FINAL

QUALITY ASSURANCE PROJECT PLAN including SAMPLING AND ANALYSIS PLAN

Appendix A
HUNTERS POINT SHIPYARD PARCEL F
ESTCP DEMONSTRATION PLAN

Prepared for:

ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM
1155 Herdon Parkway, Suite 900
Herndon, VA 20170

Prepared by:

STANFORD UNIVERSITY
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
TERMAN ENGINEERING CENTER
STANFORD, CA 94305-4020

(Adapted from original QAPP/SAP from the Final Hunters Point Shipyard Parcel F Treatability Study Work Plan prepared for SOUTHWEST DIVISION NAVAL FACILITIES ENGINEERING COMMAND located at San Diego, CA for Project No. G477702 under Contract No. N68711-01-F-6102. The original QAPP/SAP was prepared by Battelle in Duxbury, MA and Stanford University and distributed on July 22, 2004.)

December 5, 2005

This page intentionally left blank.

FINAL

QUALITY ASSURANCE PROJECT PLAN including SAMPLING AND ANALYSIS PLAN

Appendix A
HUNTERS POINT SHIPYARD PARCEL F ESTCP DEMONSTRATION PLAN

Prepared by:

STANFORD UNIVERSITY
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
TERMAN ENGINEERING CENTER
STANFORD, CA 94305-4020

December 5, 2005

REVIEW AND APPROVALS

Project QA Manager, Stanford Yeo-Myoung Cho	Yeo Myoung Cho Name	Date: 11/18/05
Project Manager, Stanford Dennis Smithenry	Dennis W. Smithenry Name	Date: 11/16/05

DISTRIBUTION LIST

This document will be distributed to the following project participants once all approval signatures have been received:

Ryan Ahlersmeyer

Todd Bridges

Yeo-Myoung Cho

Scott Dockum

Lance Dohman

Mark Fleri

Glynis Foulk

Upal Ghosh

Katie Houff

Andrea Leeson

Richard Luthy

Carole-Sue Peven

Dennis Smithenry

Barbara Sugiyama

Hunters Point Shipyard Parcel F ESTCP Demonstration Plan

U.S. EPA QA/R-5 QAPP ELEMENTS

U.S. EPA QA/R-5 QAPP ELEMENT	ESTCP Demonstration Plan QAPP/SAP
A1 Title and Approval Sheet	Title and Approval Sheet
A2 Table of Contents	Table of Contents
A3 Distribution List	Distribution List
A4 Project/Task Organization	A.2.1 Project and Task Organizations
A5 Problem Definition/Background	A.2.2 Problem Definition/Background A.2.3 Site Description
A6 Project/Task Description	A.2.4 Project/Task Description
A7 Quality Objectives and Criteria	A.2.5 Quality Objectives and Criteria
A8 Special Training/Certification	A.2.6 Special Training/Certification
A9 Documents and Records	A.2.7 Documentation and Records
B1 Sampling Process Design	A.3.1 Sampling Process Design (Experimental Design)
B2 Sampling Methods	A.3.2 Field Sampling Methods
B3 Sample Handling and Custody	A.3.3 Sample Processing, Handling, and Custody
B4 Analytical Methods	A.3.4 Analytical Laboratory Methods
B5 Quality Control	A.3.5 Quality Control Requirements
B6 Instrument/Equipment Testing, Inspection, and Maintenance	A.3.6 Instrumentation/Equipment Testing, Inspection, and Maintenance
B7 Instrument/Equipment Calibration and Frequency	A.3.7 Instrument/Equipment Calibration and Frequency
B8 Inspection/Acceptance of Supplies and Consumables	A.3.8 Inspection/Acceptance of Supplies and Consumables
B9 Nondirect Measurements	A.3.9 Nondirect Measurements
B10 Data Management	A.3.10 Data Management
C1 Assessment and Response Actions	A.4.1 Assessment and Response Actions
C2 Reports to Management	A.4.2 Reports to Management
D1 Data Review, Verification, and Validation	A.5.1 Data Review, Validation, and Oversight
D2 Validation and Verification Methods	
D3 Reconciliation with User Requirements	A.5.2 Data Quality Assessment Reconciliation with Planning Objectives

CONTENTS

ATTACHMENTS 8
FIGURES 9
TABLES 9
ACRONYMS AND ABBREVIATIONS 10
A.1.0 INTRODUCTION 12
A.2.0 PROJECT MANAGEMENT 13
A.2.1 Project and Task Organization 13
A.2.2 Problem Definition/Background 15
A.2.3 Site Description 16
A.2.4 Project/Task Description 16
A.2.4.1 Application of Activated Carbon 17
A.2.4.2 Assessment of Reductions in Aqueous PCB Availability and PCB Bioaccumulation 19
A.2.4.3 Assessment of Resuspension Potential 19
A.2.5 Quality Objectives and Criteria 19
A.2.5.1 Data Quality Objectives 19
A.2.5.2 Measurement Quality Objectives 19
A.2.6 Special Training/Certification 21
A.2.6.1 Training Requirements 21
A.2.6.2 Special Training 21
A.2.6.3 Navy Evaluation 22
A.2.6.4 State of California Environmental Laboratory Approval Program 22
A.2.7 Documentation and Records 22
A.2.7.1 Document Control 22
A.2.7.2 Documentation Standards 22
A.2.7.2.1 Changes and Deviations 23
A.2.7.2.2 Definition of Raw Data 23
A.2.7.3 Field Documentation and Forms 23
A.2.7.4 Laboratory Documentation 24
A.2.7.5 Contents of Data Packages 24
A.2.7.6 Electronic Data Deliverable 26
A.2.7.7 Reports 26
A.2.7.8 Storage and Disposal 26
A.3.0 STUDY DESIGN, DATA GENERATION AND ACQUISITION 27
A.3.1 Sampling Process Design (Experimental Design) 27
A.3.2 Field Sampling Methods 28
A.3.2.1 Plot Locations 29
A.3.2.2 Testing Material Deployment and Sampling of Environmental Media for Chemical Analysis 29
A.3.2.2.1 SPMD Deployment and Retrieval 29
A.3.2.2.2 Macoma Tube Deployment and Retrieval 29
A.3.2.2.3 Indigenous Amphipod Sample Collection 29
A.3.2.2.4 Quadrat Surface Sediment Collection and Sieving 30
A.3.2.2.5 Surface Water Sample Collection 30
A.3.2.2.6 Sediment Core Sample Collection 30
A.3.2.2.7 Equipment Decontamination 31

