantitation list. The window must be established at a minimum of 0.06 relative retention time units.

11.9 Data Interpretation.

11.9.1 Executing Qualitative Searches. The target compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.1 The search procedure will identify peaks within the search window using the primary ion only. Secondary ions and the relative retention are used to determine “the best match”. If the best match contains secondary ions outside the relative abundance window, they will be flagged with a # sign.

11.9.2 Qualitative Identification. The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Compounds are identified when the following criteria are met.

11.9.2.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.9.2.2 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criterion is the RRT of sample component must be within ± 0.06 RRT units of the standard.

11.9.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

11.9.2.3.1 If a chromatographic peak exhibits a spectrum containing an ion with relative abundance outside the relative abundance window is selected for reporting, the analyst must annotate the spectra that the compound qualified based on his/her best judgement. This circumstance will most often occur from coeluting compounds with similar ions or background matrix interferences.

11.9.3 Quantitative Analysis.

11.9.3.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 6). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.3.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. The secondary ion must be used to generate a new response factor.

11.10 Library Search for Tentatively Identified Compounds.

11.10.1 If a library search is requested, the analyst should perform a forward library search of the NIST98 mass spectral library to tentatively identify 10 to 15 non-reported compounds (15 for base, 10 for acid, 25 for base/acid fraction).

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds should have a response greater than 10% of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) should be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions should agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.3 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.4 The resulting concentration should be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.10.5 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched and reported but not counted towards the total TIC count.

11.10.6 Any peak naming as “System artifact” (from the column bleedings) or “Internal Standard” (added by lab for other test, like SIM analysis) shall be searched and reported but not counted towards the total TIC count.

11.11 Selected Ion Monitoring (SIM) Option

11.11.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a, Table 8a) Select a mass dwell time of 50 milliseconds for all compounds.

11.11.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 6 calibration standards of 0.02, 0.05, 0.10, 0.20, 1.0, 2.5, 5.0 ug/ml. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs using the procedures and criteria described in Section 10.1.6, 10.1.7.3 and 10.1.7.4.

11.11.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 1.0 ug/ml calibration standard purchased or prepared from a second standards reference

materials source. The initial calibration verification must meet the criteria of Section 10.2.2.

11.11.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 1.0 or 2.5 ug/ml calibration. The continuing calibration verification must meet the criteria of Section 10.3.

11.11.5 Sample Extract Analysis: Each extract has been previously spike with the SIM internal standard at 4 ug/ml. Analyze the sample extracts for the compounds of interest using the SIM scan parameters employed for the calibration standards.

11.11.6 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis at 50 ug/ml.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary.

Daily GC/MS Performance Checks	Beginning of the analytical shift and every 12 hours
Initial Calibration	Whenever needed.
Second Source Calibration Check	Following initial calibration
Continuing Calibration Verification	Every 12 hours.
Method Blank	One per extraction batch*.
Blank Spike	One per extraction batch*.
Matrix Spike	One per extraction batch*.
Matrix Spike Duplicate	One per extraction batch*.
Surrogate	Every sample extract and standard.
Internal Standard	Every sample extract and standard.

*The maximum number of samples per batch is twenty or per project specification.

12.2 Daily GC/MS Performance Checks.

12.2.1 Refer to Section 11.2.

12.3 Initial Calibration.

12.3.1 Refer to Section 10.1.

12.4 Initial Calibration Verification (ICV) - Source Calibration Check.

12.4.1 Refer to Section 10.2.

12.5 Continuing Calibration Verification.

12.5.1 Refer to section 10.3.

12.6 Method blank.

12.6.1 The method blank is either reagent water or anhydrous sodium sulfate (depending on the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank is then extracted and carried through all stages of the sample preparation and measurement.

12.6.2 If the method blank contains a target analyte above its MDL (Appendix I), the entire batch must be re-extracted and re-analyzed.

12.6.3 Surrogate compounds are added to the method blank prior to extraction. If the surrogate accuracy in the method blank does not meet in house criteria (Appendix I), it must be reanalyzed. If the reanalysis confirms the original data, the entire batch should be re-extracted.

12.7 Blank Spike

12.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same volume. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

12.7.2 The blank spike recoveries should be assessed using in house limits specified in Appendix I.

12.7.3 If a blank spike is out of control, the following corrective actions must be taken and all the associated samples must be re-extracted and reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required.

12.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

12.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

12.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

12.8 Matrix Spike(MS) / Matrix Spike Duplicate(MSD)

12.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, and determinative procedures.

12.8.2 Matrix spikes are prepared by spiking an actual sample at a concentration of 50 µg/l for both base/neutral and acids.

12.8.3 Assess the matrix spike recoveries (% R) (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the control limits in Appendix I.

12.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. In such case, matrix interference is assumed and the data is reported with footnote (e.g., spike recovery indicates possible matrix interference). No further corrective action is required.

12.9 Surrogates

12.9.1 All standards, blanks, sample extracts, and matrix spikes contain surrogate compounds which are used to monitor the performance of the extraction and analytical system.

12.9.2 The recoveries (Section 13.5) of the surrogates must be evaluated to determine whether or not they fall within surrogate control limits (Appendix I) developed by the laboratory annually.

12.9.3 If the recovery of any surrogate compound does not meet the control limits, the calculation must be checked for possible error. The surrogate solution should be checked for degradation. Contamination and instrument performance should also be reviewed.

12.9.3.1 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

12.9.3.2 If the data from the reanalysis is also out of control, re-extract and reanalyze the sample.

12.9.3.3 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

12.9.3.4 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

12.9.4 If the sample exhibits matrix interference, defined as excessive signal where target or non-target responses are greater than the response of the internal standards. In this case, reanalysis may not be required following team leader/manager approval; the surrogates will be qualified as outside the limits due to matrix interference. Alternatively, sample may be reanalyzed on dilution, if the reanalysis is again not within the limit, the sample should be reported with a footnote indicating that there were possible matrix interference.

12.10 Internal Standards.

12.10.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 μg/ml standard of initial calibration.

12.10.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area of the latest calibration standard (12 hr. time period).

12.10.3 If the area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.10.4 If the areas are acceptable upon reanalysis, the reanalysis data is reported.

12.10.5 If the areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

13.0 CALCULATION

13.1 Response Factor (RF).

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_s = Concentration of the compound being measured (μg/ml).
C_{is} = Concentration of the specific internal standard (μg/ml).

13.2 Percent Relative Standard Deviation (%RSD).

$$\%RSD = \quad SD \quad \times 100$$

RF_{av}

where:

SD = Standard Deviation.
RF_{av} = Average response factor from initial calibration.

13.3 Percent Difference (%D).

$$\% D = \frac{|RF_{av} - RF_{cv}|}{RF_{av}} \times 100$$

where: RF_{cv} = Response factor from Calibration Verification Standard.

13.4 Concentration (Conc.).

13.4.1 <u>for water:</u>

$$\text{Conc. } (\mu g/l) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times V_i}$$

13.4.2 <u>for soil/sediment</u> (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{A_s \times C_{is} \times V_f \times D \times 1000}{A_{is} \times RF_{av} \times W_s \times S}$$

where:

V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100.

13.5 Percent Recovery (%R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD).

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

where:

MSC = Matrix Spike Concentration.
MSDC = Matrix Spike Duplicate Concentration.

13.7 Percent Breakdown.

$$\% \text{ Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

where:

Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD.

13.8 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.9 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in this log.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

14.2.1 The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

14.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 DATA REVIEW AND REPORTING

15.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

15.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

15.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

15.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

15.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

15.3.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

15.3.2 Manual integration of chromatographic peaks must be identified by the analysts. Upon review, the supervisor will initial and date the changes made to the report.

15.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

15.4.1 Compare the printed values to the original values to verify transfer accuracy.

15.4.2 If transfer errors occurred, the errors must be corrected before the data is re-submitted.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.
16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes

Table 1 – Target Compounds by SW846 8270C			
Benzenethiol (1)	4-Bromophenyl phenyl ether	Di-n-octyl phthalate	5-Nitro-o-toluidine (1)
Benzoic Acid	Butyl benzyl phthalate	Diethyl phthalate	Naphthalene
2-Chlorophenol	Benzyl Alcohol	Dimethyl phthalate	Nitrobenzene
4-Chloro-3-methyl phenol	1,1'-Biphenyl (1)	2,3-Dichloroaniline (1)	n-Nitrosodimethylamine
2,4-Dichlorophenol	Butyl Stearate (1)	Decane	4-Nitroquinoline 1-Oxide (1)
2,4-Dimethylphenol	2-Chloronaphthalene	Octadecane (1)	N-Nitroso-di-n-propylamine
2,4-Dinitrophenol	4-Chloroaniline	bis(2-Ethylhexyl)phthalate	N-Nitrosodi-n-butylamine
2,6-Dichlorophenol	Carbazole	Ethyl methanesulfonate	N-Nitrosodiethylamine
4,6-Dinitro-2-methylphenol	Caprolactam (1)	Famphur	N-Nitrosodiphenylamine
Dinoseb	Chlorobenzilate	Fluoranthene	N-Nitrosomethylethylamine
2-Methylphenol	Chrysene	Fluorene	N-Nitrosomorpholine
3&4-Methylphenol	Cumene (1)	Hexachlorobenzene	N-Nitrosopiperidine
2-Nitrophenol	bis(2-Chloroethoxy)methane	Hexachlorobutadiene	N-Nitrosopyrrolidine
4-Nitrophenol	bis(2-Chloroethyl)ether	Hexachlorocyclopentadiene	O,O,O-Triethyl phosphorothioat
Pentachlorophenol	bis(2-Chloroisopropyl)ether	Hexachloroethane	2-Picoline
Phenol	4-Chlorophenyl phenyl ether	Hexachlorophene	Parathion
2,3,4,6-Tetrachlorophenol	1,2-Dichlorobenzene	Hexachloropropene	Pentachloroethane (1)
2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	Indene (1)	Pentachlorobenzene
2,4,6-Trichlorophenol	1,3-Dichlorobenzene	Indeno(1,2,3-cd)pyrene	Pentachloronitrobenzene
2-Acetylaminofluorene	1,4-Dichlorobenzene	Isodrin	Phenacetin
4-Aminobiphenyl	2,4-Dinitrotoluene	Isophorone	Phenanthrene
Acenaphthene	2,6-Dinitrotoluene	Isosafrole	Phorate
Acenaphthylene	3,3'-Dichlorobenzidine	Kepone	Pronamide
Acetophenone	3,3'-Dimethylbenzidine	1-Methylnaphthalene	Pyrene
Aniline	1,4-Dioxane (1)	2-Methylnaphthalene	Pyridine
Anthracene	7,12-Dimethylbenz(a)anthracene	3-Methylcholanthrene	p-Phenylenediamine
Aramite	Dimethylnaphthalenes (total) (1)	4,4'-Methylenebis(2-chloroaniline)	Quinoline (1)
Atrazine (1)	Diallate	Methapyrilene	Safrole
alpha-Terpineol	Dibenz(a,h)acridine	Methyl methanesulfonate	1,2,4,5-Tetrachlorobenzene
A,A-Dimethylphenethylamine	Dibenzo(a,h)anthracene	Methyl parathion (1)	1,2,4-Trichlorobenzene
Benzidine	Dibenzofuran	6-Methyl Chrysene (1)	1,2,3-Trichlorobenzene (1)
Benzaldehyde (1)	Dimethoate	1,4-Naphthoquinone	1,3,5-Trichlorobenzene (1)
Benzo(a)anthracene	Diphenylamine	1-Naphthylamine	Thionazin (1)
Benzo(a)pyrene	Disulfoton	2-Naphthylamine	o-Toluidine
Benzo(b)fluoranthene	m-Dinitrobenzene	2-Nitroaniline	sym-Trinitrobenzene (1)

Benzo(g,h,i)perylene	p-(Dimethylamine) azobenzene (1)	3-Nitroaniline	Tetraethyl dithiopyrophosphate (1)
Benzo(k)fluoranthene	Di-n-butyl phthalate	4-Nitroaniline	

(1) NELAC Accreditation is not offered for this compound.

Table 2 – RECOMMENDED OPERATING CONDITIONS: Gas Chromatograph/ Mass Spectrometer	
Injection Type	Splitless
Carrier Gas (linear velocity)	Helium at 30 cm/sec*
Mass range	35-500 AMU
Electron Energy	70 volts (nominal)
Scan time	not to exceed 1 sec. per scan
Injection port temperature	200-300 °C
Source temperature	220-270 °C
Transfer line temperature	250-300 °C
Analyzer temperature	220-250 °C
Gas Chromatograph Temperature Program*	
Initial temperature	40-50 °C*
Time 1	2-4 minutes*
Column temperature rate	8-25 degrees/min*
Final temperature	290-320 °C according to column type*
Total run time	*20-40 minutes*

***** Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 2a – SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 7.8	150, 64, 93, 82, 152, 99, 63, 128, 112, 42, 95
2	7.8 – 11	150, 128, 225, 142, 172, 152, 129, 223, 141, 171, 122, 127, 227, 115, 170
3	11 – 13.8	172, 152, 166, 182, 334, 266, 176, 153, 165, 330, 284, 264, 174, 154, 77, 332, 286, 268
4	13.8 – 18	266, 179, 202, 122, 268, 212, 203, 284, 178, 213, 244, 286
5	18 – 22	244, 229, 167, 122, 226, 202, 228, 149, 203
6	22 – 34.7	264, 149, 253, 278, 263, 150, 250, 139, 265, 252, 276, 138

Table 3 - DFTPP KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	**Ion Abundance Criteria**
51	30-60 of mass 198
68	<2 % of mass 69
70	<2 % of mass 69
127	40-60 % of mass 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	>1 % of mass 198
441	Present but less than mass 443
442	>40 % of mass 198

443	17-23 % of mass 442

Table 4 – INTERNAL STANDARDS	
Internal Standard (Full Scan)	**Prim/Sec. ions**
1,4-Dichlorobenzene-d4	152 / 150, 115
Naphthalene-d8	136 / 68
Acenaphthene-d10	164 / 162, 160
Phenanthrene-d10	188 / 94, 80
Chrysene-d12	240 / 120, 236
Perylene-d12	264 / 260, 265
Internal Standard (SIM)	**Prim/Sec. ions**
1,2-Dichlorobenzene-d4	152/ 150
1-Methylnaphthalene-d10	150/ 152, 122
Fluorene-d10	174/ 176
Fluoranthene-d10	212/ 213
Benzo(a)pyrene- d12	264/ 263, 265

Table 5 - Criteria for CCC and SPCC	
Initial Calibration: CCC % RSD is ≤ 30 %.	Continuing Calibration: CCC % D is ≤ 20 %
Calibration Check Compounds (CCC)	
Base Neutral	**Acid**
1,4-Dichlorobenzene	Phenol
Hexachlorobutadiene	2,4-Dichlorophenol
Acenaphthene	2-Nitrophenol
Fluoranthene	4-Chloro-3-methylphenol
N-Nitrosodiphenylamine	2,4,6-Trichlorophenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo (a) pyrene	
System Performance Check Compounds (SPCC)	
Base Neutral	**Acid**
N-Nitroso-di-n-propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol
Minimum acceptable average relative response factor (RRF) is 0.050 for SPCC.	