A.3.2.2.8 Management and Disposal of Investigation-Derived Waste 31
A.3.3 Sample Processing, Handling, and Custody 31
A.3.3.1 Sample Processing 31
A.3.3.2 Field Sample Containers and Labeling 31
A.3.3.3 Sample Handling 32
A.3.3.3.1 SPMD Sample Handling 32
A.3.3.3.2 M. nasuta Sample Handling 32
A.3.3.3.3 Indigenous Amphipod Sample Handling 33
A.3.3.3.4 Benthic Community Sample Handling 33
A.3.3.3.5 Surface Water Sample Handling 33
A.3.3.3.6 Sediment Core Processing and Sample Handling 33
A.3.3.3.7 Sample Homogenization 34
A.3.3.4 Field Sample Preservation, Packaging, and Shipment 34
A.3.3.5 Chain-of-Custody Records 34
A.3.3.6 Sample Receipt 35
A.3.4 Analytical Laboratory Methods 36
A.3.4.1 Analytical/Testing Methods for Stanford 36
A.3.4.1.1 PCB Uptake in SPMDs 36
A.3.4.1.2 Sediment Core Processing and Analyses 36
A.3.4.1.3 Stanford PCB Congener Analysis 37
A.3.4.2 Analytical/Testing Methods for ERDC 37
A.3.4.2.1 Extraction of PCBs in Clam and Amphipod Samples 37
A.3.4.2.2 Community Structure Analysis of Benthic Organisms from Surface Sediment Quadrats 38
A.3.4.2.3 ERDC PCB Congener Analysis 39
A.3.4.3 Analytical/Testing Methods for UMBC 39
A.3.4.3.1 Measurement of Aqueous and Suspended Particulate PCB Concentrations in Field Water 39
A.3.4.3.2 PCB Desorption Characteristics of Field Sediments 39
A.3.4.3.3 UMBC PCB Congener Analysis 39
A.3.4.4 Analytical/Testing Methods for BDO 39
A.3.4.4.1 Analysis of PCB Congeners in Archived Sample Splits 40
A.3.4.4.2 Tissue Lipids 41
A.3.4.4.3 Percent Moisture 41
A.3.4.5 General Requirements 41
A.3.5 Quality Control Requirements 41
A.3.5.1 Field Quality Control 41
A.3.5.2 Analytical Laboratory Quality Control 42
A.3.5.3 Control Charts 42
A.3.6 Instrumentation/Equipment Testing, Inspection, and Maintenance 42
A.3.6.1 Field Equipment 42
A.3.6.2 Laboratory Equipment 42
A.3.7 Instrument/Equipment Calibration and Frequency 43
A.3.7.1 Field Equipment 43
A.3.7.2 Laboratory Equipment and Instruments 43
A.3.8 Inspection/Acceptance of Supplies and Consumables 44
A.3.9 Nondirect Measurements 44
A.3.10 Data Management 44
A.3.10.1 Field Data 45
A.3.10.2 Laboratory Data 45
A.3.10.3 Electronic Data Deliverables 45

A.4.0 ASSESSMENTS/OVERSIGHT 47
A.4.1 Assessment and Response Actions 47
A.4.1.1 Assessment Actions 47
A.4.1.1.1 Assessment of Field Activities 47
A.4.1.1.2 Assessment of Laboratory Operations 47
A.4.1.2 Response Actions 48
A.4.1.2.1 Field Corrective Actions 48
A.4.1.2.2 Laboratory Corrective Action 49
A.4.2 Reports to Management 49
A.4.2.1 Project Progress Report 49
A.4.2.2 Quality Control Summary Report 49
A.5.0 DATA VALIDATION AND USABILITY 50
A.5.1 Data Review, Validation, and Oversight 50
A.5.1.1 Data Verification 50
A.5.1.2 Data Validation 50
A.5.1.2.1 Level-III Data Validation 51
A.5.1.2.2 Level-IV Data Validation 51
A.5.1.2.3 Results of Data Validation 51
A.5.2 Data Quality Assessment Reconciliation with Planning Objectives 52
A.6.0 REFERENCES 53

ATTACHMENTS

Attachment 1: Field Data Collection Forms
Attachment 2: Field SOPs

FIGURES

Figure A-1. Organizational Structure for the ESTCP DP 13
Figure A-2. Proposed Demonstration Area 17
Figure A-3. "Aquamog" with Rotovator Arm 18
Figure A-4. CEI System with Injector Arm 18
Figure A-5. Schematic of ESTCP DP Plots C, D, E, F, and G in Parcel F Demonstration Area 28

TABLES

Table A-1. Schedule of Plot Sampling and Analysis 55
Table A-2. Data Quality Objectives for Primary Quantitative Performance Criteria of ESTCP DP 56
Table A-3. Data Quality Objectives for Secondary Quantitative Performance Criteria of ESTCP DP 58
Table A-4. Primary and Secondary Quantitative Performance Criteria Measurements for the ESTCP DP 60
Table A-5. Total Number of Samples and Intended Analyses for the ESTCP DP 61
Table A-6. Container, Sample Size, Preservation, and Shipping Information for the ESTCP DP 62
Table A-7. PCB Congeners, Detection Limits, Reporting Limits, and Benchmarks for *M. nasuta* and *Corophium spp*. (All concentrations are ng/g wet weight.) 63
Table A-8. BDO Standard Operating Procedures for the Critical Data Collection from Archived Tissue Sample Splits 64
Table A-9. Definitions, Requirements, and Frequency for Quality Control Samples 64
Table A-10. Measurement Quality Criteria for Measurements of PCB Congeners 65
Table A-11. Navy Environmental Data Transfer Standard (NEDTS) Data Qualifiers for PCB Congener Analysis 65
Table A-12. Calibration Procedures for Laboratory Equipment 66
Table A-13. Level III Data Validation Assessment Parameters 67

ACRONYMS AND ABBREVIATIONS

AC	–	activated carbon
AEI	–	Aquatic Environments, Inc.
ASCII	–	American Standard Code for Information Interchange
ASTM	–	American Society for Testing and Materials
BDO	–	Battelle Duxbury Operations
BRAC	–	Base Realignment and Closure (Act)
CD	–	compact disc
CEI	–	Compass Environmental, Inc.
CERCLA	–	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	–	Code of Federal Regulations
COC	–	chain of custody
DGPS	–	differential global positioning system
DoD	–	Department of Defense
DP	–	demonstration plan
DQA	–	data quality assessment
DQO	–	data quality objective
EB	–	equipment blank
EDD	–	electronic data deliverable
ELAP	–	Environmental Laboratory Accreditation Program
ERDC	–	Engineering Research and Development Center
EST	–	Environmental Sampling Technologies
ESTCP	–	Environmental Security Technology Certification Program
FS	–	feasibility study
FSP	–	field sampling plan
GC	–	gas chromatography
GC/ECD	–	gas chromatograph/electron capture detector
GC/MS	–	gas chromatography/mass spectroscopy
GPS	–	global positioning system
HASP	–	Health and Safety Plan
HAZWOPER	–	Hazardous Waste Operations and Emergency Response
HPS	–	Hunters Point Shipyard
HSO	–	Site Health and Safety Officer
ID	–	identification
LCS	–	laboratory control sample
LCSD	–	laboratory control sample duplicate
LIMS	–	laboratory information management system
LM	–	Laboratory Manager
MB	–	method or procedural blank

MDL	–	method detection limit
mL	–	milliliter
MLLW	–	mean lower low water
MQO	–	Management Quality Objective
MS	–	matrix spike
MSD	–	matrix spike duplicate
NA	–	not available
NEDTS	–	Navy Environmental Data Transfer Standards
NELAC	–	National Environmental Laboratory Accreditation Conference
NFESC	–	Naval Facilities Engineering Service Center
NIST	–	National Institute of Standards and Technology
NOAA	–	National Oceanic and Atmospheric Administration
NPL	–	National Priorities List
NS&T	–	National Status and Trends
PC	–	personal computer
PCB	–	polychlorinated biphenyl
QA	–	quality assurance
QAPP	–	quality assurance project plan
QC	–	quality control
QSM	–	quality systems manual
RIS	–	recovery internal standard
RL	–	reporting limit
RPD	–	relative percent difference
RPM	–	Remedial Project Manager
RSD	–	relative standard deviation
RSO	–	Radiation Safety Officer
SA	–	selective availability
SAP	–	sampling and analysis plan
SARA	–	Superfund Amendments and Reauthorization Act
SDG	–	sample delivery group or analytical batch
SERDP	–	Strategic Environmental Research Development Program
SIS	–	surrogate internal standard
SOP	–	standard operating procedure
SPMD	–	semi-permeable membrane device
SWDIV	–	Southwest Division Naval Facilities Engineering Command
SWG	–	Sediment Work Group
TOC	–	total organic carbon
UMBC	–	University of Maryland Baltimore County
U.S. EPA	–	U.S. Environmental Protection Agency

A.1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP), which contains the Sampling and Analysis Plan (SAP), has been developed for the Environmental Security Technology Certification Program (ESTCP) Demonstration Plan (DP) prepared by Stanford. The original proposal to ESTCP was titled *Field Testing of Activated Carbon Mixing and In Situ Stabilization of PCBs in Sediment*. The ESTCP DP will be completed at Hunters Point Shipyard (HPS) Parcel F (offshore sediment) in San Francisco, California.

In recent Strategic Environmental Research Development Program (SERDP)-funded work with sediment from Hunters Point, San Francisco Bay, Dr. Richard G. Luthy's research group at Stanford found that the polychlorinated biphenyls (PCBs) in the sediment tend to preferentially accumulate in coal-derived and char particles where the compounds may be strongly bound (Ghosh et al., 2003a; Luthy et al., 2004 Zimmerman et al., 2004). In addition, the Stanford team, along with researchers at the United States Army Corps of Engineers Engineering Research Development Center (USACE-ERDC), demonstrated in laboratory experiments that large reductions in PCB aqueous concentrations and PCB bioaccumulation (clams, polychaetes, and crustaceans) occurred in Hunters Point sediment treated with activated carbon (AC) (Ghosh et al., 2003b; Luthy et al., 2004; Millward et al., 2004; Zimmerman et al., 2004). These observations suggest that mixing AC into sediment may provide a new technology for contaminated sediment management.

This QAPP describes the ESTCP DP that will be conducted during FY2005-2007. The overall purpose of this project is to demonstrate that AC sorbent mixed with sediment is a cost-effective, in situ, non-removal, management strategy for reducing the bioavailability of PCBs in offshore sediments at HPS site. The scope of the ESTCP DP is to:

1) Demonstrate and compare the effectiveness, in terms of AC application and ease of use, of two available large-scale mixing technologies,
2) Demonstrate that AC treatment reduces PCB bioaccumulation results in field tests, and
3) Demonstrate no significant sediment resuspension and PCB release after the large-scale mixing technologies are used.