Table 6 – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d4	**Ions**	**Acenaphthene-d10**	**Ions**
Aniline	(93/66,65)	Acenaphthene	(154/153,152)
Benzaldehyde	(105)	Acenaphthylene	(152/151,153)
Benzenethiol	(110)	1-Chloronaphthalene	(162/127,164)
Benzyl alcohol	(108/79,77)	2-Chloronaphthalene	(162/127,164)
Bis(2-chloroethyl)ether	(93/63,95)	4-Chlorophenylphenyl ether	(204/206,141)
Bis (2-chloroisopropyl)ether	121	Dibenzofuran	(168/139)
2-Chlorophenol	(128/64,130)	Diethyl phthalate	(149/177,150)
Cumene	(105,120)	Dimethyl phthalate	(163/149,164)
Decane	(43)	m-Dinitrobenzene	(168)
1,3-Dichlorobenzene	(146/148,111)	2,4-Dinitrophenol	(184/63,154)
1,4-Dichlorobenzene	(146/148,111)	2,4-Dinitrotoluene	(165/63,89)
1,2-Dichlorobenzene	(146/148,111)	2,6-Dinitrotoluene	(165/63,89)
1,4 Dioxane	(88)	Fluorene	(166/165,167)
Ethyl methanesulfonate	(79/109,97)	Hexachlorocyclopentadiene	(295/237,142)
2-Fluorophenol (SURR.)	(112)	1,4 – Naphthoquinone	(158)
Hexachloroethane	(117/201,199)	1- Naphthylamine	(143/115,116)
Indene	(116)	2- Naphthylamine	(143/115,116)
Methyl methanesulfonate	(80/79,64)	2-Nitroaniline	(65/92,138)
2-Methylphenol	(108/107,79)	3-Nitroaniline	(138/108,92)
4-Methylphenol	(108/107,79)	4-Nitroaniline	(138/108,92)
N-Nitrosodiethylamine	(102)	4-Nitrophenol	(139/109,65)
N-Nitrosodimethylamine	(74/42)	5 Nitro-o-toluidine	(152)
N-Nitroso-di-n-propylamine	(70/101,130)	Pentachlorobenzene	(250/252,248)
N-Nitrosomethyethylamine	(42)	Pentachloronitrobenzene	(237/235,272)
N-Nitrosomorpholine	(56)	Phenacetin	(108/109,179)
N-Nitrosoptrrolidine	(41)	Phorate	(75)
O-Toluidine	(106)	Pronamide	(173/175,145)
Petachloroethane	(167)	1,2,4,5-Tetrachlorobenzene	(216/214,218)
Phenol	(94)	2,3,4,6-Tetrachlorphenol	(232/230,131)
Phenol-d5 (SURR.)	(99)	Tetraethyldithiopyrophosphate	(322)
2-Picoline	(93/66,92)	Thioazin	(143)
Pyridine	(79)	2,4,6-Trichlorophenol	(196/198,200)
		2,4,5-Trichlorophenol	(196/198,200)

Table 6 (cont'd) – Full Scan Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Naphthalene-d8	**Ions**	**Phenanthrene-d10**	**Ions**
A,A-Dimethylphenethylamine	(58)	4-Aminobiphenyl	(169/168,170)
Acetophenone	(105/77,51)	Anthracene	(178/176,179)
Benzoic acid	(184/92,185)	Atrazine	(58)
Bis(2-chloroethoxy)methane	(93/95,123)	4-Bromophenyl phenyl ether	(248/250,141)
Caprolactam	(55)	Carbazole	(167)
4-Chloroaniline	(127)	Diallate	(86)
4-Chloro-methylphenol	(107/144)	Dimethoate	(87)
2,3 Dichloroaniline	(161)	Di-n-Butyl phthalate	(149/150)
2,4-Dichlorophenol	(162/164,98)	4,6-Dinitro-2-methylphenol	(198/51,105)
2,6-Dichlorophenol	(162/164,98)	Dinoseb	(211)
Dimethylnaphthalene	(156)	Diphenylamine	(169/168,167)
2,4-Dimethylphenol	(122/107)	1,2-Diphenylhydrazine	(77/105)
a,a-Dimethyl-phenethylamine	(58/91,42)	Disulfoton	(88)
Hexachlorobutadiene	(225/223,227)	Fluoranthene	(202/101,203)
Hexachloroprene	(213)	2-Fluorobiphenyl (SURR)	(172)
Isophorone	(82/95,138)	Hexachlorobenzene	(284/142,249)
Isosafrole	(127)	Isodrin	(193)
1-Methylnaphthalene	(142)	Methapyriline	(58)
2-Methylnaphthalene	(142/141)	Methyl Parathion	(125)
Naphthalene	(128/129,127)	N-Nitrosodiphenylamine	(169/168,167)
Nitrobenzene	(77/123,65)	4-Nitroquinoline 1-oxide	(190)
Nitrobenzene-d5 (SURR.)	(82)	Octadecane	(57)
N-Nitroso-di-n-butylamine	(84/57/41)	Parathion	(109)
2-Nitrophenol	(139/109,65)	Pentachlorophenol	(266/264,268)
Quinoline	(129)	Phenanthrene	(178/179,176)
N-Nitrosopiperidine	(42/114,55)	Pronamide	(173)
p-Phenylenediamine	(108)	sym- Trinitrobenzene	(213)
O,O,O-Triethylphosphorthioat	(198)	2,4,6 Tribromophenol (SURR)	(330)
Safrole	(162)		
alpha –Terpineol	(128)	**Perylene-d12**	**Ions**
1,2,3-Trichlorobenzene	(180/182,145)	Benzo(b)fluoranthene	(252/125)
1,2,4-Trichlorobenzene	(180/182,145)	Benzo(k)fluoranthene	(252/125)
1,3,5-Trichlorobenzene	(180/182,145)	Benzo(g.h.i)perylene	(276/138,277)
		Benzo(a)pyrene	(252/253,125)
Chrysene-d12	**Ions**	Dibenz(a,j)acridine	(279/280)
2 –Acetylaminofluorene	(181)	Dibenz(a,h)anthracene	(278/139,279)
Aramite	(194)	7,12-Dimethylbenz(a)anthracene	(256/241,257)
Benzidine	(184)	Di-n-Octyl Phthalate	(149)
Benzo(a)anthracene	(228/229/226)	Hexachlorophene	(196)
Bis(2-ethylhexyl)phthalate	(149/167,279)	Indeno(1,2,3-d)pyrene	(276)
Butylbenzyl phthalate	(149/91)	3-Methylchloanthrene	(268/253)
Chlorobenzilate	(251)		
Chrysene	(228/226,229)		
3,3'-Dichlorobenzidine	(252/254,126)		
p-Dimethylaminoazobenzene	(120/225,77)		
3,3 Dimethylbenzidine	(212)		

Famphur	(218)		
Kepone	(272)		
Methyl Chrysene	(242)		
Pyrene	(202/200,203)		
Terphenyl-d14 (SURR.)	(244)		
Table 6a – SIM Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation			
1,4-Dichlorobenzene-d4	**Ions**	**Fluoranthene-d10**	**Ions**
2-Fluorophenol (Surr)	(112)	Fluoranthene	202, 101, 203
Phenol-d5 (Surr)	(99)	Pyrene	202, 203
Bis-(2-chloro-ethyl)ether	93, 63, 95	Terphenyl-d14 (Surr)	(244)
Nitrobenzene-d5 (Surr)	(82)	Benzo(a)anthracene	228, 229, 226
		Chrysene	228, 226, 229
1-Methylnaphthalene-d10	**Ions**	Bis(2-ethylhexylphthalate	149, 167, 279
Naphthalene	128, 129, 127		
Hexachlorobutadiene	225, 223, 227	**Benzo(a) pyrene-d12**	**Ions**
2-Methyl Naphthalene	142, 141, 115	Di-n-octyl phthalate	149, 150, 43
2-Fluorobiphenyl (Surr)	(172)	Benzo(b)fluoranthene	252, 253
		Benzo(k)fluoranthene	252, 125
Fluorene-d10	**Ions**	Benzo(a)pyrene	252, 253, 125
Acenaphthylene	152, 151, 153	Indeno(1,2,3-cd)pyrene	276, 277, 138
Acenaphthene	153, 152, 154	Dibenzo(a,h)anthracene	278, 139, 279
Fluorene	166, 165, 167	Benzo(g,h,i)perylene	276, 138, 277
1,2-Diphenylhydrazine	77, 105, 182		
2,4,6-Tribromophenol (Surr)	(330)		
Hexachlorobenzene	284, 286		
Pentachlorophenol	266, 264		
Phenanthrene	178, 179, 176		
Anthracene	178, 176, 179		

Table 7. STANDARD PREPARATION

Table 7A – Intermediate Calibration Standard Solution

Stock Solution	Stock Conc., µg/ml	Volume Added, µl	Final Vol. in $MeCl_2$, ml	Final Conc. µg/ml
Semivolatile Standard Mix # 1	2,000	500	10	100
Semivolatile Standard Mix # 2	2,000	500	10	100
Semivolatile Standard Mix # 4	2,000	500	10	100
Semivolatile Standard Mix # 5	2,000	500	10	100
Semivolatile Standard Mix # 6	2,000	500	10	100
Semivolatile Standard Mix # 7	2,000	500	10	100
PAH Mixture #2	2,000	500	10	100
Semivolatile Standard Mix # 8	2,000	500	10	100
Additional Requested Compound(s) Mix	2,000	500	10	100
Pyridines Mixture	2,000	500	10	100
1,2,3-Trichlorobenzene	1,000	1,000	10	100
1,3,5-Trichlorobenzene	1,000	1,000	10	100
Butyl Stearate	10,000	200	10	200
Pentachlorophenol	1,000	1,000	10	100

B/N Surrogate Standard Mix	5,000	200	10	100
Acid Surrogate Standard Mix	7,500	134	10	100.5

Table 7B – Intermediate Calibration Standard Solution -SIM

Stock Solution	Stock Conc., µg/ml	Volume Added, µl	Final Vol. in $MeCl_2$, ml	Final Conc. µg/ml
Semivolatile Standard Mix # 1	2,000	50	10	10
Semivolatile Standard Mix # 2	2,000	50	10	10
Toxic #2	2,000	50	10	10
PAH Mixture #2	2,000	50	10	10
Semivolatile Standard Mix # 8 (Acids)	2,000	250	10	50
1-Methynaphthalene	1,000	100	10	10
B/N Surrogate Standard Mix	5,000	100	10	50
Acid Surrogate Standard Mix (Full Scan)	7500	67	10	50

Table 7C – Initial Calibration Standards Prep Scheme

Standard Solution	Intermediate Conc., µg/ml	Intermediate added, µl Full Scan	Final Volume in $MeCl_2$, ml	Final Conc., µg/ml – Full Scan
STD 1	100	1,000	1	100
STD 2	100	800	1	80
STD 3	100	500	1	50
STD 4	100	250	1	25
STD 5	100	200	1	20
STD 6	100/10 (SIM)	100	1	10
STD 7	100	50	1	5
STD8	100	20	1	2

Table 7D Initial Preparation Standards Prep Scheme - SIM

Standard Solution	Intermediate Conc., µg/ml	Intermediate added, µl SIM	Final Volume in $MeCl_2$, ml	Final Conc., µg/ml – SIM Scan
STD 1	10/50	500	1	5 BN / 25 Acids
STD 2	10/50	250	1	2.5 BN / 12.5 Ac
STD 3	10/50	100	1	1 BN / 5 Acids
STD 4	1	200	1	0.2 BN / 1 Acids
STD 5	1	100	1	0.1 BN / 0.5 Acids
STD7	0.1	500	1	0.05 BN / 0.25 AC
STD 6	0.1	200	1	0.02 BN / 0.1 AC

Table 7E– ICV -Second Source Calibration Check Standard

Intermediate	Intermediate Conc., µg/ml	Volume Used, µl (Full/SIM)	Final Volume in Acetone, ml	Final Conc., µg/ml (Full/SIM)
Base Neutrals Mixture	100	500/ 50	1	50/ 5
Acid Mixture	100	500/ 50	1	50/ 5

Table 8a –Selected Ion Monitoring: Masses and Dwell Times

Compound	Mass Ion (m/z)	Dwell Time (ms)
Acenaphthene	153, 152, 154	50
Acenaphthylene	152, 151, 153	50
Anthracene	178, 176, 179	50
Benzo(a)anthracene	228, 229, 226	50
Benzo(a)pyrene	252, 253, 125	50
Benzo(b)fluoranthene	252, 253	50
Benzo(g,h,i)perylene	276, 138, 277	50
Benzo(k)fluoranthene	252, 125	50
Chrysene	228, 226, 229	50
Dibenzo(a,h)anthracene	278, 139, 279	50
Fluoranthene	202, 101, 203	50
Fluorene	166, 165, 167	50
Indeno(1,2,3-cd)pyrene	276, 277, 138	50
Naphthalene	128, 129, 127	50
Phenanthrene	178, 179, 176	50
Pyrene	202, 203	50
2-Methyl Naphthalene	142, 141, 115	50
Bis-(2-chloro-ethyl)ether	93, 63, 95	50
Pentachlorophenol	266, 264	50
Hexachlorobutadiene	225, 223, 227	50
1,2-Diphenylhydrazine	77, 105, 182	50
Bis(2-ethylhexylphthalate	149, 167, 279	50
Di-n-octyl phthalate	149, 150, 43	50
Hexachlorobenzene	284, 286	50
2-Fluorophenol	112, 64, 63	50
Phenol-d5	99, 42	50
Nitrobenzene-d5	82, 128	50
2-Fluorobiphenyl	172, 171, 170	50
2,4,6-Tribromophenol	330, 332, 334	50
Terphenyl-d14	244, 122	50

Lab Manager:_____

QA Manager:_____

Effective Date:_____

TEST NAME: CLEANUP OF ORGANIC EXTRACTS BY GEL PERMEATION CHROMATOGRAPHY

METHOD REFERENCE: SW846 Method 3640A. Sept 1994

Revised Sections*: *1.1, 5.1, 7.2 Deleted Section 7.3

1.0 SCOPE AND APPLICATION

1.1 This method is designed for the cleanup of organic extracts of water, sediment, and soil from hazardous waste sites prior to their analysis for semi-volatile base neutral organics, chlorinated pesticides and PCBs. GPC cleanup is employed primarily for extracts of soils/sediments and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds. GPC Cleanup may be used for other samples if required.

1.2 This SOP describes the analytical procedures used by Accutest laboratories to perform sample extract cleanup prior to analysis in aqueous and solid matrices using SW 846 3640A and the USEPA Contract Laboratory Program Organics Statement of Work.

1.3 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules.

1.4 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.5 This method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

1.6 This method is used to cleanup extracts obtained from the extraction of aqueous samples using continuous liquid/liquid extract (Accutest SOP EOP008-02) and solid samples using sonication extraction (Accutest SOP EOP012-02)

2.0 SUMMARY OF METHOD

2.1 Sample extracts that contain the presence higher molecular weight compounds are present that interfere with the analyses of target compounds are required to be cleaned up by GPC. The GPC column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer or electron capture detector to the target compounds.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards, and surrogate standards (or SMCs for VOA), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest.

RESOLUTION - also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RETENTION TIME (RT) - the time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's retention time falling within the specified retention time window established for that compound. Retention time is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. All reagents and glassware must be free of contamination from the compounds of interest and other extraneous compounds that could interfere with the analysis.

4.2 Method blanks are analyzed each day samples are prepared (extraction) to demonstrate that all equipment and reagents are not contaminated with any target compound at concentrations above the CRQL.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. Accutest maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method, which is accessible by the staff. A reference file of material safety data handling sheets is available to all personnel involved in these analyses. Use reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.3 Many of the analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the Aroclors. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 SAMPLE PRESERVATION AND HOLDING TIME

6.1 Procedure for Sample Extract Storage. Sample extracts must be protected from light and stored at $4^{o}C$ ($\pm 2\ ^{o}C$). Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants. Samples, sample extracts, and standards must be stored separately.

6.2 Contract Required Holding Times. Analysis of sample extracts must be completed within 40 days following the start of extraction. GPC can be performed anytime within the 40 day period.

7.0 APPARATUS AND MATERIALS

7.1 Gel Permeation Chromatography System.

GPC, Waters Instruments, consisting of a Waters Model 501 HPLC pump, a Waters Model 717 auto sampler, a Waters Model 441 UV detector and a Waters fraction collector.

7.2 Chromatographic Columns - Envirogel GPC Cleanup Column, 19 mm x 150 mm and Envirogel GPC Cleanup Column 19 mm x 150 mm, connected in series. The columns are packed with high

performance, fully porous, highly cross-linked, styrene divinylbenzene copolymer particles with 100A
pore size and a nominal particle size of 15um.

7.3 Ultraviolet detector – Waters 441, fixed wavelength (254 nm) with a semi-prep flow-through cell.

7.4 Strip chart recorder - recording integrator, BBC SE 120

7.5 Syringe Filter Assembly, disposable – SRI "Prep Disc" sample filter assembly – 25 mm, 0.45um and 5 um filter discs as needed. Rinse each filter assembly prior to use with methylene chloride.

8.0 REAGENTS AND STANDARDS

8.1 GPC Calibration and Calibration Verification Solutions. Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below:

Analyte	Concentration mg/ml
Corn oil	25.0
Bis-2-ethylhexyl phthalate	0.5
Methoxychlor	0.1
Perylene	0.02
Sulfur	0.08

8.1.1 Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Weigh the corn oil after warming and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

8.2 GPC Pesticides & PCB Calibration Verification Solution.

8.2.1 Prepare a GPC calibration verification solution in methylene chloride that contains the following compounds. The concentrations listed below are used or a 5 ml GPC injection loop.

Compound	Concentration ug/ml
gamma-BHC (Lindane)	0.1
Heptachlor	0.1
Aldrin	0.1
4,4'-DDT	0.2
Endrin	0.2
Dieldrin	0.2

The Aroclor mixture contains 2 ug/ml each of Aroclor 1016 and 1260 in methylene chloride.

8.2.2 Store the GPC calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4 ^{o}C (± 2 ^{o}C) and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every six months, or more frequently if necessary.

8.2.3 Store all other working standard solutions in amber glass bottles or vials with Teflon lined screw caps at 4 °C (± 2 °C) and protect from light. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months, or sooner if comparison with quality control check samples indicates a problem, except for the PEM solution which must be prepared weekly. Allow all standard solutions to equilibrate to room temperature before use.