This QAPP documents the policies, the project organization, quality assurance (QA) requirements, and quality control (QC) procedures to be implemented for the ESTCP DP to ensure that the data are valid for use. The QAPP is incorporated as Appendix A to the ESTCP Demonstration Plan, and is not an independent document. This QAPP addresses all U.S. Environmental Protection Agency (U.S. EPA) requirements for a quality assurance project plan (QAPP) (U.S. EPA, 2001) with the elements of a field sampling and analysis plan (SAP) so that field and laboratory activities are described in one document. It defines the QA/QC methods that must be implemented to ensure that data meets the requirements of the Data Quality Objectives (DQO). The Health and Safety Plan in Appendix B, which is issued as a separate document, defines the preventative and prophylactic procedures that will be implemented during the field survey to ensure the safety of the field team.

The Navy has indicated that the AC treatment technology is being considered as an alternative for detailed analysis in an upcoming Feasibility Study (FS). Any data that the Navy may use to make a decision about assessing the AC treatment technology in the FS must be generated by a Navy-certified lab. Since the laboratories at Stanford, University of Maryland Baltimore County (UMBC), and USACE-ERDC that are involved in this ESTCP DP are not Navy-certified laboratories, The Navy Remedial Project Manager (RPM) of the HPS Parcel F site has requested that an archive of sample splits be created for the clams and amphipods that are collected to assess the AC treatment effects on PCB bioaccumulation. These samples splits will be analyzed by Battelle Duxbury Operations (BDO), a Navy-certified laboratory. The resulting PCB bioaccumulation data from BDO has been identified by the Navy

as "critical data" that must be of known and sufficient quality for decision making. The decision to analyze this archive will be made by the Navy RPM as part of the FS.

A.2.0 PROJECT MANAGEMENT

A.2.1 Project and Task Organization

Figure A-1 presents the organizational structure of the ESTCP DP project.

Dr. Andrea Leeson is the Environmental Restoration Program Manager at the ESTCP office. She is responsible for approval of the Demonstration Plan and executing Environmental Restoration contracts with Stanford and ERDC.

Mr. Ryan Ahlersmeyer is the Navy Remedial Project Manager (RPM) at Hunters Point Shipyard Parcel F. He is responsible for reviewing the Demonstration Plan to ensure that it meets Navy requirements for the site. He will also provide support for the field activities that occur at HPS Parcel F. Mr. Ahlersmeyer will decide if critical data for the HPS FS is to be obtained from the samples splits that are archived in this ESTCP Demonstration.

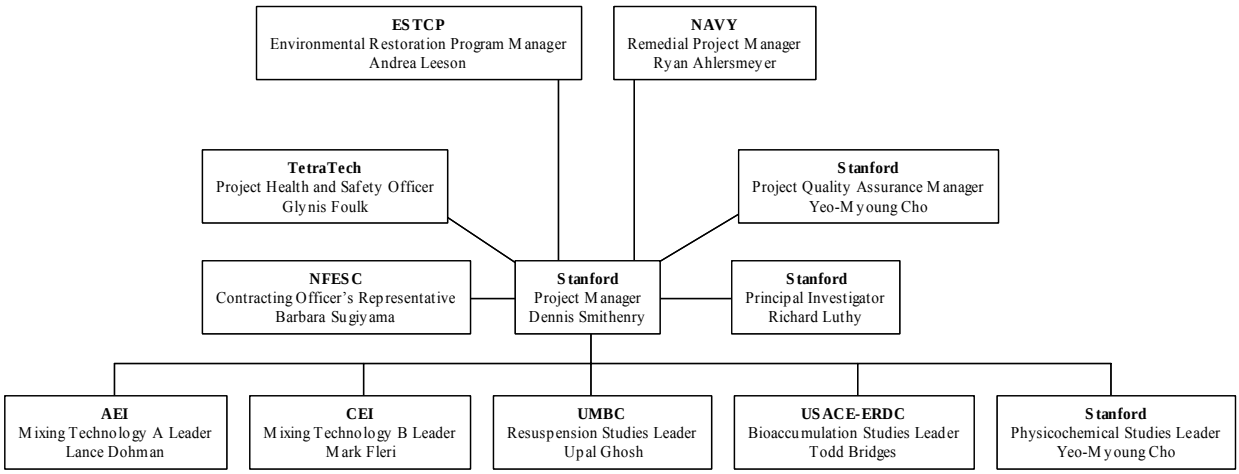

Figure A-1. Organizational Structure for the ESTCP DP

Dr. Richard G. Luthy is the Principal Investigator (PI) for the ESTCP DP. He is a professor at Stanford University whose lab studies support the in situ technology of applying AC to PCB-contaminated sediment. He will provide expertise and guidance to the Project Manager in the development and implementation of the QAPP. His team at Stanford (Dr. Luthy, Ms. Cho, and Dr. Smithenry) is responsible for assessment of proposed carbon application by AEI and CEI, deployment of semi-permeable membrane devices (SPMDs), analysis of sediment PCB concentrations, and analysis of aqueous equilibrium PCB concentrations.

Dr. Dennis W. Smithenry is the Project Manager. Dr. Smithenry, a postdoctoral researcher at Stanford University, is responsible for coordinating field efforts outlined in the QAPP between the various groups involved in the project. He is responsible for overall preparation and coordination of the study planning documents: the demonstration plan, QAPP, and supporting documents. He coordinates technical activities as a liaison between the ESTCP Environmental Restoration Manager, Navy RPM, Stanford PI, Project

Health and Safety Officer, Project QA Manager, and NFESC DoD Contracting Officer's Representative. He is responsible for ensuring that communication of all decisions, which impact field or laboratory activities, are dispatched in real time. He is responsible for responding to QA reports and either implementing or requiring corrective action to address systematic problems. He communicates directly with the ESTCP Environmental Restoration Program Manager and the Navy RPM to coordinate activities and enforce schedules and deadlines.