8.2.4 Samples, sample extracts, and standards must be stored separately

8.3 Solvents - Ultra pure, pesticide residue analysis grade: Methylene chloride, Methanol, Toluene, and Acetone.

8.3.1 Methylene Chloride, Hexane, Acetone, Toluene, and Iso-octane - pesticide quality or equivalent. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

9.0 COLUMN PREPARATION

9.1 GPC Column Preparation.

9.1.1 Purchase pre-packed GPC columns containing Bio Beads (SX-3).

9.1.2 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube to force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x O.010" ID x 2". Pump methylene chloride through the column at a rate of 5 ml/min for one hour.

9.1.3 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as the one in Section 9.1.2) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline.

9.1.4 The restrictor will not affect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

9.1.5 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

10.0 CALIBRATION

10.1 Instrument Operation

10.1.1 Turn on HPLC pump

10.1.1.1 Set pressure to 5000 PSI.

10.1.1.2 Allow pressure to equilibrate, verify the absence of leaks or clogs by observing pressure readings.

10.1.2 Open auto sampler and load extract vials. Close door when finished.

10.1.3 Program system for a 2ml injection volume and a run tike of 32 minutes.

10.1.4 Establish dump and collection times based on the calibration retention time data.

10.1.5 Turn on the UV detector, allow absorbances to zero.

10.1.6 When all operating systems have achieved equilibrium, push the start button to initiate the GPC cleanup run.

10.1.7 Always follow Water's instructions for operating the GPC system. Monitor changes in pressure, solvent flow rate, and temperature conditions will affect analyte retention times and affect dump and collection times.

10.2 Calibration of GPC for Semi-Volatile Organics.

10.2.1 The GPC calibration procedure and GPC CCV procedure require monitoring the elution of standards with a UV detector connected to the GPC column.

10.2.2 Using the auto sampler, load the calibration solution (Section 8.3.1) onto the GPC. Establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis (2-ethylhexyl) phthalate and after the elution of corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur.

10.2.3 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.2.4 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may indicate problems with the system during sample processing.

10.2.5 Analyze a GPC blank of methylene chloride after each GPC calibration or each GPC CCV. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (K-D) evaporator. Add internal standards at the appropriate concentration and analyze the concentrate by GC/MS.

10.3 Calibration of GPC for Pesticides Analyses.

10.3.1 Follow the GPC calibration procedure above (10.2) with the following exceptions.

10.3.1.1 Using the auto sampler, load the calibration solution onto the GPC. Determine the elution times for the phthalate, methoxychlor, and perylene. Phthalate will elute first; perylene, last.

10.3.1.2 Choose a "DUMP" time which removes > 85 percent of the phthalate. Choose a "COLLECT" time so that > 95 percent of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a “WASH" time of 10 minutes. Adjust the dump and collect times to compensate for the difference in volume of the lines between the detector and the collection flask.

10.3.1.3 Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the collect cycle using Kuderna-Danish (K-D) evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/EC according to the procedures in EGCPCLP. Assuming that the blank represents a 1 L water sample extract, calculate the analyte concentrations using Equation 13.

10.3.1.4 The analyte concentrations in a GPC blank must be less than the CRQL of any pesticide compound in Table 1.

10.4 GPC Calibration Verification: Pesticides & PCBs

10.4.1 The GPC calibration must be routinely verified with two check mixtures.

10.4.2 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples, including matrix spikes, matrix spike duplicates, and blanks are cleaned up using the GPC.

10.4.3 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every seven days.

10.4.4 Procedure for GPC Calibration Verification: Pesticides & PCBs

10.4.4.1 The instructions below are for a GPC injection loop of 5 ml. If a 2 ml injection loop is used, adjust the volume to 4 ml instead of 10 ml before injection extract on the GPC.

10.4.4.2 The pesticide GPC calibration verification solution contains the following six compounds in methylene chloride: gamma-BHC (Lindane), Heptachlor, and Aldrin each at a concentration of 0.1 ug/ml for a 5 ml GPC loop (0.25 ug/ml when a 2 ml GPC loop is used) and 4,4'-DDT , Endrin, and Dieldrin at 0.2 µg/ml (0.50 ug/ml for a 2 ml loop). The Aroclor mixture contains 2 ug/ml each of Aroclor 1016 and 1260 in methylene chloride (5.0 ug/ml when a 2 ml GPC loop is used).

10.4.4.3 Load sample vial number one with 8 ml of the pesticide GPC calibration verification solution. Load sample vial number two with 8 ml of the Aroclor calibration verification solution. Collect individual fractions using the auto sequence from the GPC program established be the UV detector calibration procedure.

10.4.4.4 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 ml portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced and exchanged to hexane after cooling following (SOP EOP008, sec 9.3.3). The final volume is adjusted to 10 ml, and the sample is analyzed by GC. Analysis on the confirmatory column is unnecessary.

10.4.4.5 The pattern of the Aroclor quantitation peaks and the recovery of each single component analyte must be determined for evaluation and reporting purposes.

10.4.4.6 The recovery of each of the single component analytes must be between 80 - 110 percent.

10.4.4.7 The Aroclor patterns must be the same as those from the Aroclor 1016 and Aroclor 1260 standards in the initial calibration sequence.

10.4.4.8 If the recoveries are out of the acceptance window or if changes in the relative peak heights of the patterns of the Aroclor are observed, the columns must be replaced and the GPC recalibrated before proceeding with the GPC cleanup of any extracts.

10.5 Corrective Action for GPC Calibration

10.5.1 If the requirements in Section 10.3.4 cannot be met, clean the column may by processing several 5 ml volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts.

10.5.2 If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated.

10.5.3 A UV trace that does not meet criteria also indicates that a new column is needed.

10.5.4 If the GPC blank is equal to or exceeds the CRQL of any pesticide compound in Table 1, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.6 Technical Acceptance Criteria for GPC Calibration and GPC CCV

10.6.1 The GPC system must be calibrated and verified at the prescribed frequency. The UV trace must meet the following requirements:

- Symmetrical peaks must be present for all compounds in the calibration solution.

- Corn oil and the phthalate peaks must exhibit > 85.0 percent resolution.
- The phthalate and methoxychlor peaks must exhibit > 85.0 percent resolution.
- Methoxychlor and perylene peaks must exhibit > 85.0 percent resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit > 90.0 percent baseline resolution.

10.6.2 If the retention time shift is > 5.0 percent between calibrations take corrective action. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.6.3 Submit a copy of the two most recent UV traces of the calibration solution with the data for the associated samples.

10.6.4 The analyte concentrations in the GPC blank must be less than the CRQL for all semivolatile target compounds in Table 1, except phthalate esters, which must be less than 5 times the CRQL.

11.0 PROCEDURE

11.1 GPC is required for all soil/sediment extracts. It is also required for water extracts containing high molecular weight contaminants that interfere with the analysis of the target analytes.

11.1.1 Maintain laboratory temperatures at approximately 22 ^{o}C to prevent outgassing of the methylene chloride. To avoid retention time shifts, maintain a constant laboratory temperature , which will cause the dump and collect times to become unsynchronized.

11.2 Reduce the volume of all soil/sediment extracts that have not been cleaned-up using GPC to 0.5 ml (if possible) to remove most of the acetone using the nitrogen evaporation technique. The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Adjust the soil/sediment extract volume to 4 ml with methylene chloride.

11.3 Sample Extract Cleanup by GPC

11.3.1 Dilute highly viscous sample extracts prior to cleanup In order to prevent overloading of the GPC column. Dilute and Load any sample extract with a viscosity greater than that of a 1:1 glycerol:water into several loops. Similarly, dilute and load extracts containing more than 40 mg/ml of non-volatile residue into several loops. Determine the non-volatile residue by evaporating a 100 uL aliquot of the extract to dryness in a tared aluminum weighing pan. Carefully monitor the GPC system to assure that the required amount is being injected on the column. Viscous extracts or extracts containing a large amount of non-volatile residue will cause problems with an automated injection system's ability to inject the proper amount of sample extract on a column. After the sample extract has been processed, check the remaining sample extract in the injection vial before proceeding with extract cleanup to assure that the proper amount was injected on the column. If the proper amount of extract was not injected, the sample must be re-prepared and the sample extract must be diluted and loaded into several loops. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected from each run.

11.3.2 Procedure for GPC Sample Cleanup

11.3.2.1 Filter the extract through either a 5 micron or 0.5 micron filter disc (depending on the extract appearance) by attaching a syringe filter assembly containing the filter disc to a 10 ml syringe. Particles greater than 5 microns may scratch the valve resulting in system leaks and cross contamination of extracts in the sample loops. Draw the sample extract through the filter assembly and into the 10 ml syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container with a Teflon-lined screw cap. Draw a minimum of 4 ml of extract into a 10 ml syringe.

11.3.2.2 Avoid introducing particulates or glass wool into the GPC switching.

11.3.2.3 Follow the steps in sections 10.1 and 10.2 for operation of the GPC system.

11.3.2.4 If the sample does not load, part of the system may be blocked. Take appropriate corrective action following manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

11.3.2.5 After loading the autosampler, process each sample using the collect and dump cycle time initially established.

11.3.2.6 Collect each sample in a glass sample tube using the automatic fraction collector. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems.

- Solvent flow rate change caused by column channeling or column pressure changes
- Increase in column operating pressure due to the absorption of particles or gel fines onto the guard column (if used) or the analytical column gel.
- Leaks in the system or significant variances in room temperature.

11.3.1 Recombine any samples that were split into two or more autosampler vials before proceeding with concentration.

11.4 Sample Cleanup by GPC: Pesticides & PCBs

11.4.1 After the appropriate GPC fraction has been collected for each sample, concentrate the extract following the steps in EOP012 Section 9.3. Proceed to solvent exchange to hexane as described in Section 9.3.3 and Florisil cleanup in Section 9.6.

11.4.2 Any samples that were split into two or more vials must be recombined before proceeding with concentration.

11.4.3 Concentrate the hexane extract of samples, which have been subjected to GPC cleanup, to 5 ml using nitrogen evaporation using the steps in EOP012 Section 9.4. Proceed to EOP012- Section 9.6 for Florisil cartridge cleanup.

13.0 Pollution Prevention & Waste Management

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, ESM003. This document describes the proper disposal of all wastes generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 Documentation

14.1 Record the analytical sequence in the instrument logbook prior to initiating the analysis.

14.2 Document reasons for re-analysis in the comments section of the log book.

14.3 Record all standards preparation data in the standards logbook. All columns must be completed and countersigned by a supervisor. Cross reference the Accutest lot number on the standard vial.

14.4 The instrument maintenance logbook must be completed whenever maintenance is performed on the instrument. There is a separate logbook for each instrument.

Table 1

Pesticides/ PCB (Aroclors) Target Compound List (TCL)
Contract Required Quantitation Limits (CRQLs)

Pesticides/ PCBs (Aroclors)	CAS No.	Quantitation Limits		
		Water ug/l	Soil ug/kg	On Column pg
alpha-BHC	319-84-6	0.05	1.7	5
beta-BHC	319-85-7	0.05	1.7	5
delta-BHC	319-86-8	0.05	1.7	5
gamma-BHC (Lindane)	58-89-9	0.05	1.7	5
Heptachlor	76-44-8	0.05	1.7	5
Aldrin	309-00-2	0.05	1.7	5
Heptachlor epoxide	1024-57-3	0.05	1.7	5
Endosu1fan I	959-98-8	0.05	1.7	5
Dieldrin	60-57-1	0.1	3.3	10
4,4'-DDE	72-55-9	0.1	3.3	10
Endrin	72-20-8	0.1	3.3	10
Endosulfan II	33213-65-9	0.1	3.3	10
4,4'-DDD	72-54-8	0.1	3.3	10
Endosulfan sulfate	1031-07-8	0.1	3.3	10
4,4'-DDT	50-29-3	0.1	3.3	10
Methoxychlor	72-43-5	0.5	17	50
Endrin ketone	53494-70-5	0.1	3.3	10
Endrin aldehyde	7421-93-4	0.1	3.3	10
alpha-Chlordane	5103-71-9	0.05	1.7	5
gamma-Chlordane	5103-74-2	0.05	1.7	5
Toxaphene	8001-35-2	5	170	500
Aroclor-1016	12674-11-2	1	33	100
Aroclor-1221	11104-28-2	2	67	200
Aroclor-1232	11141-16-5	1	33	100
Aroclor-1242	53469-21-9	1	33	100
Aroclor-1248	12672-29-6	1	33	100
Aroclor-1254	11097-69-1	1	33	100
Aroclor-1260	11096-82-5	1	33	100

Analysis of PCB Congeners
By USEPA Method 1668A

Samples are spiked with isotopically labelled surrogate standards, solvent extracted and cleaned up on a series of chromatographic columns which may include silica, Florisil, alumina, carbon/Celite and gel permeation columns. The final extract is spiked with isotopically labelled recovery (internal) standards prior to instrumental analysis. Analysis of the extract is performed on high-resolution mass spectrometer (HRMS) coupled to a high-resolution gas chromatograph (HRGC) equipped with a SPB-Octyl chromatography column (30 m, 0.25 mm i.d., 0.25 µm film thickness). Resolution of the PCB 156/157 coelution may be achieved by high resolution GC/MS using a DB-1 chromatography column (30 m, 0.25 mm id, 0.25 µm film thickness). The method is carried out in accordance with the protocols described in EPA Method 1668A *with changes and correction through to August 20, 2003*, incorporating the AXYS modifications described below. Details of all procedures are documented in AXYS method MLA-010, *Analytical Method for Determination of 209 PCB Congeners by EPA Method 1668A*.

Method Modifications:

Section 4.2.1, 4.2.2: The protocol for washing reusable glassware includes a detergent wash, water rinse and baking at a minimum of 300℃ for 8 hours. Immediately prior to use, glassware is solvent rinsed with toluene and hexane.

Section 4.7: The first cleanup column for tissue extracts is a gravity gel permeation column (SX-3 Biobeads). An anthropogenic isolation column 7.5.3 is not used.

Section 6.5.1: Glass wool is cleaned by rinsing twice with toluene and twice with hexane.

Section 7.12, 7.13, 9.0, 11.0: The concentration of the labeled toxics/LOC and the cleanup standard spiking solutions is 100 ng/mL and the sample spiking volume is 20 µL. The resulting final concentrations in the extracts are as specified in the method.

Section 7.14: Concentration of the labeled injection internal standard spiking solution (recovery standard) is modified so that a volume of 5 µL is added. The resulting amount of standard added to the final extract is the same as specified in the method. The solution is spiked into a 15 µL extract volume for a final extract volume of 20 µL.

*Section 7.*2.1: Powdered, not granular, sodium sulphate is baked at a minimum of 300℃ for 8 hrs rather than at 600℃ for 24 hrs.

Section 7.5.1: Silica is activated by baking at 450℃ in a muffl e oven for at least 8 hrs.

Section 7.5.4.1.1: Florisil is baked at 450℃ in a muffle over for a t least 8 hrs, and then deactivated with water to 2.1% deactivation.

*Section 10.*3.3, *15.3.3:* A S:N ratio of 3:1 for di-PCBS and nona-PCBs in CS0.2 calibration solution is acceptable.

Section 11.5.6: Unless requested by the client, the aqueous portion after filtration of aqueous samples with >1% solids is not discarded but is extracted.

Section 11.5, 11.5.2, 11.5.5 12.3 Solid samples are dried by mixing with anhydrous sodium sulphate. The dried solid is extracted using a soxhlet extraction apparatus. The surrogate

spike is incorporated after the drying step. Equilibration time is 30 minutes. The extracting solvent for solids is dichloromethane.

Section 11.8, 12.4: The surrogate spike is incorporated into the sample after the drying step to eliminate the possibility of disproportional loss of volatile labeled and target compounds.

Section 12.4.2: The pre-cleaning of the soxhlet apparatus is carried out using toluene instead of dichloromethane.

Section 12.4.9: Lipid analysis is carried out by sub-sampling two 2g portions of the extract from a total 30 g extract weight. The cleanup standard is spiked into the extract after soxhlet extraction and before any lipid analysis or rotary evaporation is done. The percent recoveries are corrected for the amount of extract used for lipid analysis.

Section 12.6.1.1: Rotary evaporation is done at 30℃. Daily cleanin g of the rotary evaporators include dismantling and rinsing/soaking in solvent. Mimic proofs are run periodically but are not archived daily.

Section 12.7.4: Before Florisil or alumina cleanup procedures, a solvent exchange is done by reducing under nitrogen to 300 uL and bulking up to 1mL in hexane. If toluene is present the extract is reduced to 50 uL under nitrogen and bulked up to 1mL.

Section 12.7.7: Toluene (1 mL) is added to the eluate from the final column prior to rotary evaporation and nitrogen blow down concentration steps.

Section 13.1.1: GPC chromatography, by a gravity column, is routinely used only for tissue extracts. The GPC cleanup is optional for all other matrices.

Section 13.3.1: Routine layered silica column is as follows: 0.5 g neutral silica, 2 g 28% basic silica, 0.5 g neutral silica, 4 g 44% acidic silica, 4 g 22% acidic silica, 1 g neutral silica.

Section 13.3.4: The sample is loaded onto the column followed by 2-3 rinses of a least 1 mL, and eluted with 100 mL of hexane.

Section 14.2: The volume of labeled injection internal standard (recovery standard) added to the extract is 5 µL, for a final extract volume of 20 µL. Hexane rather than nonane is used as the solvent to bring extract back to volume for re-analysis or to dilute extracts.

Section 15.3: The calibration solution containing all 209 PCB congeners is used as the CAL/VER solution.

*Section 17.*5: Extracts are diluted with hexane. The concentration of the labeled injection internal (recovery) standard is not re-adjusted to 100 pg/uL when dilutions are performed.

Section 17.0

$Conc_i$ - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:
Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%\text{Recovery} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

Table 1. QC Acceptance Criteria for PCBs in CAL/VER, IPR, OPR, and Samples[1]

Congener	Cong. No.[2]	Test conc ng/mL	CAL/VER[4] (%)		IPR[5] (%)		OPR[6] (%)		Labelled compound recovery in samples	
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
2-MoCB	1	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4-MoCB	3	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'-DiCB	4	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4,4'-DiCB	15	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6-TrCB	19	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4'-TrCB	37	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6,6'TeCB	54	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4'-TeCB	77	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4',5-TeCB	81	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,6,6'-PeCB	104	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4'-PeCB	105	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,4,4',5-PeCB	114	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5-PeCB	118	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2',3,4,4',5-PeCB	123	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5-PeCB	126	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,4',6,6'-HxCB	155	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5-HxCB[3]	156	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5'-HxCB[3]	157	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5,5'-HxCB	167	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5,5'-HxCB	169	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,4',5,6,6'-HpCB	188	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5'-HpCB	189	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',5,5',6,6'-OcCB	202	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5',6-OcCB	205	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',4,4',5,5',6-NoCB	206	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3,'4,5,5',6,6'-NoCB	208	50	75-125	70-130	40	60-140	70-130	50-150	-	-
DeCB	209	50	75-125	70-130	40	60-140	70-130	50-150	-	-
Labelled Compounds										
$^{13}C_{12}$-2-MoCB	1L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-4-MoCB	3L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,3',4,4'-TCB	77L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5-HxCB[3]	156L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[3]	157L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
Cleanup Standard										
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
2. Suffix "L" indicates labelled compound.
3. PCBs 156 and 157 are tested as the sum of two concentrations

4. CAL VER: Calibration Verification test run at least every 12 hours
5. IPR: Initial Precision and Recovery demonstration
6. OPR: Ongoing Precision and Recovery test run with every batch of samples.

Table 1 con't

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)[1]
Procedural Blank	Analyte concentrations in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be less than 2 pg/congener/sample, and concentrations of PCB congeners 156, 157, 167 and 189 must be less than 10 pg/congener/sample. Concentrations of all other individual PCB congeners or coelutions must be less than 50 pg/congener/sample in blank samples. The sum of all 209 congeners must be less than 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10x the blank levels.
Detection Limit	Typical sample specific detection limits for individual congeners, determined from chromatographic noise, range from 0.5 to 2.0 pg.
Initial Calibration	For 6-point calibration, a relative standard deviation of the RRF's ≤20% for all compounds. Ion ratios for all congeners must be within ±15% of theoretical for CS 0.2. Minimum S:N ratio 10:1 for all calibration standards, except for CS0.2, where the S:N may be as low as 3:1 for di-PCBs and nona-PCBs.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within ±15% of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for all calibration standards except for CS0.2, where the S:N may be as low as 3:1 for di-PCBs and nona-PCBs .

[1.] Duplicate criterion is a guideline, final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

ANALYSIS OF POLYCHLORINATED DIOXINS AND FURANS BY EPA METHOD 1613B

Samples are spiked with a suite of isotopically labelled surrogate standards prior to analysis, solvent extracted, and cleaned up through a series of chromatographic columns that may include gel permeation, silica, Florisil, carbon/Celite, and alumina columns. The extract is concentrated and spiked with an isotopically labelled recovery (internal) standard. Analysis is performed using a high-resolution mass spectrometer coupled to a high-resolution gas chromatograph equipped with a DB-5 capillary chromatography column (60 m, 0.25 mm i.d., 0.1 µm film thickness). A second column, DB-225 (30 m, 0.25 mm i.d., 0.15 µm film thickness), is used for confirmation of 2,3,7,8-TCDF identification. All procedures are carried out according to protocols as described in EPA Method 1613B, with the significant modifications summarized below. The data are evaluated against QC criteria presented in Tables 1 and 2.

Method Modifications:

Section 2.1.2

Non-aqueous liquid from multiphase sample is combined with the solid phase and extracted by Dean Stark soxhlet.

Section 7.2.1

Anhydrous sodium sulphate (Na_2SO_4) is purchased in powder form (not granular) and is baked overnight prior to use. There is no solvent rinse with dichloromethane.

Section 7.10

The concentration of the labelled compound spiking solution is 100 ng/mL (except for OCDD which is 200 ng/mL) and the sample spiking volume is 20 µL. The resulting concentrations in the final extracts are as specified in the method.

Section 7.11

The concentration of the clean-up standard spiking solution is 10 ng/mL and the sample spiking volume is 20 µL. The resulting concentration in the final extracts are as specified in the method.

Sections 7.13, 14.0, 15.0

An additional lower level calibration solution, 0.2 times the concentration of CS1, is prepared and included in the initial calibration series. Initial calibration is based on a six-point series.

Section 7.14

The concentration of the PAR spiking solutions is 0.2/1.0/2.0 ng/mL for tetra/penta, hexa, hepta, hexa/octas respectively and the spiking volume is 1 mL. The resulting final concentration in the extracts are as specified in the method.

Section 9.3.3, Table 7

Acceptance criteria for the percent recovery of surrogate standards in samples have been revised. Criteria that are higher than 130% have been lowered to 130%, as presented in Table 1.

Section 11.5

Aqueous samples containing >1% visible solids are prepared and extracted using the same procedure as samples containing ≤1% visible solids. This involves extracting the solids by soxhlet and the filtrate by separatory funnel extraction and combining the extract from the two phases.

Section 12.0

Samples with sufficiently low moisture content may be mixed with Na_2SO_4 and extracted using regular soxhlet apparatus in 80:20 toluene:acetone.

Section 12.4

The equilibration time for the sodium sulphate drying step is that required to produce a dry, free flowing powder (minimum thirty minutes). This may be less than the 12-hour minimum specified in EPA 1613B.

Section 12.5.1

Samples are spiked with cleanup standard right after extraction and before reduction; not spiked into the separatory funnels containing the extracts prior to the acid/base wash.

Section 12.6.1.1

Rotary evaporator baths are maintained at 35ºC. Mimic proofs are collected instead of collecting proofs each day and archiving.

Section 13.0

Extracts may be cleaned up on silica, alumina and carbon chromatographic columns using a Fluid Management System (FMS) automated cleanup system.

Section 13.7

Gravimetric lipid analysis is carried out on two subsamples of the extract.

Sections 14.0, 15.0, 16.0, Table 8, Table 9

M/Z channels 354/356 and 366/368 are used to confirm and quantify the native and surrogate penta-substituted dioxins, respectively; this change from the method's specification is made in the instrument method in order to avoid a persistent interference in the 356/358 and 368/370 M/Z channels. The theoretical ratio for the P5CDD M/M+2 ions is 0.61; therefore, the acceptance range is 0.52 - 0.70.

Section 15.3.5, Table 6

Acceptance criteria for calibration verification concentrations have been modified, as presented in Table 1, so that ranges do not exceed 70-130% of the test concentration.

Section 15.5.3 Table 6

Acceptance specifications for OPR concentrations have been modified, as presented in Table 1, so that ranges do not exceed 70-130%.

Section 17.0

$Conc_i$ - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:

Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%\mathrm{Recovery} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;

M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;

$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

.

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

Section 17.5

Extracts may be diluted with solvent and re-analyzed by GC/MS isotope-dilution to bring the instrumental response to within the linear range of the instrument. For very high-level samples where a smaller sample aliquot may not be representative, extracts may be diluted and re-spiked with labelled quantification standards and re-analyzed by GC/MS to bring the instrumental response analytes within range. Final results may be recovery corrected using the mean recovery of labelled quantification standards.

Table 1. QC Acceptance Criteria for PCDD/F in CAL/VER, IPR, OPR and Test Samples[1]

	Test Conc ng/mL	IPR[2]		OPR[3] (%)	I-CAL %	CAL/VER[4] (%)	Labelled Cmpd %Rec. in Sample	
		RSD (%)	X(%)				Warning Limit	Control Limit
Native Compound								
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-129	-	-
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-130	-	-
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-
2,3,4,7,8-PeCDF	50	17	72-150	70-130	20	82-122	-	-
1,2,3,4,7,8-HxCDD	50	19	78-152	70-130	20	78-128	-	-
1,2,3,6,7,8-HxCDD	50	15	84-124	76-130	20	78-128	-	-
1,2,3,7,8,9-HXCDD	50	22	74-142	70-130	35	82-122	-	-
1,2,3,4,7,8-HxCDF	50	17	82-108	72-130	20	90-112	-	-
1,2,3,6,7,8-HxCDF	50	13	92-120	84-130	20	88-114	-	-
1,2,3,7,8,9-HxCDF	50	13	84-122	78-130	20	90-112	-	-
2,3,4,6,7,8-HxCDF	50	15	74-158	70-130	20	88-114	-	-
1,2,3,4,6,7,8-HpCDD	50	15	76-130	70-130	20	86-116	-	-
1,2,3,4,6,7,8-HpCDF	50	13	90-112	82-122	20	90-110	-	-
1,2,3,4,7,8,9-HpCDF	50	16	86-126	78-130	20	86-116	-	-
OCDD	100	19	86-126	78-130	20	79-126	-	-
OCDF	100	27	74-146	70-130	35	70-130	-	-
Surrogate Standards								
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-130	35	72-130	40-120	23-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130
$^{13}C_{12}$-OCDD	200	48	20-138	25-130	35	70-130	25-120	17-130
Cleanup Standard								
$^{37}Cl_4$-2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130

[1] QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
[2] IPR: Initial Precision and Recovery demonstration
[3] OPR: Ongoing Precision and Recovery test run with every batch of samples.
[4] CAL VER: Calibration Verification test run at least every 12 hours

Table 2. QC Specifications for QC Samples, Instrumental Analysis, and Analyte Quantification

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)[1]
Procedural Blank	**Blood:** TCDD/F <0.2 pg/sample, PeCDD/F <0.5 pg/sample, HxCDD/F and HpCDD/F <1.0 pg/ sample, OCDD/F<5 pg/sample **Other Matrices:** TCDD/F <0.5 pg/sample, PeCDD/F, HxCDD/F, HpCDD/F <1.0 pg/sample, OCDD/F <5 pg/sample Higher levels acceptable where all sample concentrations a >10X the blank
Detection Limit	SDL Requirements **Blood:** Tetra-penta-CDD/F 0.2 pg/sample Hexa-octa-CDD/F 0.5 pg/sample **Other Matrices**: 1 pg/sample
Instrument Carryover: **Toluene Blank** **Samples**	 A. 1st toluene blank following CAL-VER must have <0.6 pg TCDD and <25 pg OCDD B. 2nd toluene blank following CAL-VER must have <0.2 pg TCDD and <0.8 pg Pe – HpCDD/f, and <0.5 pg OCDD. <10% contribution from preceding sample (based on observed instrument carryover
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Must be within ±15% of theoretical
Sensitivity	S:N≥10:1 for all compounds for 0.1 pg/µL (CS-0.2), plus For bloods: S:N≥3:1 for 0.025 pg/µL 2,3,7,8-T4CDD

[1] Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

METHOD SUMMARY

ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) and ALKYLATED PAHs BY METHOD MLA-021

This method summary describes the determination of concentrations of PAHs, and alkylated PAHs in solid (sediment, soil, ash), tissue (including blood), aqueous, XAD-2 column (resin and filters), air, and oil samples and in solvent extracts by MLA-021. This method can also be used to analyze alkanes and hopanes.

List of Analytes

Analyte List of Standard PAH Parents and Select Alkylated PAHs determined by linearity method

Parent	
Naphthalene	Benzo(b)fluoranthene
Acenaphthylene	Benzo(j/k)fluoranthenes
Acenaphthene	Benzofluoranthenes
Fluorene	Benzo(e)pyrene
Phenanthrene	Benzo(a)pyrene
Anthracene	Perylene
Fluoranthene	Dibenzo(ah)anthracene
Pyrene	Indeno(1,2,3-cd)pyrene
Benz(a)anthracene	Benzo(ghi)perylene
Chrysene	
Alkylated PAHs	
2-Methylnaphthalene	1-Methylphenanthrene
2,6-Dimethylnaphthalene	Dibenzothiophene
2,3,5-Trimethylnaphthalene	

Analyte List of Alkylated PAHs determined by linearity method

1-Methylnaphthalene	C1-Phenanthrenes/Anthracenes
C1-Naphthalenes	1,7-Dimethylphenanthrene
1,2-Dimethylnaphthalene	1,8-Dimethylphenanthrene
C2-Naphthalenes	2,6-Dimethylphenanthrene
2,3,6-Trimethylnaphthalene	3,6-Dimethylphenanthrene
C3-Naphthalenes	C2-Phenanthrenes/Anthracenes
1,4,6,7-Tetramethylnaphthalene	1,2,6-Trimethylphenanthrene
C4-Naphthalenes	C3-Phenanthrenes/Anthracenes
2-Methylphenanthrene	Retene
3-Methylphenanthrene	C4-Phenanthrenes/Anthracenes
9/4-Methylphenanthrenes	Biphenyl
2-Methylanthracene	

Analyte List Extended alkylated PAHs determined by bracketing method

C1-Biphenyls	C1-Fluoranthenes/Pyrenes
C2-Biphenyls	C2-Fluoranthenes/Pyrenes
C1-Acenaphthenes	C3-Fluoranthenes/Pyrenes
2-Methylfluorene	C4-Fluoranthenes/Pyrenes
C1-Fluorenes	1-Methylchrysene
1,7-Dimethylfluorene	5/6-Methylchrysenes
C2-Fluorenes	C1-Benz(a)anthracenes/Chrysenes
C3-Fluorenes	5,9-Dimethylchrysene
2/3-Methyldibenzothiophenes	C2-Benz(a)anthracenes/Chrysenes
C1-Dibenzothiophene	C3-Benz(a)anthracenes/Chrysenes
2,4-Dimethyldibenzothiophene	C4-Benz(a)anthracenes/Chrysenes
C2-Dibenzothiophene	7-Methylbenzo(a)pyrene
C3-Dibenzothiophene	C1-Benzofluoranthenes/Benzopyrenes
C4-Dibenzothiophene	C2-Benzofluoranthenes/Benzopyrenes
3-Methylfluoranthene/Benzo(a)fluorene	

1. EXTRACTION PROCEDURES

Aqueous sample extraction

Up to 1 L clear, aqueous sample is spiked with a suite of perdeuterated surrogate standards and extracted by shaking with dichloromethane. The extract is dried over anhydrous sodium sulphate.

Samples with visible particulates are spiked with a suite of perdeuterated surrogate standards and filtered prior to extraction. The filtrate is extracted separately as above and the filter with the particles is Soxhlet extracted as solids (see below). The two extracts are combined.

Soxhlet extraction of solids (sediment, soil, ash and tissue)

Sediments are thawed and homogenized and the moisture is determined. Up 10 g of the sample is dried by mixing with anhydrous sodium sulphate. The sample is spiked with a suite of perdeuterated surrogate standards (table 1) and extracted with dichloromethane (sediment and soil) or toluene (ash) by Soxhlet extraction.

Fly ash is digested with dilute hydrochloric acid and filtered. The filtrate is extracted by shaking with dichloromethane. The filter with the particles is spiked with surrogate standards and Soxhlet extracted with toluene. The two extracts are combined.

Base digest extraction of tissue, soil and sediment

10-30 g of homogenized, wet sample is mixed with 100 mL methanol and spiked with a suite of perdeuterated surrogate standards. Potassium hydroxide solution is added and the mixture is boiled under reflux for 1 hour. Ultra pure water is added and the boiling is continued for 1½ hour. The liquid phase is extracted by shaking with pentane. The pentane extract is washed with ultra pure water and dried over anhydrous sodium sulphate.

XAD-2 columns and filters

XAD-2 resin and associated filters are spiked with surrogate standards and separately extracted by Soxhlet extraction or Dean-Stark Soxhlet extraction.