Ms. Glynis Foulk of Tetra Tech is the Project Health and Safety Officer (HSO). She is responsible for reviewing the project Health and Safety Plan (HASP), ensuring that the field personnel have received appropriate health and safety training for work at the study site, and that the training is documented. She may also conduct inspections during field operations. She reports issues and concerns directly to the Project Manager and has the authority to stop work.

Ms. Yeo-Myoung Cho is the Project QA Manager. She is responsible for reviewing the QAPP to ensure that all elements are addressed in adequate detail and must approve the final version. She ensures that project reviews are conducted frequently enough to ensure that the work is being conducted according to the QAPP and SOPs, and that corrective action plans are implemented to address any deficiencies identified. She reports the results of these oversight activities to the Project Manager. She is authorized to stop work if data quality or staff safety is threatened. She ensures that all SOPs cited in the QAPP are approved and available, and that appropriate training is documented for team members. She verifies that adequate forms and labels are designed for the sampling and analysis effort. She reviews chain of custody (COC) forms to verify that custody is maintained, and conducts field and laboratory inspections as appropriate to ensure that the QAPP is implemented. She prepares reports of inspections and audits, and communicates findings to the Project Manager. Ms. Cho will also serve as Physicochemical Studies Leader. In this role, she will be responsible for assessment of proposed carbon application by AEI and CEI, deployment of semi-permeable membrane devices (SPMDs), analysis of sediment PCB concentrations, and analysis of aqueous equilibrium PCB concentrations.

Dr. Upal Ghosh, an Assistant Professor at University of Maryland Baltimore County, will serve as Resuspension Studies Leader. He is responsible for carrying out field water quality tests that will assess if PCB resuspension occurs as a result of mixing the AC into the sediment. He will also conduct laboratory tests that assess the change in PCB availability for desorption to the aqueous phase after treatment. He will implement these tests in coordination with the Project Manager. Dr. Ghosh will be present to assist with and oversee the proper deployment of the two remediation technologies that will be tested at Hunters Point. Dr. Ghosh will assist with the evaluation of the technologies. Dr. Ghosh and his team at UMBC will also assist with technology scale-up and cost estimation for full-scale application. Dr. Ghosh will assist in preparing the ESTCP Cost and Performance Report, ESTCP Final Technical Report, and will be available to make presentations to the user community, regulatory community, and industry.

Dr. Todd S. Bridges will represent USACE-ERDC and serve as Bioaccumulation Studies Leader. He is responsible for carrying out field clam bioaccumulation tests that will assess whether the bioavailability of PCBs is reduced by the mixing AC into sediments. He will coordinate and implement these tests in coordination with the Project Manager.

Ms. Barbara Sugiyama will serve as DoD Contracting Officer's Representative to help prepare the full proposal and Phase II briefing. Ms. Sugiyama will take care of contract issues between Stanford and the ESTCP office.

Mr. Lance Dohman will represent Aquatic Environments, Inc. (AEI) and serve as Mixing Technology A Leader. He will be responsible for the mobilization, storage, and demobilization of the Aquamog, an ARGO amphibious support vehicle, and auxiliary equipment to the demonstration site. He will supervise

and be responsible for the safe operation of equipment provided and used by Aquatic Environments, Inc. employees. He will provide technical assistance in using the Aquamog to distribute and mix AC and sediment through rotovation onto the demonstration plot.

Mr. Mark Fleri will represent Compass Environmental, Inc. (CEI) and serve as Mixing Technology B Leader. H will be responsible for the mobilization, storage, operation, and demobilization of its patented rake injector and other equipment necessary to support the injection of a dose of carbon in the upper one foot of tidal zone sediments at Hunters Point. He will supervise and be responsible for the safe operation of equipment provided and used by CEI's employees.

Ms. Sarah Brennan is the Database Manager at BDO should the decision be made to analyze the archived sample splits. She is responsible for ensuring that the database construction and output meet the needs of the ESTCP DP for analysis and report preparation. She is responsible for overseeing accurate and complete loading of data to the database, sample tracking, and providing sample identification codes. She provides database exports to the Navy contractor validation firm for data validation upon request.

Dr. Carole-Sue Peven is the Chemistry Laboratory Leader at BDO should the decision be made to analyze the archived sample splits. She is responsible for ensuring that appropriate and comparable technical procedures for sample analysis are used by BDO. She will coordinate with the Project Manager and appropriate labs to ensure that holding times are met and that reporting schedules are not compromised for the archived sample splits. Ms. Peven ensures that the status of laboratory analyses and potential problems are reported to the Project Manager. She is responsible for performing a management review of analytical data reports produced.

The field sampling crew is responsible for conducting all field activities according to the QAPP and for communicating problems to the Project Manager.

All critical data from the archived sample splits that may be used in the HPS FS will be generated by BDO. BDO is responsible for conducting all analytical activities according to Naval Facilities Engineering Service Center (NFESC, 1999), the Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories (DoD, 2002), and the QAPP.

A.2.2 Problem Definition/Background

Contaminated sediments pose challenging cleanup and management problems. Hydrophobic organic compounds such as PCBs associate with fine-grained, organic-rich, sediment material. This serves as a contaminant reservoir in shallow estuarine and coastal regions from which fish and bottom-dwelling organisms accumulate toxic compounds that may be passed up the food chain. However, work at Stanford University and elsewhere proposes that hydrophobic organic contaminants in sediment may be of more or less concern depending on how weakly or strongly they are sorbed to sediment organic matter (e.g., Bucheli and Gustafsson, 2001).

Portions of the offshore sediment at HPS have elevated concentrations of PCBs that could pose a potential human health and ecological risk. Currently the standard approach to addressing contaminated marine "mud flat" sediments is the expensive ex situ process of dredging and disposal. Previous laboratory experiments (Ghosh et al., 2003b; Luthy et al., 2004; Millward et al., 2004; Zimmerman et al., 2004) have shown that large reductions in PCB aqueous concentrations and PCB bioaccumulation (clams, polychaetes, and crustaceans) occurred in HPS sediment treated with AC. Based on these observations, this project will entail mixing AC into sediment as a new technology for contaminated sediment management.

A.2.3 Site Description

HPS is situated on a peninsula in the southeast corner of San Francisco, CA. The peninsula is bounded on the north, east, and south by San Francisco Bay and on the west by the Bayview Hunters Point district. HPS comprises about 928 acres, with approximately 400 acres of offshore sediments. From 1945 to 1974, the Navy used HPS predominantly for ship repair and maintenance. HPS was deactivated in 1974 and remained relatively unused until 1976, when it was leased to Triple A Machine Shop, a private ship repair company. In 1986, the Navy resumed occupancy of HPS, but closed the Base in 1991.

Historical site activities at HPS resulted in the release of chemicals to the environment, including offshore sediments. Environmental restoration activities are conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA). The facility was closed under the Defense Base Realignment and Closure Act of 1990 (BRAC) and is in the process of conversion to nonmilitary use.

Five plots, as shown in Figure A-2, having areas of 370 ft^2 will be used as the test plots for the ESTCP DP. The plots will be located within the tidal flat region of Hunters Point South Basin, in the southeast portion of the cove; this location is accessible from the shore and away from possible impacts of any potential on-going PCB releases on the north side of the cove (Battelle, 2003) as shown in Figure A-2.

A.2.4 Project/Task Description

The scope of the ESTCP DP is to compare the effectiveness of two available large-scale mixing technologies, demonstrate that AC treatment reduces the aqueous PCB availability and PCB bioaccumulation results in field tests, and evaluate sediment resuspension and PCB release.

There are primary quantitative performance criteria that have been identified to measure the success of the AC treatment technology demonstration:
1) PCB bioaccumulation in test organisms (clams),
2) PCB bioaccumulation in indigenous organisms (amphipods),
3) Homogeneity of AC application, and
4) PCB Resuspension.

The procedures developed to implement the scope of the ESTCP DP are described below in Sections A.2.4.1 through A.2.4.3. The schedule of sampling and analysis related to these procedures is summarized in Table A-1.