PUF and filters

Polyurethane foam (PUF) samplers and associated filters are spiked with surrogate standards and extracted together by Soxhlet extraction with dichloromethane.

Oil

The oil sample is dissolved in pentane and spiked with a suite of perdeuterated surrogate standards. The solution is backwashed by shaking with water and dried over anhydrous sodium sulphate.

Blood samples

The blood sample is spiked with a suite of perdeuterated surrogate standards and extracted by shaking with a mixture of ethanol, hexane and saturated ammonium sulphate solution. The hexane extract is backwashed by shaking with water and dried over anhydrous sodium sulphate.

2. CLEAN-UP CHROMATOGRAPHY

A solid extract is treated with activated copper to remove sulphur. Sample extracts are loaded onto a silica gel column and eluted into two fractions with pentane followed by dichloromethane. The pentane fraction contains the alkanes (if required) and the dichloromethane fraction contains the PAHs. Each fraction is concentrated to a small volume and recovery (internal) standards are added.

Sample extracts for PAH analysis containing lipids may benefit from being cleaned up by gel permeation (Biobead) before silica column cleanup. If necessary, extracts may also be cleaned up by alumina column chromatography to remove interferences.

3. INSTRUMENTAL ANALYSIS

HRGC/LRMS analysis is conducted on a low-resolution mass spectrometer (MS) equipped with a high-resolution gas chromatograph. A splitless/split injection sequence is used on a Restek Rt_x-5 chromatography column (30 m, 0.25 mm i.d., 0.25 µm film thickness) coupled directly to the MS source. The MS is operated at a unit mass resolution in the electron impact (EI) ionization mode using multiple ion detection (MID) acquiring at least one characteristic ion for each target analyte and surrogate standard.

4. ANALYTE QUANTIFICATION

Concentrations of target PAHs are calculated using the isotope dilution method of quantification. Compounds are quantified by comparing the area of the quantification ion to that of the corresponding deuterium-labelled standard and correcting for response factors. Response factors are determined daily using authentic PAHs. Calculations are carried out using HP EnviroQuant and Prolab MS-Extended for targeting and quantification.

$$\text{Concentration of Target} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}}\right) \times \left(\frac{\text{weight of Surr Std (ng)}}{\text{RRF}}\right) \times \left(\frac{1}{\text{weight of sample (g or L)}}\right)$$

(ng/g or ng/L)

$$\textit{where} \quad \text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}}\right) \times \left(\frac{\text{concentration of Surr Std}}{\text{concentration of Target}}\right)$$

and the Surr Std is either the surrogate or the internal standard

Table 1: Surrogates Used and RRF Determination for PAH

TARGET ANALYTES	SURROGATE	RRF DETERMINED FROM
Naphthalene	d_8-Naphthalene	Naphthalene
Acenaphthylene	d_8-Acenaphthylene	Acenaphthylene
Acenaphthene	d_8-Acenaphthylene	Acenaphthene
Fluorene	d_{10}-Phenanthrene	Fluorene
Phenanthrene	d_{10}-Phenanthrene	Phenanthrene
Anthracene	d_{10}-Phenanthrene	Anthracene
Fluoranthene	d_{10}-Fluoranthene	Fluoranthene
Pyrene	d_{10}-Fluoranthene	Pyrene
Benz[a]anthracene	d_{12}-Benz[a]anthracene	Benz[a]anthracene
Chrysene[1]	d_{12}-Chrysene	Chrysene
Benzo[b]fluoranthene	d_{12}-Benzo[b]fluoranthene	Benzo[b]fluoranthene
Benzo[j,k]fluoranthenes	d_{12}-Benzo[k]fluoranthene	Benzo[k]fluoranthene
Benzo[e]pyrene	d_{12}-Benzo[a]pyrene	Benzo[e]pyrene
Benzo[a]pyrene	d_{12}-Benzo[a]pyrene	Benzo[a]pyrene
Perylene	d_{12}-Perylene	Perylene
Dibenzo[ah]anthracene[2]	d_{14}-Dibenzo[ah]anthracene	Dibenz[ah]anthracene
Indeno[1,2,3-cd]pyrene	d_{12}-Indeno[1,2,3,cd]pyrene	Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene	d_{12}-Benzo[ghi]perylene	Benzo[ghi]perylene
Biphenyl[3]	d_{10}- Biphenyl	Biphenyl
Dibenzothiophene[3]	d_{10}-Phenanthrene	Dibenzothiophene
1-Methylnaphthalene[3]	d_{10}-2-Methylnaphthalene	1-Methylnaphthalene
2-Methylnaphthalene[3]	d_{10}-2-Methylnaphthalene	2-Methylnaphthalene
C1-Naphthalenes[3]	d_{10}-2-Methylnaphthalene	1- & 2-Methylnaphthalene
2,6-Dimethylnaphthalene[3]	d_{12}-2,6 Dimethylnaphthalene	2,6-Dimethylnaphthalene
1,2-Dimethylnaphthalene	d_{12}-2,6 Dimethylnaphthalene	1,2-Dimethylnaphthalene
C2-Naphthalenes[3]	d_{12}-2,6 Dimethylnaphthalene	2,6- & 1,2-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene[3]	d_{12}-2,6 Dimethylnaphthalene	2,3,5- Trimethylnaphthalene
2,3,6-Trimethylnaphthalene	d_{12}-2,6 Dimethylnaphthalene	2,3,6- Trimethylnaphthalene

[1] Coelutes with Triphenylene
[2] Coelutes with Dibenz[ac]anthracene
[3] These compounds are in addition to the regular suite of analytes, and are analyzed by client request only.
[4] Secondary ion confirmation procedures do not apply
[5] RRT ranges apply to alkylated PAH Totals

TARGET ANALYTES	SURROGATE	RRF DETERMINED FROM
C3-Naphthalenes[3]	d_{12}-2,6 Dimethylnaphthalene	2,3,5- & 2,3,6-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene	d_{12}-2,6 Dimethylnaphthalene	1,4,6,7-Tetramethylnaphthalene
C4-Naphthalene	d_{12}-2,6 Dimethylnaphthalene	1,4,6,7-Tetramethylnaphthalene
2-Methylanthracene	d_{10}-Phenanthrene	2-Methylanthracene
3-Methylphenanthrene	d_{10}-Phenanthrene	1- & 2-Methylphenanthrene & 2-Methylanthracene
2-Methylphenanthrene	d_{10}-Phenanthrene	2-Methylphenanthrene
9/4-Methylphenanthrenes	d_{10}-Phenanthrene	1- & 2-Methylphenanthrene & 2-Methylanthracene
1-Methylphenanthrene[3]	d_{10}-Phenanthrene	1-Methylphenanthrene
C1-Phenanthrenes/Anthracenes[3]	d_{10}-Phenanthrene	1- & 2-Methylphenanthrene & 2-Methylanthracene
3,6-Dimethylphenanthrene[3]	d_{10}-Fluoranthrene	3,6-Dimethylphenanthrene
2,6-Dimethylphenanthrene	d_{10}-Fluoranthrene	3,6- & 1,7-Dimethyl-phenanthrenes
1,7-Dimethylphenanthrene	d_{10}-Fluoranthrene	1,7-Dimethylphenanthrene
1,8-Dimethylphenanthrene	d_{10}-Fluoranthrene	3,6- & 1,7-Dimethyl-phenanthrenes
C2-Phenanthrenes/Anthracenes[3]	d_{10}-Fluoranthrene	3,6- & 1,7-Dimethyl-phenanthrenes
1,2,6-Trimethylphenanthrene	d_{10}-Fluoranthrene	1,2,6-Trimethylphenanthrene
C3-Phenanthrenes/Anthracenes	d_{10}-Fluoranthrene	1,2,6-Trimethylphenanthrene
Retene[3]	d_{10}-Fluoranthene	Retene
C4-Phenanthrenes/Anthracenes	d_{10}-Fluoranthrene	Retene
C1-Biphenyls	d_{10}- Biphenyl	Biphenyl
C2-Biphenyls	d_{10}- Biphenyl	Biphenyl
C1-Acenaphthenes	d_8-Acenaphthylene	Acenaphthene
2-Methylfluorene	d_8-Acenaphthylene	2-Methylfluorene
C1-Fluorenes	d_8-Acenaphthylene	2-Methylfluorene
1,7-Dimethylfluorene	d_8-Acenaphthylene	1,7-Dimethylfluorene
C2-Fluorenes	d_8-Acenaphthylene	1,7-Dimethylfluorene
C3-Fluorenes	d_8-Acenaphthylene	1,7-Dimethylfluorene
2/3-Methyldibenzothiophenes	d_{10}-Phenanthrene	2/3-Methyldibenzothiophenes
C1-Dibenzothiophenes	d_{10}-Phenanthrene	2/3-Methyldibenzothiophenes
2,4-Dimethyldibenzothiophene	d_{10}-Phenanthrene	2,4-Dimethyldibenzothiophene
C2-Dibenzothiophenes	d_{10}-Phenanthrene	2,4-Dimethyldibenzothiophene
C3-Dibenzothiophenes	d_{10}-Phenanthrene	2,4-Dimethyldibenzothiophene
C4-Dibenzothiophenes	d_{10}-Phenanthrene	2,4-Dimethyldibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene	d_{10}-Fluoranthrene	3-Methylfluoranthene
C1-Fluoranthenes/Pyrenes	d_{10}-Fluoranthrene	3-Methylfluoranthene
C2-Fluoranthenes/Pyrenes	d_{10}-Fluoranthrene	3-Methylfluoranthene
C3-Fluoranthenes/Pyrenes	d_{10}-Fluoranthrene	3-Methylfluoranthene
C4-Fluoranthenes/Pyrenes	d_{10}-Fluoranthrene	3-Methylfluoranthene
5/6-Methylchrysenes	d_{12}-Chrysene	6-Methylchrysene
1-Methylchrysene	d_{12}-Chrysene	1-Methylchrysene
C1-Benz(a)anthracenes/Chrysenes	d_{12}-Chrysene	1- & 6-Methylchrysenes
5,9-Dimethylchrysene	d_{12}-Chrysene	5,9-Dimethylchrysene
C2-Benz(a)anthracenes/Chrysenes	d_{12}-Chrysene	5,9-Dimethylchrysene
C3-Benz(a)anthracenes/Chrysenes	d_{12}-Chrysene	5,9-Dimethylchrysene
C4-Benz(a)anthracenes/Chrysenes	d_{12}-Chrysene	5,9-Dimethylchrysene
7-Methylbenzo(a)pyrene	d_{12}-Benzo[a]pyrene	7-Methylbenzo(a)pyrene
C1-Benzofluoranthenes/Benzo-pyrenes	d_{12}-Benzo[a]pyrene	7-Methylbenzo(a)pyrene

TARGET ANALYTES	SURROGATE	RRF DETERMINED FROM
C2-Benzofluoranthenes/Benzo-pyrenes	d_{12}-Benzo[a]pyrene	7-Methylbenzo(a)pyrene
LABELLED SURROGATE STANDARDS	**RECOVERY CALCULATED AGAINST**	
d_8-Naphthalene	d_{10}-Acenaphthene	
d_{10}-2-Methylnaphthalene	d_{10}-Acenaphthene	
d_{10}-Biphenyl	d_{10}-Acenaphthene	
d_{12}-2,6-Dimethylnaphthalene	d_{10}-Acenaphthene	
d_8-Acenaphthylene	d_{10}-Acenaphthene	
d_{10}-Phenanthrene	d_{10}-Pyrene	
d_{10}-Fluoranthene	d_{10}-Pyrene	
d_{12}-Benz[a]anthracene	d_{10}-Pyrene	
d_{12}-Chrysene	d_{10}-Pyrene	
d_{12}-Benzo[b]fluoranthene	d_{12}-Benzo[e]pyrene	
d_{12}-Benzo[k]fluoranthene	d_{12}-Benzo[e]pyrene	
d_{12}-Benzo[a]pyrene	d_{12}-Benzo[e]pyrene	
d_{12}-Perylene	d_{12}-Benzo[e]pyrene	
d_{12}-Indeno[1,2,3,cd]pyrene	d_{12}-Benzo[e]pyrene	
d_{14}-Dibenzo[ah]anthracene	d_{12}-Benzo[e]pyrene	
d_{12}-Benzo[ghi]perylene	d_{12}-Benzo[e]pyrene	
LABELLED RECOVERY STANDARDS		
d_{10}-Acenaphthene		
d_{10}-Pyrene		
d_{12}-Benzo[e]pyrene		

5. QUALITY ACCEPTANCE CRITERIA

Table 2: QC Acceptance Criteria

	Typical Sample Specific* Detection Limits							Procedural Blank Level (ng)	Acceptable Matrix Spike % Recovery
MATRIX	Solid	Aqueous	Tissue	XAD Column	PUF	Filter	Oil		
Analyte:	ng/g	ng/L	ng/g	ng	ng	ng	ng/g		
Naphthalene	0.5	5	0.1	5	5	5	50	<10	70-130
Acenaphthylene	0.5	5	0.1	5	5	5	50	<5	70-140
Acenaphthene	0.5	5	0.1	5	5	5	50	<5	70-130
Fluorene	0.5	5	0.1	5	5	5	50	<5	60-140
Phenanthrene	0.5	5	0.1	5	5	5	50	<10	70-130
Anthracene	0.5	5	0.1	5	5	5	50	<5	70-130
Fluoranthene	0.5	5	0.1	5	5	5	50	<5	70-130
Pyrene	0.5	5	0.1	5	5	5	50	<5	70-130
Benz(a)anthracene	0.5	5	0.1	5	5	5	50	<5	70-130
Chrysene	0.5	5	0.1	5	5	5	50	<5	70-130
Benzo(b)fluoranthene	0.5	5	0.1	5	5	5	50	<5	70-130
Benzo(j/k)fluoranthenes	0.5	5	0.1	5	5	5	50	<5	70-130
Benzo(e)pyrene	0.5	5	0.1	5	5	5	50	<5	70-130
Benzo(a)pyrene	0.5	5	0.1	5	5	5	50	<5	70-130
Perylene	1.0	10	0.2	10	10	10	100	<5	70-130
Dibenzo(ah)anthracene	1.0	10	0.2	10	10	10	100	<5	70-130
Indeno(1,2,3-cd)pyrene	1.0	10	0.2	10	10	10	100	<5	70-130
Benzo(ghi)perylene	1.0	10	0.2	10	10	10	100	<5	70-130
Biphenyl	1.0	10	0.2	10	10	10	100	<5	70-130
Dibenzothiophene	1.0	10	0.2	10	10	10	100	<5	60-140
1-Methylnaphthalene	1.0	10	0.2	10	10	10	100	<5	70-130
2-Methylnaphthalene	1.0	10	0.2	10	10	10	100	<5	70-130
2,6-Dimethylnaphthalene	1.0	10	0.2	10	10	10	100	<10	70-130
1,2-Dimethylnaphthalene	1.0	10	0.2	10	10	10	100	<10	60-140
2,3,5-Trimethylnaphthalene	1.0	10	0.2	10	10	10	100	<10	50-150
2,3,6-Trimethylnaphthalene	1.0	10	0.2	10	10	10	100	<10	50-150
1,4,6,7-Tetramethyl-naphthalene	1.0	10	0.2	10	10	10	100	<10	50-200
2-Methylanthracene	1.0	10	0.2	10	10	10	100	<5	50-150
3-Methylphenanthrene	1.0	10	0.2	10	10	10	100	<10	N.A.
2-Methylphenanthrene	1.0	10	0.2	10	10	10	100	<10	50-150
9/4-Methylphenanthrenes	1.0	10	0.2	10	10	10	100	<10	N.A.
1-Methylphenanthrene	1.0	10	0.2	10	10	10	100	<10	50-150
3,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	100	<10	50-150
2,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	100	<10	N.A.
1,7-Dimethyl-phenanthrenes	1.0	10	0.2	10	10	10	100	<10	50-150
1,8-Dimethylphenanthrene	1.0	10	0.2	10	10	10	100	<10	N.A.
1,2,6-Trimethyl-phenanthrene	1.0	10	0.2	10	10	10	100	<10	50-150
Retene	1.0	10	0.2	10	10	10	100	<5	50-150
2-Methylfluorene	1.0	10	0.2	10	10	10	100	<5	50-150
1,7-Dimethylfluorene	1.0	10	0.2	10	10	10	100	<5	50-150

2/3-Methyldibenzo-thiophenes	1.0	10	0.2	10	10	10	100	<10	50-150
2,4-Dimethyl-dibenzothiophene	1.0	10	0.2	10	10	10	100	<5	50-150
3-Methylfluoranthene/ Benzo(a)fluorene	1.0	10	0.2	10	10	10	100	<5	50-150
5/6-Methylchrysenes	1.0	10	0.2	10	10	10	100	<5	50-150
1-Methylchrysene	1.0	10	0.2	10	10	10	100	<5	50-150
5,9-Dimethylchrysene	1.0	10	0.2	10	10	10	100	<5	50-150
7-Methylbenzo(a)pyrene	1.0	10	0.2	10	10	10	100	<5	50-150
Typical Sample Size	10 g	1 L	10 g	1 col	1 PUF	1 filter	0.1 g		
Typical Final Volume (µL)	500	100	100	500	500	500	500		

* Detection limits quoted are those routinely achieved. Lower detection limits can be achieved if required.
NOTE: QC Acceptance criteria do not apply to alkylated PAH total values (e.g. C1-phenanthenes/anthracenes). These should be flagged as TIC (Tentatively Identified Compounds).