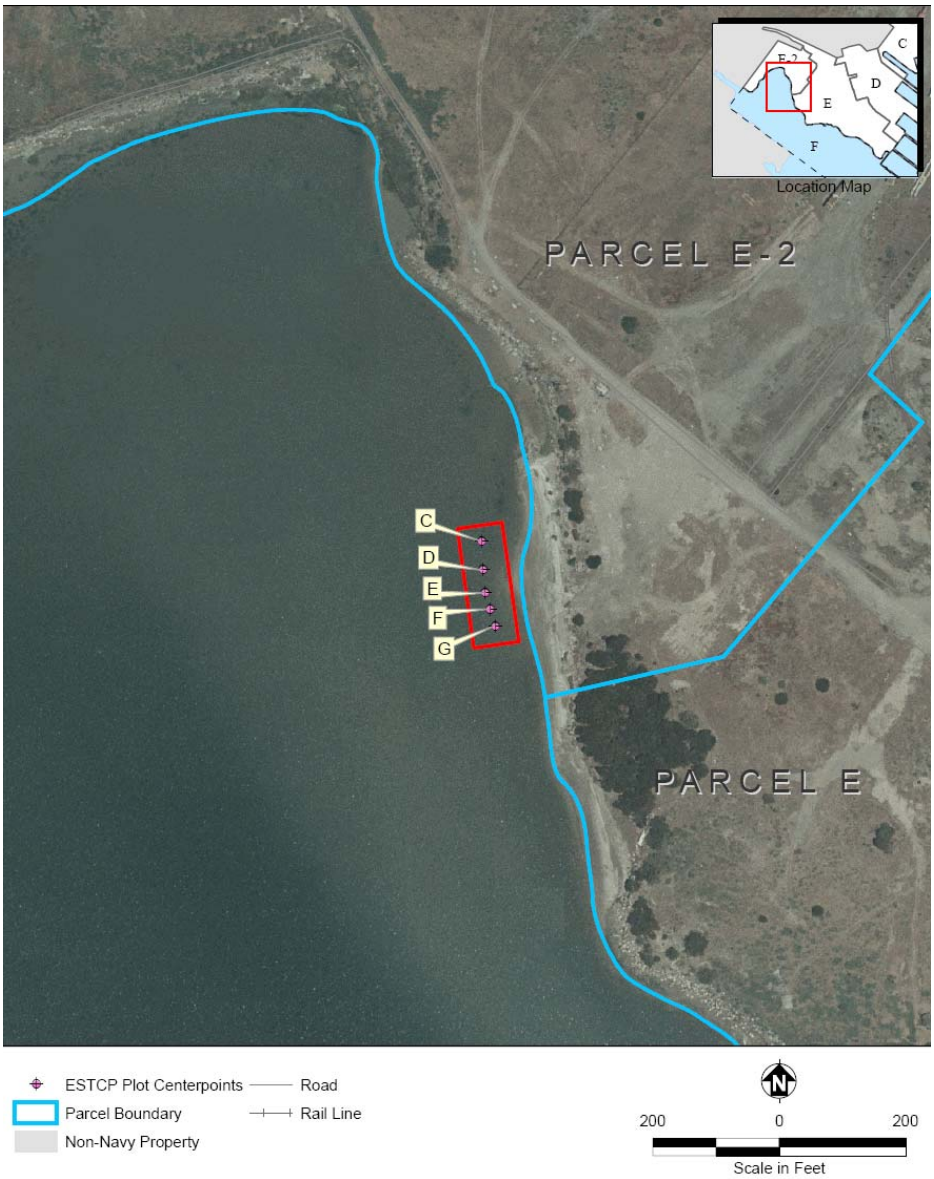

Figure A-2. Proposed Demonstration Area

A.2.4.1 Application of Activated Carbon

The first contractor, Aquatic Environments, Inc. (AEI), has a barge-like machine (called an Aquamog, Figure A-3) with a rotovator attachment that is typically used to disrupt weed growth in marshy areas. In the field demonstration, AEI will be responsible for the mobilization, storage, operation, and demobilization of the Aquamog to the Hunters Point Naval Shipyard field site in January 2006. In the field demonstration, the Aquamog will be deployed on the water during high tide and allowed to settle onto the sediment surface at low tide to do treatments on Plots C and D as shown in Figure A-2. AEI will supply an ARGO amphibious support vehicle and any auxiliary equipment to the demonstration site that will be necessary to complete the treatments. Before mobilization of the Aquamog, AEI is also responsible for the design, development, and testing of a delivery system for transferring AC from the deck of the Aquamog to the plot surface. Besides delivering AC to the sediment surface, the Aquamog has a rotovator attachment that will be used to mix transferred AC into sediments into Plot D to an

approximate depth of one foot. The depth of the mixing can be controlled by the speed and downward pressure of the rotovator. The rotovator attachment will also be used to mix (only) the sediments in Plot C to a depth of one foot.

The second contractor, Compass Environmental, Inc. (CEI) [formerly Williams Environmental Services, Inc. (WESI)], owns an injection system used traditionally for sediment solidification with cement mortar (Figure A-4). In Jan. 2006, CEI will provide its patented rake injector and other equipment necessary to support the treatments of Plots F and G. This equipment will be located on the shore with the injector arm reaching out to Plots F and G. Via a slurry, AC will be injected and mixed into the upper one foot of tidal zone sediments for Plot F. For Plot G, the sediments will be mixed using the rake injector mixers with no application of a AC slurry. CEI will provide the data necessary to demonstrate that the requisite carbon mass has been added to Plot F. CEI will record data such as slurry flow rate, slurry density, pump time, and slurry volume pumped into each test plot.

The field sampling and analysis methods that will be used to assess the depth and homogeneity of the AC application are provided in Section A.3.2 through A.3.5.

Figure A-3. "Aquamog" with Rotovator Arm

Figure A-4. CEI System with Injector Arm

A.2.4.2 Assessment of Reductions in Aqueous PCB Availability and PCB Bioaccumulation

To determine that the AC treatments lead to a reduction in aqueous PCB availability and PCB bioaccumulation, the following assessments will be completed during the course of the ESTCP DP project:

a) PCB bioaccumulation in test clams and indigenous amphipods retrieved from plots (ERDC),
b) AC treatment effects on indigenous benthic community structure (ERDC), and
c) in situ PCB stabilization using physicochemical tests of PCB availability (Stanford/UMBC).

Further details of these field sampling and analysis methods associated with the above assessments are provided in Sections A.3.2 through A.3.5.

A.2.4.3 Assessment of Resuspension Potential

The overlying water above the five plots will be sampled during high tide once before and thrice after treatments to evaluate possible sediment and PCB resuspension and measure suspended and dissolved PCB concentrations. The sampling and analysis methods associated with this assessment are provided in Sections A.3.2 through A.3.5.

A.2.5 Quality Objectives and Criteria

A.2.5.1 Data Quality Objectives

The development of the DQOs for the ESTCP DP followed U.S. EPA's Guidance for the Data Quality Objectives Process (U.S. EPA QA/G-4, 2000b). The DQOs have been divided into two categories that relate to those defined in the ESTCP DP. The DQOs for primary quantitative performance criteria are defined in Table A-2; the DQOs for secondary performance criteria are defined in Table A-3. Table A-4 defines the measurements that will be completed to assess the primary performance criteria and secondary performance for the ESTCP DP. Measurements that will be done by BDO on the archived sample splits and will produce critical data for the Navy are identified Table A-4.

A.2.5.2 Measurement Quality Objectives

Measurement quality objectives for critical analyses conducted for this study can be expressed in terms of accuracy, precision, completeness, and sensitivity goals. Accuracy and precision are monitored through the analysis of QC samples (Section A.3.5). Completeness is a calculated value. Sensitivity is monitored through instrument calibration (Section A.3.7) and the determination of method detection limits (MDLs) and reporting limits (Section A.2.5.2). Qualitative quality objectives, expressed in terms of comparability and representativeness, are addressed as part of the sampling design.

> **Accuracy** is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.
>
> **Precision** is defined as degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.
>
> **Completeness** is the amount of data collected as compared to the amount needed to ensure that the uncertainty or error is within acceptable limits. The goal for data completeness is 100%.

However, the project will not be compromised if 90% of the samples collected are analyzed with acceptable quality.

Comparability is a measure of the confidence with which one data set can be compared to another. This is a qualitative assessment and is addressed primarily in sampling design through use of comparable sampling procedures or, for monitoring programs, through accurate resampling of stations over time. In the laboratory, comparability is ensured through the use of comparable analytical procedures and ensuring that project staff are trained in the proper application of the procedures. Within-study comparability will be assessed through analytical performance (QC samples).

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population. This is a qualitative assessment and is addressed primarily in the sample design, through the selection of sampling sites and procedures that reflect the project goals and environment being sampled. It is ensured in the laboratory through (1) the proper handling, homogenizing, compositing, and storage of samples and (2) analysis within the specified holding times so that the material analyzed reflects the material collected as accurately as possible.

Sensitivity is the capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. Sensitivity is addressed primarily through the selection of appropriate analytical methods, equipment, and instrumentation. The methods selected for this study were chosen to provide the sensitivity required for the end-use of the data. This is a quantitative assessment and is monitored through the instrument calibrations and calibration verification samples and the analysis of procedural blanks with every analytical batch.