SURROGATE STANDARD RECOVERIES:	**% RECOVERY RANGES ALL MATRICES**
d_8-naphthalene	15 – 130
d_8-acenaphthylene	20 – 130
d_{10}-phenanthrene	30 – 130
d_{10}-fluoranthene	30 – 130
d_{12}-benz[a]anthracene	30 – 130
d_{12}-chrysene	30 – 130
d_{12}-benzo[b]fluoranthene	30 – 130
d_{12}-benzo[k]fluoranthene	30 – 130
d_{12}-benzo[a]pyrene	30 – 130
d_{12}-perylene	30 – 130
d_{14}-dibenz[ah]anthracene	30 – 130
d_{12}-indeno[1,2,3-cd]pyrene	30 – 130
d_{12}-benzo[ghi]perylene	30 – 130
d_{10}-2-methylnaphthalene	20 – 130
d_{12}-2,6-dimethylnaphthalene	20 – 130
d_{10}-biphenyl	15 – 130

Parameter	Acceptance Specification
Procedural Blank	Refer to Table 2 above, or 5 times lower than analogous analyte value detected in the samples.
Analysis Duplicate	Duplicates must fall within ±20% of the mean (applicable to concentrations >10 times the DL) These are guidelines – departures based on professional judgement allowed.
Instrument Sensitivity	S/N 3:1 for 10 pg of acenaphthene, dibenzo(a,h)anthracene.
Instrument Resolution	*AXYS Method*: For calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220, Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220. *EPA Regulatory Method*: In accordance with the specification of the EPA Method.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present and all labelled compounds, ≤35% for targets with no labelled analog present.
Bracketing Cal	RRFs for the opening and closing calibrations over a 12 hour period must agree to within +/- 20% of the mean (ie <40 RPD between RRFs and for the opening and closing calibrations).
Continuing Cal Ver	Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within ±25% of expected values for all targets. Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%
GC Resolution	Benzo[b] & [k]fluoranthene valley height must be ≤75% for equal concentrations. Phenanthrene/anthracene valley height must be ≤30% for equal concentrations.
Chromatogram Quality	Maximum peak width must be ≤15 seconds for dibenzo[ghi]perylene peak at 10% peak height.
Retention Time Window (RRT)	RRT are ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). A second requirement is that an authentic elute after its labelled analog.
Ion Abundance Ratios	CAL VER: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL All other native analytes and labelled surrogates must be ±20% of the mid-point of the I-CAL Samples: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the 12 hour CAL (CAL VER or Bracketing) calibration standard. All other native analytes and labelled surrogates must be ±20% of the 12 hour CAL (CAL VER or Bracketing) calibration standard.

METHOD SUMMARY

ANALYSIS OF ORGANOCHLORINE PESTICIDES BY HRGC/HRMS BY METHOD MLA-028

This method is for determination of the organochlorine pesticides in water, solids (soil, sediment, sludge), tissue (including blood and milk), aqueous samples, XAD-2 water sampling columns, air samples and solvent extracts by HRGC/HRMS instrumentation.

*List of Analytes (*Chlorinated Pesticides)

E1 Pesticides by HRGC/MS	E2 Pesticides by HRGC/MS
1,4-dichlorobenzene (1,3-Cl_2-BZ)	Heptachlor epoxide
1,3-dichlorobenzene (1,4-Cl_2-BZ)	alpha-Endosulphan
1,2-dichlorobenzene(1,2-Cl_2-BZ)	delta-HCH[1]
1,2,4-trichlorobenzene (1,2,4-Cl_3-BZ)	Dieldrin
1,2,3-trichlorobenzene (1,2,3-Cl_3-BZ)	Endrin
1,3,5-trichlorobenzene (1,3,5-Cl_3-BZ)	Methoxychlor
1,2,4,5-tetrachlorobenzene (1,2,4,5-Cl_4-BZ)	Endosulphan sulphate
1,2,3,5-tetrachlorobenzene (1,2,3,5-Cl_4-BZ)	Endrin ketone
1,2,3,4-tetrachlorobenzene (1,2,3,4-Cl_4-BZ)	beta-Endosulphan
Pentachlorobenzene (Cl_5-BZ)	Endrin aldehyde
Hexachlorobenzene (HCB)	
alpha-HCH	
beta-HCH	
gamma-HCH	
delta-HCH[1]	
Heptachlor	
Aldrin	
Oxychlordane	
trans-Chlordane	
Cis-Chlordane	
o,p'-DDE	
p,p'-DDE	
trans-Nonachlor	
Cis-Nonachlor	
o,p'-DDD	
p,p'-DDD	
o,p'-DDT	
p,p'-DDT	
Mirex	
Hexachlorobutadiene (Cl_6-Butadiene upon request)	
Octachlorostyrene (upon request)	
Toxaphene (upon request -organochlorine scan or separate ECNI GC/MS analysis)	

[1] delta-HCH can be found in both E1 and E2 Fractions

1. Extraction and Cleanup Procedures

Samples are spiked with a suite of isotopically labelled surrogate standards before extraction. Water is extracted by shaking with dichloromethane. Solids and tissue are dried with sodium sulphate and Soxhlet extracted with dichloromethane. XAD-2 resin is Soxhlet extracted with dichloromethane. Filters are extracted with toluene in a Dean-Stark extractor. Milk and blood are extracted into hexane. Gel permeation chromatography is performed on some sample extracts. The extracts are cleaned up and separated into two fractions, E1 and E2, using Florisil. Each fraction is spiked with isotopically labelled recovery (internal) standard(s) and analysed for a suite of organochlorine pesticides by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

2. HRGC/HRMS Analysis

Instrumental analysis of the E1 and E2 fractions is performed on a high-resolution gas chromatograph (HRGC) equipped with a J&W DB-5 chromatography column (60 m, 0.25 mm i.d., 0.10 µm film thickness) coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at a static (8000) mass resolution (10% valley) in the electron ionization (EI) mode using multiple ion detection (MID).

Initial calibration is performed using a multi-point calibration series of solutions that encompass the working concentration range. Calibration is verified at least once every twelve hours by analysis of a mid-level calibration solution.

3. Quantification Procedures

Target concentrations are determined with respect to labelled surrogate standards as shown in Tables 1 and 2. Mean relative response factors (RRF) determined from the initial calibration runs are used to convert raw peak areas in sample chromatograms to final concentrations as follows:

$$\text{Concentration of target} = \left(\frac{\text{area of Target}}{\text{area of Surrogate}}\right) \times \left(\frac{\text{weight of Surrogate}}{\text{weight of Sample}}\right) \times \left(\frac{1}{\text{RRF}}\right)$$

$$\text{where} \quad \text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Surrogate}}\right) \times \left(\frac{\text{concentration of Surrogate}}{\text{concentration of Target}}\right)$$

Final concentrations are recovery corrected by the method of quantification.

Sample specific detection limits (SDLs) reported with the analytical results are determined from the analysis data by converting the minimum detectable signal to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as three times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labelled surrogate peak.

Recoveries of surrogates are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality.

Table 1: Surrogates Used and RRF Determination for Total Toxaphene by GC/MS

Compound Name	Surrogate	RRF Determined From
Toxaphene Peaks T1, T2, T3, T4,T5, T6, T7	^{13}C-PCB 138	Toxaphene Peaks T1, T2, T3, T4,T5, T6, T7
Surrogate Standard		
^{13}C-PCB 180	^{13}C-PCB 138	Toxaphene Peaks T1, T2, T3, T4,T5, T6, T7
Recovery Standard		
^{13}C-PCB 138		

Table 2:. Surrogates Used, and RRF Determination for E1 Pesticides by HR GC/MS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Quantification and Retention Time Reference	RRF Determination
1,3-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ	
1,4-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ	
1,2-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ	
1,3,5-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ	
1,2,4-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ	
1,2,3-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ	
1,2,4,5/3,5-Cl_4-BZ	$^{13}C_6$-1,2,3,4-Cl_4-BZ	
1,2,3,4-Cl_4-BZ	$^{13}C_6$-1,2,3,4-Cl_4-BZ	
Cl_5-BZ	$^{13}C_6$-Cl_5-BZ	
HCB	$^{13}C_6$-HCB	
TCMX	$^{13}C_6$-HCB	
Cl_6-Butadiene	$^{13}C_6$-1,2,3-Cl_3-BZ	1,2,3-Cl_3-BZ
alpha-HCH	$^{13}C_6$-gamma-HCH	
beta-HCH	$^{13}C_6$-beta-HCH	
gamma-HCH	$^{13}C_6$-gamma-HCH	
delta-HCH[2]	$^{13}C_6$-delta-HCH	
Heptachlor	$^{13}C_{10}$-Heptachlor	
Aldrin	$^{13}C_{12}$-Aldrin	
Octachlorostyrene	$^{13}C_{10}$-trans-Chlordane	
Oxychlordane	$^{13}C_{10}$-Oxychlordane	
trans-Chlordane	$^{13}C_{10}$-trans-Chlordane	
cis-Chlordane	$^{13}C_{10}$-trans-Chlordane	
o,p-DDE	$^{13}C_{12}$-o,p-DDE	
p,p-DDE	$^{13}C_{12}$-p,p-DDE	
trans-Nonachlor	$^{13}C_{10}$-trans-Nonachlor	
cis-Nonachlor	$^{13}C_{10}$-cis-Nonachlor	

[2] delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of ^{13}C-delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of ^{13}C-delta-HCH are observed in the E1 fraction.

o,p-DDD	$^{13}C_{12}$-p,p-DDD	
p,p-DDD	$^{13}C_{12}$-p,p-DDD	
o,p-DDT	$^{13}C_{12}$-o,p-DDT	
p,p-DDT	$^{13}C_{12}$-p,p-DDT	
Mirex	$^{13}C_{10}$-Mirex	

Cont'd

Analyte Name	Quantification and Retention Time Reference	RRF Determination
$^{13}C_6$-1,4-Cl_2-BZ	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-1,2,3-Cl_3-BZ	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-1,2,3,4-Cl_4-BZ	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-Cl_5-BZ	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-HCB	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-beta-HCH	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-gamma-HCH	$^{13}C_{12}$-PCB-52	
$^{13}C_6$-delta-HCH	$^{13}C_{12}$-PCB-52	
$^{13}C_{10}$-Heptachlor	$^{13}C_{12}$-PCB-52	
$^{13}C_{10}$-Aldrin	$^{13}C_{12}$-PCB-52	
$^{13}C_{10}$-Oxychlordane	$^{13}C_{12}$-PCB-52	
$^{13}C_{10}$-trans-Chlordane	$^{13}C_{12}$-PCB-138	
$^{13}C_{10}$-trans-Nonachlor	$^{13}C_{12}$-PCB-138	
$^{13}C_{10}$-cis-Nonachlor	$^{13}C_{12}$-PCB-138	
$^{13}C_{12}$-o,p-DDE	$^{13}C_{12}$-PCB-138	
$^{13}C_{12}$-p,p-DDE	$^{13}C_{12}$-PCB-138	
$^{13}C_{12}$-p,p-DDD	$^{13}C_{12}$-PCB-138	
$^{13}C_{12}$-o,p-DDT	$^{13}C_{12}$-PCB-138	
$^{13}C_{12}$-p,p-DDT	$^{13}C_{12}$-PCB-138	
$^{13}C_{10}$-Mirex	$^{13}C_{12}$-PCB-138	
Recovery Standards		
$^{13}C_{12}$-PCB-52		
$^{13}C_{12}$-PCB-138		
Lock Masses		
Lock Mass		
Lock Mass		
Lock Mass		
Lock Mass		

Table 3:. Surrogates Used and RRF Determination for E2 Pesticides by GC/MS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Quantification and Retention Time Reference	RRF Determination
delta-HCH	$^{13}C_6$-delta-HCH	
Heptachlor epoxide	$^{13}C_9$-Heptachlor-Epoxide	
alpha-Endosulphan	$^{13}C_9$-alpha-endosulphan	
Dieldrin	$^{13}C_{12}$-Dieldrin	
Endrin	$^{13}C_{12}$-Endrin	
beta-Endosulphan	$^{13}C_9$-beta-Endosulphan	
Endosulphan sulphate	$^{13}C_9$-beta-Endosulphan	
Endrin aldehyde	$^{13}C_{12}$-Endrin aldehyde	
Endrin ketone	$^{13}C_{12}$-Endrin	
Methoxychlor	$^{13}C_{12}$-Methoxychlor	
Labelled Surrogates		
$^{13}C_6$-delta-HCH	$^{13}C_{12}$-PCB-153	
$^{13}C_9$-Heptachlor-Epoxide	$^{13}C_{12}$-PCB-153	
$^{13}C_9$-alpha-endosulphan	$^{13}C_{12}$-PCB-153	
$^{13}C_{12}$-Dieldrin	$^{13}C_{12}$-PCB-153	
$^{13}C_{12}$-Endrin	$^{13}C_{12}$-PCB-153	
$^{13}C_9$-beta-Endosulphan	$^{13}C_{12}$-PCB-153	
$^{13}C_{12}$-Endrin aldehyde	$^{13}C_{12}$-PCB-153	
$^{13}C_{12}$-Methoxychlor	$^{13}C_{12}$-PCB-153	
Recovery Standard		
$^{13}C_{12}$-PCB-153		
Lock Masses		
Lock Mass		
Lock Mass		
Lock Mass		
13C_{12}-Endrin ketone	breakdown check	

4. QUALITY ACCEPTANCE CRITERIA

Samples are analyzed in batches consisting of a maximum of twenty samples, one procedural blank and one spiked matrix (OPR) sample. Sample duplicates or matrix spike/matrix spike duplicate (MS/MSD) pairs may be analyzed on an individual contract basis. The batch is carried through the complete analytical process as a unit. For sample data to be reportable, the batch QC data must meet the established acceptance criteria presented on the analysis reports.

All aspects of the method are described in detail in AXYS' document MLA-028 "Analytical Procedures for Organochlorine Pesticides by Isotope Dilution HRGC/HRMS".

Table 4: QC Criteria for E1 Chlorinated Pesticides

Analyte	Typical Sample Specific Detection LImits					Procedural Blank Level	Acceptable Matrix Spike
	Solid	Aqueous	Tissue	Pulp	XAD Column		
	ng/g	ng/L	ng/g	ng/g	ng	ng	% Recovery
Dichlorobenzenes	0.1	1.0	0.1	0.05	1.0	<1.0	60-130
Trichlorobenzenes	0.1	1.0	0.1	0.05	1.0	<1.0	60-130
Tetrachlorobenzenes	0.1	1.0	0.1	0.05	1.0	<0.5	60-130
Pentachlorobenzene	0.01	0.1	0.01	0.05	0.1	<0.1	70-130
Hexachlorobenzene	0.01	0.1	0.01	0.05	0.1	<0.1	70-130
alpha-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
beta-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
gamma-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
delta-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
Heptachlor	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
Aldrin	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
Oxychlordane	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
trans-Chlordane	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
cis-Chlordane	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDE	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDE	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
trans-Nonachlor	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
cis-Nonachlor	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDD	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDD	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDT	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDT	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
Mirex	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
Total Toxaphene	0.05	0.5	0.05	NA	0.5	<0.5	60-150
Typical Sample Size:	10 g	1 L	10 g	20 g	1 Column		
Typical Final Vol, µL *	200	200	200	200	200		

*Extract volumes may range from 20 µL to 200 µL. To avoid excessive loss of volatile compounds, where recovery of volatile compounds is critical, extract volumes lower than 100 µL are not recommended.

SURROGATE STANDARD RECOVERIES:	% RECOVERY RANGES ALL MATRICES
$^{13}C_6$-Chlorobenzene	10-130
$^{13}C_6$-1,4-dichlorobenzene	15-130
$^{13}C_6$-1,2,3-trichlorobenzene	20-130
$^{13}C_6$-1,2,3,4-tetrachlorobenzene	20-130
$^{13}C_6$-Pentachlorobenzene	20-150
$^{13}C_6$-Hexachlorobenzene	20-150
$^{13}C_6$-beta-HCH	30-150
$^{13}C_6$-delta-HCH[3]	30-150
$^{13}C_6$-gamma-HCH	30-150
$^{13}C_{10}$-Heptachlor	30-150
$^{13}C_{12}$-Aldrin	30-150
$^{13}C_{10}$-Oxychlordane	30-200
$^{13}C_{10}$-trans-Chlordane	30-200
$^{13}C_{12}$-o,p'-DDE	40-150
$^{13}C_{12}$-p,p'-DDE	40-150
$^{13}C_{10}$-trans-Nonachlor	30-150
$^{13}C_{10}$-cis-Nonachlor	30-150
$^{13}C_{12}$-p,p'-DDD	40-150
$^{13}C_{12}$-o,p'-DDT	40-150
$^{13}C_{12}$-p,p'-DDT	40-150
$^{13}C_{10}$-Mirex	30-150

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL).
Procedural Blank	See Table 4 or <10% of analyte value <0.1 ng for toxaphene.
Instrument Sensitivity	S/N ≥3:1 for 2-4 pg injected for all target analytes (See Table 4). S/N ≥2:1 for 1.6 ng of technical toxaphene.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present, ≤35% for targets with no labelled analog present and all labelled compounds.
Bracketing Cal Ver	RRFs from calibration standards must agree to ±25% over a 12-hour period.
Continuing Cal Ver	Concentrations of native compounds must be within ±20% of expected values for targets with a labelled analog present, ±35% for targets with no labelled analog present. Concentrations of labelled must be within ±35% of expected values.
Chromatogram Quality **Max Peak Width:** **Resolution:**	1. Separation between p,p'-DDD and o,p-DDT □20% of valley height. 2. p,p-DDT breakdown must be ≤15%.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Times	RRT windows are calculated from daily calibration verification run data using RRT references and fixed RT window brackets in seconds are specified in tables 9 and 10.
Ion Ratios	Ion ratios must fall within ±20% (±30% for 13C10-Oxychlordane) of the theoretical values for positive identification of all E1 targets in the calibration standards.

[3] delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of ^{13}C-delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of ^{13}C-delta-HCH are observed in the E1 fraction.

Table 5: QC Criteria for E2 Chlorinated Pesticides

Analyte:	Typical Sample Specific Detection Limits					Procedural Blank Level ng	Acceptable Matrix Spike % Recovery[1]
	Solid	Aqueous	Tissue	Pulp	XAD column		
	ng/g	ng/L	ng/g	ng/g	ng		
Delta-HCH	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Heptachlor epoxide	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
alpha-Endosulphan	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Dieldrin	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Endrin	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Endosulphan sulphate	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Endrin ketone	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
beta-Endosulphan	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Endrin aldehyde	0.05	0.5	0.05	0.05	0.5	<0.5	50-130
Methoxychlor	0.1	1	0.1	0.1	1.0	<1	60-130
Typical Sample Size:	10 g	1 L	10 g	20 g	1 column		
Typical Final Vol, µL*	200	200	200	200	200		

* Extract volumes may range from 20 µL to 200 µL. To avoid excessive loss of volatile compounds, where recovery of volatile compounds is critical, extract volumes lower than 100 µL are not recommended.

[1] Recoveries quoted are guidelines only and vary according to matrix. Consult detailed method performance data available with method documentation for specific criteria.

SURROGATE STANDARD RECOVERIES:	% RECOVERY RANGES ALL MATRICES
$^{13}C_6$-delta-HCH	30-150
$^{13}C_{12}$-Dieldrin	30-150
$^{13}C_{12}$-Endrin	30-150
$^{13}C_{12}$-Endrin aldehyde	30-150
$^{13}C_{10}$-Heptachlor epoxide	30-150
$^{13}C_{12}$-Methoxychlor	30-150
$^{13}C_9$-alpha-Endosulphan	30-150
$^{13}C_9$-beta-Endosulphan	30-150

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL).
Procedural Blank	See Table 5 or <10% of analyte value.
Instrument Sensitivity	S/N ratio ≤3:1 for 4 pg of all analytes.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present, ≤35% for targets with no labelled analog present and all labelled compounds.
Bracketing Cal Ver	RRFs from calibration standards must agree to ±25% over a 12-hour period.
Continuing Cal Ver	Concentrations of native compounds must be within ±20% of expected values for targets with a labelled analog present, ±35% for targets with no labelled analog present. Concentrations of labelled must be within ±35% of expected values.
Chromatogram Quality (GC Resolution)	13C-labelled endrin breakdown must be ≤20%.
Analyte /Surrogate Ratios	Response ratio must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Times	RRT windows are calculated from daily calibration verification run data using RRT references and fixed RT window brackets in seconds are specified in tables 9 and 10.
Ion Ratios	Ion ratios must fall within ±20% of the theoretical values for positive identification of all E2 targets and surrogates (with the exception of labelled methoxychlor which is ±50%) in the calibration standards (Levels C-F) and samples, and within ±50% for calibration standard Level B.

STANDARD OPERATING PROCEDURE

10-Day static whole sediment bioassay using *Chironomus dilutus* or *Chironomus riparius*

OBJECTIVE

To determine the acute toxicity of sediments to the midge larvae, *Chironomus dilutus* or *Chironomus riparius*

ASSOCIATED SOPS

- Sample Collection (GENTOX001.0)
- Dilution Water Collection (GENTOX002.0)
- Cleaning of Laboratory Glassware (GENLAB002.0)
- Preparing of EPA Moderately Hard Water (GENLAB001.0)

MATERIALS

- 300 mL high form lipless beakers
- Tygon tubing siphon
- Refilling disc
- Sieves
- Glass Pasteur pipettes
- Temperature controlled bath or room
- Natural or synthetic freshwater
- Physical chemistry instruments
- Fish flake food
- Weigh pans
- Balance
- Forceps
- Oven
- Muffle furnace
- Desiccator

PROCEDURE

- Test chambers will be prepared by adding 100 mL of sieved and thoroughly mixed sediment to each marked replicate beaker. A total of 175 mL of diluent will be added to the chambers and allowed to settle overnight.

- Samples will be maintained at 2-4 ^{o}C in original containers or new HDPE containers after sieving, if required. Holding time not to exceed client's requirements. Samples may be sieved as per client's instruction.

- Control sediment will be provided by culture facility or will be locally collected from a site of known quality and will be handled as described above.

- A minimum of five replicates of each test sample, reference sample and control sample will be tested employing 10 chironomids per test chamber for a total of 50 organisms per sample. The organisms must be third instar or younger with at least 50 % of the organisms at third instar.

- Length or weight should be measured on a subset of at least 20 organisms prior to test start.

- One hour after organism introduction, the test chambers will be observed for floaters (organisms trapped in the surface film). Floaters will be removed and replaced with new organisms.

- Dissolved oxygen concentrations in each chamber should not fall below 40 % saturation. If the dissolved oxygen levels do fall below acceptable limits begin gentle aeration of all chambers with an oil free air source with a maximum of 100 bubbles/minute. Care must be taken to ensure that the sediment is not disturbed.

- During the test, the organisms in each chamber will be fed 4.0 mg fish food flakes daily.

- Behavioral observations should be made upon the introduction of the organisms to the test. If any larvae do not commence burrowing activities or if any organisms linger on the surface of the sediments for extended periods of time, this should be noted by the investigator on the bench sheet. Dead organisms that appear on the surface of the sediment should be removed as soon as they are noticed. Counts of any emergent flies or pupae should be recorded.

- Tests will be run for 10 days, during which dissolved oxygen, pH and temperature will be measured daily. Alkalinity, ammonia, conductivity and hardness shall be measured in all treatments at the beginning and end of the test.

- Test chamber temperatures will be maintained within 1.0 °C of the test temperature, 23.0° C.

- Twice daily approximately 80% of the overlying water will be removed using a siphon and replaced using a refilling disc to minimize disturbance of the sediment. Renewal of the overlying water is started when the sediment is placed into the test chambers.

- At the conclusion of the test, the surviving organisms will be removed from the test chambers. Many of the organisms can be pipetted from the water column or upper 1 cm of sediment before sieving the samples using a US Standard No. 25 (710μm) sieve.

- The organisms will then be rinsed from the screen into collecting pans and final mortality counts will be made. Surviving organisms will be divided into three separate categories for statistical analysis: percent survival, percent emergence, and percent pupae mortality.

- The organisms will then be rinsed from the screen into collecting pans and final mortality counts will be made. Surviving organisms will be sacrificed test organisms will be placed into tared aluminum weighing boats. The organisms and boats will be dried at 100° C for a minimum of six hours and placed in a desiccator to cool to room temperature. Weights will be measured to the nearest 0.01 mg. If required, ash free dry weights will be determined by placing the dried and weighed test organisms and pans in a muffle furnace for two hours at 550 ^{o}C. Tissue mass will be determined as the difference between the weight of the dried larvae plus pan and the weight of the ashed larvae plus pan.

REFERENCES

- Environmental Protection Agency March 2000. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates. Office of Research and Development US Environmental Protection Agency, Duluth, NM (EPA/600/R-99/064).

STANDARD OPERATING PROCEDURE

28-Day static whole sediment bioassay using *Hyalella azteca*

OBJECTIVE

To determine the chronic toxicity of sediments to the amphipod, *Hyalella azteca*.

ASSOCIATED SOPS

- YCT Preparation (GENCUL002.1)
- Sample Collection (GENTOX001.1)
- Dilution Water Collection (GENTOX002.1)
- Cleaning Laboratory Glassware (GENLAB002.0)
- Preparation of EPA Moderately Hard Water (GENLAB001.0)

MATERIALS

- 300 mL high form lipless beakers
- Tygon tubing siphon
- Refilling disc
- Sieves
- Glass Pasteur pipettes
- Temperature controlled bath or room
- Natural or synthetic freshwater
- Physical chemistry instruments
- YCT (yeast-cerophyll-trout chow food mixture)
- Weigh pans
- Balance
- Forceps
- Oven
- Desiccator

PROCEDURE

- Test chambers will be prepared by adding 100 mL of sieved and thoroughly mixed sediment to each marked replicate beaker. A total of 175 mL of diluent will be added to the chambers and allowed to settle overnight.

- Samples will be maintained at 2-4 ^{o}C in original containers or new HDPE containers after sieving, if required. Holding time not to exceed client's requirements. Samples may be sieved as per client's instruction.

- Control sediment will be provided by culture facility or will be locally collected from a site of known quality and will be handled as described above

- A minimum of five replicates of each test sample, reference sample and control will be tested employing 10 amphipods per test chamber for a total of 50 organisms per sample. The organisms must be 7 to 14 days old at the start of the test.

- Length and/or weight should be measured on a subset of at least 20 organisms used to start the test.

- One hour after organism introduction, the test chambers will be observed for floaters (organisms trapped in the surface film). Floaters will be removed and replaced with new test organisms.

- Dissolved oxygen concentrations in each chamber should not fall below 40% saturation. If the dissolved oxygen levels do fall below acceptable limits begin aeration of all chambers with an oil free air source with a maximum of 100 bubbles/minute. Care must be taken to ensure that the sediment is not disturbed.

- During the test, the organisms in each chamber will be fed 1.5 mL of YCT daily.

- Behavioral observations should be made upon the introduction of the organisms to the test. If any organisms do not commence burrowing activities or if any organisms linger on the surface of the sediments for extended periods of time, this should be noted by the investigator on the bench sheet. Dead organisms that appear on the surface of the sediment should be removed as soon as they are noticed.

- Test will be run for 28 days, during which dissolved oxygen, pH and temperature will be measured daily. Alkalinity, ammonia, conductivity and hardness shall be measured in all treatments at the beginning and end of the test.

- Test chamber temperatures will be maintained within 1.0° C of the test temperature 23° C.

- Twice daily approximately 80% of the overlying water will be removed using a siphon and replaced using a refilling disc to minimize disturbance of the sediment. Renewal of the overlying water is started when the sediment is placed into the test chambers.

- At the conclusion of the test, the surviving organisms will be removed from the test chambers. Many of the organisms can be pipetted from the water column or upper 1 cm of sediment before sieving the samples using a US Standard No. 25 (710 μm) sieve.

- The organisms will then be rinsed from the screen into collecting pans and final mortality counts will be made. Surviving organisms will be sacrificed and length will be determined, if required, measuring from the base of the first antennae to the end of the third uropod. Following length determination, test organisms will be placed into tared aluminum weighing boats. The organisms and boats will be dried at 100° C for a minimum of six hours and placed in a desiccator to cool to room temperature. Weights will be measured to the nearest 0.01 mg.

REFERENCES

- Environmental Protection Agency March 2000. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates. Office of Research and Development US Environmental Protection Agency, Duluth, MN (EPA/600/R-99/064).

STANDARD OPERATING PROCEDURE

10-Day static whole sediment bioassay using the amphipod *Ampelisca abdita*

OBJECTIVE

To determine the acute toxicity of sediments to the amphipod, *Ampelisca abdita*.

ASSOCIATED SOPS

- YCT Preparation (GENCUL002.1)
- Sample Collection (GENTOX001.1)
- Dilution Water Collection (GENTOX002.1)
- Cleaning Laboratory Glassware (GENLAB002.0)
- Preparation of EPA Moderately Hard Water (GENLAB001.0)

MATERIALS

- 1000 mL beakers with or without overflow spouts
- Tygon tubing siphon
- Refilling disc
- Sieves
- Glass Pasteur pipettes
- Temperature controlled bath or room
- Artificial saltwater
- Aeration system
- Physical chemistry instruments
- Weigh pans
- Balance
- Forceps
- Oven
- Desiccator

PROCEDURE

- Test chambers will be prepared by adding ~ 2 cm (175 mL) of sieved and thoroughly mixed sediment to each marked replicate beaker. A total of 175 mL of diluent will be added to the chambers and allowed to settle overnight.

- Overlying water is artificial saltwater at the required salinity generated at the laboratory unless otherwise instructed by the client.

- Control sediment will be provided by culture facility.

- *A. abdita* will be immature individuals, 2-4 mm in length.

- Sediment pore water unionized ammonia must be below 0.4 mg/L. Ammonia analyses will be performed on centrifuged samples prior to test initiation and if levels are above 0.4 mg/L, two volume exchanges of overlying water will be performed daily in the affected samples until the ammonia values are reduced to below 0.4 mg/L.

- A minimum of five replicates of each test sample, reference sample and control will be tested employing 20 amphipods per test chamber for a total of 100 organisms per sample. Care must be take with *A. abdita when* assigning to counting cups and test chambers to insure that they are introduced below the waterline and do not stick to chamber sides.

- Length and/or weight should be measured on a subset of at least 20 organisms used to start the test.

- One hour after organism introduction, the test chambers will be observed for floaters (organisms trapped in the surface film). Floaters will be removed and replaced with new test organisms.

- 24-hour illumination is required for the 10-day exposure at 50-100 ft/candles.

- Behavioral observations should be made upon the introduction of the organisms to the test. If any organisms do not commence burrowing activities or if any organisms linger on the surface of the sediments for extended periods of time, this should be noted by the investigator on the bench sheet. Dead organisms that appear on the surface of the sediment should be removed as soon as they are noticed.

- Test will be run for 10 days. At test initiation and conclusion dissolved oxygen, salinity, pH and temperature will be measured in all chambers. During test conduct a surrogate chamber will be used to measure dissolved oxygen, salinity, pH and temperature. Pore water and overlying water ammonia measurements will be done at test initiation, day 3 (from the surrogate chamber) and at the conclusion of the test.

- Test chamber temperatures will be maintained within 1.0° C of the test temperature 20° C. All chambers will be aerated to maintain dissolved oxygen levels at 90% saturation or better.

- Overlying water exchanges will be made on days 3, 5, and 8, unless otherwise specified by client. Water will be removed using a siphon and replaced using a refilling disc to minimize disturbance of the sediment. Renewal of the overlying water is started when the sediment is placed into the test chambers.

- At the conclusion of the test, the surviving organisms will be removed from the test chambers. Many of the organisms can be pipetted from the water column or upper 1 cm of sediment before sieving the samples using a US Standard No. 25 (710 μm) sieve.

- The organisms will then be rinsed from the screen into collecting pans and final mortality counts will be made. Control survival must ≥ 90%.

REFERENCES

- Environmental Protection Agency 1994. Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine and Amphipods. (EPA/600/R-94/025).
- American Society of Testing and Materials 2008. Standard Test Method for Measuring the Toxicity Sediment-associated Contaminants with Estuarine and Marine Invertebrates. E-1367-03

Attachment 8

Axys Analytical Services PCB Congener Co-Elution List

Attachment 8: AXYS Analytical Services PCB Congener Co-Elution List

USEPA 1668A
TYPICAL DETECTION LIMITS, METHOD DETECTION LIMITS, LOW CALIBRATION LIMITS, AND REPORTING LIMITS
for PCBs

AXYS Method: MLA-010
Instrument Type: High Resolution GC/MS
MDL Protocol: Federal Register 40 CFR Part 136, Appendix B, no iteration

Matrix	SOIL/SEDIMENT/BIOSOLIDS/ASH					TISSUE				
Units/Sample Size	pg/g based on 10g sample					pg/g based on 10g sample				
Analyte	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL
CL1-PCB-1	0.2	0.18	2.0	0.4	0.005	0.2	0.19	2.0	0.4	0.005
CL1-PCB-2	0.2	0.19	2.0	0.4	0.005	0.2	0.16	2.0	0.4	0.005
CL1-PCB-3	0.2	0.19	2.0	0.4	0.005	0.2	0.27	2.0	0.4	0.005
CL2-PCB-4	0.2	0.47	2.0	0.4	0.005	0.2	0.34	2.0	0.4	0.005
CL2-PCB-5	0.2	0.12	2.0	0.4	0.005	0.2	0.20	2.0	0.4	0.005
CL2-PCB-6	0.2	0.19	2.0	0.4	0.005	0.2	0.23	2.0	0.4	0.005
CL2-PCB-7	0.2	0.30	2.0	0.4	0.005	0.2	0.25	2.0	0.4	0.005
CL2-PCB-8	0.2	0.74	2.0	0.4	0.005	0.2	0.17	2.0	0.4	0.005
CL2-PCB-9	0.2	0.16	2.0	0.4	0.005	0.2	0.25	2.0	0.4	0.005
CL2-PCB-10	0.2	0.19	2.0	0.4	0.005	0.2	0.20	2.0	0.4	0.005
CL2-PCB-11	0.2	0.56	2.0	0.4	0.005	0.2	0.43	2.0	0.4	0.005
CL2-PCB-12/13	0.2	0.25	2.0	0.4	0.005	0.2	0.28	2.0	0.4	0.005
CL2-PCB-14	0.2	0.19	2.0	0.4	0.005	0.2	0.34	2.0	0.4	0.005
CL2-PCB-15	0.2	0.37	2.0	0.4	0.005	0.2	0.20	2.0	0.4	0.005
CL3-PCB-16	0.1	0.36	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL3-PCB-17	0.1	0.38	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL3-PCB-19	0.1	0.18	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL3-PCB-21/33	0.1	0.50	2.0	0.4	0.005	0.1	0.44	2.0	0.4	0.005
CL3-PCB-22	0.1	0.35	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL3-PCB-23	0.1	0.14	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL3-PCB-24	0.1	0.13	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL3-PCB-25	0.1	0.17	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL3-PCB-26/29	0.1	0.24	2.0	0.4	0.005	0.1	0.47	2.0	0.4	0.005
CL3-PCB-27	0.1	0.15	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL3-PCB-28/20	0.1	0.94	2.0	0.4	0.005	0.1	0.53	2.0	0.4	0.005
CL3-PCB-30/18	0.1	0.67	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL3-PCB-31	0.1	0.82	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL3-PCB-32	0.1	0.27	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL3-PCB-34	0.1	0.11	2.0	0.4	0.005	0.1	0.36	2.0	0.4	0.005
CL3-PCB-35	0.1	0.16	2.0	0.4	0.005	0.1	0.44	2.0	0.4	0.005
CL3-PCB-36	0.1	0.13	2.0	0.4	0.005	0.1	0.38	2.0	0.4	0.005
CL3-PCB-37	0.1	0.23	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL3-PCB-38	0.1	0.23	2.0	0.4	0.005	0.1	0.30	2.0	0.4	0.005
CL3-PCB-39	0.1	0.21	2.0	0.4	0.005	0.1	0.37	2.0	0.4	0.005
CL4-PCB-41/40/71	0.1	0.49	2.0	0.4	0.005	0.1	0.41	2.0	0.4	0.005
CL4-PCB-42	0.1	0.19	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL4-PCB-43	0.1	0.87	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL4-PCB-44/47/65	0.1	0.57	2.0	0.4	0.005	0.1	0.72	2.0	0.4	0.005
CL4-PCB-45/51	0.1	0.57	2.0	0.4	0.005	0.1	0.33	2.0	0.4	0.005
CL4-PCB-46	0.1	0.13	2.0	0.4	0.005	0.1	0.22	2.0	0.4	0.005
CL4-PCB-48	0.1	0.28	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL4-PCB-50/53	0.1	0.26	2.0	0.4	0.005	0.1	0.38	2.0	0.4	0.005
CL4-PCB-52	0.1	0.44	2.0	0.4	0.005	0.1	0.30	2.0	0.4	0.005
CL4-PCB-54	0.1	0.15	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL4-PCB-55	0.1	0.32	2.0	0.4	0.005	0.1	0.37	2.0	0.4	0.005
CL4-PCB-56	0.1	0.27	2.0	0.4	0.005	0.1	0.72	2.0	0.4	0.005
CL4-PCB-57	0.1	0.31	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL4-PCB-58	0.1	0.41	2.0	0.4	0.005	0.1	0.33	2.0	0.4	0.005
CL4-PCB-59/62/75	0.1	0.36	2.0	0.4	0.005	0.1	0.57	2.0	0.4	0.005
CL4-PCB-60	0.1	0.51	2.0	0.4	0.005	0.1	0.24	2.0	0.4	0.005
CL4-PCB-61/70/74/76	0.1	1.1	2.0	0.4	0.005	0.1	1.32	2.0	0.4	0.005
CL4-PCB-63	0.1	0.26	2.0	0.4	0.005	0.1	0.35	2.0	0.4	0.005
CL4-PCB-64	0.1	0.21	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL4-PCB-66	0.1	0.68	2.0	0.4	0.005	0.1	0.46	2.0	0.4	0.005

Attachment 8: AXYS Analytical Services PCB Congener Co-Elution List

USEPA 1668A
TYPICAL DETECTION LIMITS, METHOD DETECTION LIMITS, LOW CALIBRATION LIMITS, AND REPORTING LIMITS
for PCBs

AXYS Method: MLA-010
Instrument Type: High Resolution GC/MS
MDL Protocol: Federal Register 40 CFR Part 136, Appendix B, no iteration

Matrix	SOIL/SEDIMENT/BIOSOLIDS/ASH					TISSUE				
Units/Sample Size	pg/g based on 10g sample					pg/g based on 10g sample				
Analyte	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL
CL4-PCB-67	0.1	0.24	2.0	0.4	0.005	0.1	0.29	2.0	0.4	0.005
CL4-PCB-68	0.1	0.22	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL4-PCB-69/49	0.1	0.41	2.0	0.4	0.005	0.1	0.62	2.0	0.4	0.005
CL4-PCB-72	0.1	0.18	2.0	0.4	0.005	0.1	0.29	2.0	0.4	0.005
CL4-PCB-73	0.1	0.20	2.0	0.4	0.005	0.1	0.30	2.0	0.4	0.005
CL4-PCB-77	0.1	0.21	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL4-PCB-78	0.1	0.36	2.0	0.4	0.005	0.1	0.33	2.0	0.4	0.005
CL4-PCB-79	0.1	0.42	2.0	0.4	0.005	0.1	0.33	2.0	0.4	0.005
CL4-PCB-80	0.1	0.32	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL4-PCB-81	0.1	0.27	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL5-PCB-82	0.1	0.18	2.0	0.4	0.005	0.1	0.24	2.0	0.4	0.005
CL5-PCB-83/99	0.1	0.60	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL5-PCB-84	0.1	0.22	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL5-PCB-88/91	0.1	0.34	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL5-PCB-89	0.1	0.12	2.0	0.4	0.005	0.1	0.24	2.0	0.4	0.005
CL5-PCB-92	0.1	0.19	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL5-PCB-94	0.1	0.21	2.0	0.4	0.005	0.1	0.13	2.0	0.4	0.005
CL5-PCB-95/100/93/102/98	0.1	4.3	2.0	0.4	0.005	0.1	0.62	2.0	0.4	0.005
CL5-PCB-96	0.1	0.14	2.0	0.4	0.005	0.1	0.08	2.0	0.4	0.005
CL5-PCB-103	0.1	0.13	2.0	0.4	0.005	0.1	0.10	2.0	0.4	0.005
CL5-PCB-104	0.1	0.13	2.0	0.4	0.005	0.1	0.14	2.0	0.4	0.005
CL5-PCB-105	0.1	0.24	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL5-PCB-106	0.1	0.21	2.0	0.4	0.005	0.1	0.14	2.0	0.4	0.005
CL5-PCB-107/124	0.1	0.36	2.0	0.4	0.005	0.1	1.19	2.0	0.4	0.005
CL5-PCB-108/119/86/97/125/87	0.1	0.70	2.0	0.4	0.005	0.1	0.79	2.0	0.4	0.005
CL5-PCB-109	0.1	0.27	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL5-PCB-110/115	0.1	0.48	2.0	0.4	0.005	0.1	0.41	2.0	0.4	0.005
CL5-PCB-111	0.1	0.12	2.0	0.4	0.005	0.1	0.11	2.0	0.4	0.005
CL5-PCB-112	0.1	0.22	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL5-PCB-113/90/101	0.1	0.56	2.0	0.4	0.005	0.1	0.35	2.0	0.4	0.005
CL5-PCB-114	0.1	0.19	2.0	0.4	0.005	0.1	0.37	2.0	0.4	0.005
CL5-PCB-117/116/85	0.1	0.40	2.0	0.4	0.005	0.1	0.40	2.0	0.4	0.005
CL5-PCB-118	0.1	0.48	2.0	0.4	0.005	0.1	0.57	2.0	0.4	0.005
CL5-PCB-120	0.1	0.20	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL5-PCB-121	0.1	0.20	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL5-PCB-122	0.1	0.26	2.0	0.4	0.005	0.1	0.22	2.0	0.4	0.005
CL5-PCB-123	0.1	0.16	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL5-PCB-126	0.1	0.29	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL5-PCB-127	0.1	0.18	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL6-PCB-128/166	0.1	0.81	2.0	0.4	0.005	0.1	0.37	2.0	0.4	0.005
CL6-PCB-130	0.1	0.18	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL6-PCB-131	0.1	0.32	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL6-PCB-132	0.1	0.31	2.0	0.4	0.005	0.1	0.29	2.0	0.4	0.005
CL6-PCB-133	0.1	0.20	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL6-PCB-134/143	0.1	0.46	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL6-PCB-136	0.1	0.42	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL6-PCB-137	0.1	0.42	2.0	0.4	0.005	0.1	0.12	2.0	0.4	0.005
CL6-PCB-138/163/129/160	0.1	1.2	2.0	0.4	0.005	0.1	1.04	2.0	0.4	0.005
CL6-PCB-139/140	0.1	0.58	2.0	0.4	0.005	0.1	0.29	2.0	0.4	0.005
CL6-PCB-141	0.1	0.21	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL6-PCB-142	0.1	0.36	2.0	0.4	0.005	0.1	0.16	2.0	0.4	0.005
CL6-PCB-144	0.1	0.29	2.0	0.4	0.005	0.1	0.22	2.0	0.4	0.005
CL6-PCB-145	0.1	0.25	2.0	0.4	0.005	0.1	0.16	2.0	0.4	0.005
CL6-PCB-146	0.1	0.37	2.0	0.4	0.005	0.1	0.36	2.0	0.4	0.005

Attachment 8: AXYS Analytical Services PCB Congener Co-Elution List

USEPA 1668A
TYPICAL DETECTION LIMITS, METHOD DETECTION LIMITS, LOW CALIBRATION LIMITS, AND REPORTING LIMITS
for PCBs

AXYS Method: MLA-010
Instrument Type: High Resolution GC/MS
MDL Protocol: Federal Register 40 CFR Part 136, Appendix B, no iteration

Matrix	SOIL/SEDIMENT/BIOSOLIDS/ASH					TISSUE				
Units/Sample Size	pg/g based on 10g sample					pg/g based on 10g sample				
Analyte	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL	Typical Detection Limit/SDL	MDL	LMCL based on CS-1	LMCL based on High Sensitivity CS-0.2	Lower RL
CL6-PCB-147/149	0.1	0.62	2.0	0.4	0.005	0.1	0.55	2.0	0.4	0.005
CL6-PCB-148	0.1	0.31	2.0	0.4	0.005	0.1	0.12	2.0	0.4	0.005
CL6-PCB-150	0.1	0.25	2.0	0.4	0.005	0.1	0.16	2.0	0.4	0.005
CL6-PCB-151/135/154	0.1	1.4	2.0	0.4	0.005	0.1	0.40	2.0	0.4	0.005
CL6-PCB-152	0.1	0.31	2.0	0.4	0.005	0.1	0.10	2.0	0.4	0.005
CL6-PCB-153/168	0.1	0.67	2.0	0.4	0.005	0.1	1.32	2.0	0.4	0.005
CL6-PCB-155	0.1	0.11	2.0	0.4	0.005	0.1	0.14	2.0	0.4	0.005
CL6-PCB-156/157	0.1	0.16	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL6-PCB-158	0.1	0.26	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL6-PCB-159	0.1	0.29	2.0	0.4	0.005	0.1	0.30	2.0	0.4	0.005
CL6-PCB-161	0.1	0.31	2.0	0.4	0.005	0.1	0.24	2.0	0.4	0.005
CL6-PCB-162	0.1	0.30	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL6-PCB-164	0.1	0.20	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL6-PCB-165	0.1	0.33	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL6-PCB-167	0.1	0.46	2.0	0.4	0.005	0.1	0.18	2.0	0.4	0.005
CL6-PCB-169	0.1	0.14	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL7-PCB-170	0.1	0.17	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005
CL7-PCB-171/173	0.1	0.44	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL7-PCB-172	0.1	0.22	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL7-PCB-174	0.1	0.16	2.0	0.4	0.005	0.1	0.24	2.0	0.4	0.005
CL7-PCB-175	0.1	0.19	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL7-PCB-176	0.1	0.13	2.0	0.4	0.005	0.1	0.10	2.0	0.4	0.005
CL7-PCB-177	0.1	0.24	2.0	0.4	0.005	0.1	0.23	2.0	0.4	0.005
CL7-PCB-178	0.1	0.12	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL7-PCB-179	0.1	0.12	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL7-PCB-180/193	0.1	0.19	2.0	0.4	0.005	0.1	0.47	2.0	0.4	0.005
CL7-PCB-181	0.1	0.72	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL7-PCB-182	0.1	0.12	2.0	0.4	0.005	0.1	0.26	2.0	0.4	0.005
CL7-PCB-183/185	0.1	0.23	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL7-PCB-184	0.1	0.15	2.0	0.4	0.005	0.1	0.15	2.0	0.4	0.005
CL7-PCB-186	0.1	0.14	2.0	0.4	0.005	0.1	0.10	2.0	0.4	0.005
CL7-PCB-187	0.1	0.10	2.0	0.4	0.005	0.1	0.28	2.0	0.4	0.005
CL7-PCB-188	0.1	0.11	2.0	0.4	0.005	0.1	0.25	2.0	0.4	0.005
CL7-PCB-189	0.1	0.07	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL7-PCB-190	0.1	0.19	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL7-PCB-191	0.1	0.08	2.0	0.4	0.005	0.1	0.14	2.0	0.4	0.005
CL7-PCB-192	0.1	0.15	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL8-PCB-194	0.1	0.11	2.0	0.4	0.005	0.1	0.12	2.0	0.4	0.005
CL8-PCB-195	0.1	0.13	2.0	0.4	0.005	0.1	0.25	2.0	0.4	0.005
CL8-PCB-196	0.1	0.14	2.0	0.4	0.005	0.1	0.34	2.0	0.4	0.005
CL8-PCB-197/200	0.1	0.21	2.0	0.4	0.005	0.1	0.36	2.0	0.4	0.005
CL8-PCB-198/199	0.1	0.16	2.0	0.4	0.005	0.1	0.21	2.0	0.4	0.005
CL8-PCB-201	0.1	0.13	2.0	0.4	0.005	0.1	0.11	2.0	0.4	0.005
CL8-PCB-202	0.1	0.15	2.0	0.4	0.005	0.1	0.19	2.0	0.4	0.005
CL8-PCB-203	0.1	0.14	2.0	0.4	0.005	0.1	0.32	2.0	0.4	0.005
CL8-PCB-204	0.1	0.17	2.0	0.4	0.005	0.1	0.20	2.0	0.4	0.005
CL8-PCB-205	0.1	0.12	2.0	0.4	0.005	0.1	0.17	2.0	0.4	0.005
CL9-PCB-206	0.1	0.19	2.0	0.4	0.005	0.1	0.12	2.0	0.4	0.005
CL9-PCB-207	0.1	0.27	2.0	0.4	0.005	0.1	0.12	2.0	0.4	0.005
CL9-PCB-208	0.1	0.25	2.0	0.4	0.005	0.1	0.11	2.0	0.4	0.005
CL10-PCB-209	0.1	0.24	2.0	0.4	0.005	0.1	0.27	2.0	0.4	0.005