Method Detection Limits for PCB congeners in tissues are determined by spiking clean, low-lipid tissue (e.g., white meat fillet from a non-bottom-feeding fish species) with all parameters of interest and processing them according to the methods defined Section A.3.4. MDLs for Gas chromatography/electron-capture detector (GC/ECD) analysis are determined on the primary column. (MDLs for PCBs must also be determined on a confirmation column if data from confirmatory analyses will be reported. In these instances, the MDLs determined from confirmation column analysis must be less than those determined from the primary column. Quantification on confirmation columns is not, however, anticipated for this investigation.)

Reporting Limits (RLs) for PCB congeners are empirical values based on a low calibration standard (≤0.005 µg/mL), instrument sensitivity, and day-to-day operations. Sample-specific reporting limits will be calculated and reported with the final data. For PCB congeners, the RL is calculated as

RL = (Low Standard Concentration) (Preinjection Volume) (Dilution Factors) (1/ Sample Size)

The DoD Quality Systems Manual (DoD, 2002) includes the following note: *There may be numbers reported to the client that are below the reporting limit. These numbers must be flagged appropriately. When the analysis demonstrates a non-detect at the MDL, the data shall be flagged with a "U." The value reported to the client is the MDL, adjusted by any dilution factor used in the analysis. When an analyte is detected between the lower quantitation limit and the MDL, the data shall be flagged with a "J." The value reported is an estimate.*

A.2.6 Special Training/Certification

A.2.6.1 Training Requirements

Documented training is required for each individual performing activities in support of environmental data collection or analysis. In order to ensure that field personnel are trained in the study sampling procedures, pre-deployment practice sessions will be conducted to ensure that clam, amphipod, water, and sediment samples can be deployed and/or collected as specified in the standard operating procedures. Each BDO laboratory technician and analyst must complete an initial demonstration of capability before processing or analyzing samples for this project. At least annually, technicians and analysts must demonstrate continued proficiency for the analyses that they are performing. The procedures used to ensure that staff training is current and documented is defined in laboratory SOPs. The laboratory manager is responsible for determining specific training and certification needs, and for ensuring that any required training is documented.

Individuals implementing this QAPP must receive, at a minimum, orientation to the project's purpose, scope, and methods of implementation. This orientation is the responsibility of the Project Manager or designee. Field and data management personnel must have documented experience or direct training in the procedures that they will be performing for this project, including any applicable SOPs.

A.2.6.2 Special Training

Special training and certification required for this study include the following:

- Any field team member involved in the operation of either large-scale mixing device will have been trained by AEI or CEI in the proper and safe operation of all equipment associated with the mixing device.

- Any field team members involved with sample collection or handling must be supervised by a Health and Safety Officer who has received certification of training in hazardous waste operations and emergency response (HAZWOPER – 29 CFR 1910.120). This is a 40-hour course.

- The Health and Safety Officer must complete an additional 8-hour supervisor training course (HAZWOPER – 29 CFR 1910.120).

- Any other safety-related training defined in the project HASP.

- Vessel operators will be experienced and have demonstrable experience in small boat handling under the conditions expected at the site.

Radioactive contamination may be present at the site. The sediment samples will be scanned for radioactivity by Tetra Tech ECI field personnel (under a separate contract to the Navy) who have been trained to perform this task.

The Project Manager is responsible for identifying worker certification needs for the field unit and ensuring that all team members are adequately trained. A field orientation must be conducted to establish guidelines for field observations between crews to ensure repeatability within the limits of this qualitative approach. This orientation is the responsibility of the Project Manager.

A.2.6.3 Navy Evaluation

Only laboratories that the Navy has evaluated and approved within the previous 18 months may perform the critical analyses of the archived sample splits described in this QAPP. Critical analyses are those upon which future decisions regarding the suitability of AC application as a remedial alternative may be based. For the ESTCP DP, critical parameters are defined as PCB congeners in the *M. nasuta* tissue and *Corophium spp.* amphipod samples that will be collected and archived in December 2005 (t = -1 months), August 2006 (t = 6 months), and August 2007 (t = 18 months) as shown in Table A-1.

Battelle Duxbury Operations (BDO) in Duxbury, MA will perform critical data analyses. The BDO laboratory has obtained general NFESC approval for the use of these methods for the BRAC program.

A.2.6.4 State of California Environmental Laboratory Approval Program

Laboratory certification through the State of California Environmental Laboratory Accreditation Program (ELAP) is required for any certifiable methods. ELAP does not certify the low-level methods required for the BDO's critical analyses that will be used for the ESTCP DP. Therefore, certification is not required for these measurements.

A.2.7 Documentation and Records

A.2.7.1 Document Control

It is critical that project personnel have the most recent versions of the QAPP and SOPs. Version control is maintained by defining the version number and date on each of these documents. A distribution list is maintained for each controlled document. When a new version is approved, it is distributed and the old versions must be marked as "Obsolete." Requests for SOPs should be submitted to the QA Officer at the authoring laboratory. Field and laboratory logbooks are controlled documents and must be permanently bound and prenumbered, dated, and distinctly labeled.

A.2.7.2 Documentation Standards

Each organization performing activities in support of environmental data collection that will be used for decision making at Hunters Point must have written procedures for the methods and procedures related to the collection, processing, analysis, reporting, and tracking of environmental data. This documentation must be in either the organization's QA Manual or in SOPs. Written procedures must describe how analytical methods are implemented, and must be readily available to personnel. SOPs are controlled documents and, as such, must be approved by management and dated. The laboratory must maintain a master list of SOPs in accordance with DoD QSM (2002) requirements. All SOPs that are used for environmental data collection activities must be reviewed annually and updated as needed. The QAPP defines procedures by reference to the SOP number or another appropriate citation.

All critical data (BDO measurements of PCB congeners in *M. nasuta* and *Corophium spp.* tissues) and supporting data (field data) generated during the course of this project must be able to withstand challenges to their validity, accuracy, and legibility. To meet this objective, data are recorded in standardized formats and in accordance with prescribed procedures. The documentation of all environmental data collection activities must meet the following minimum requirements. Other specific documentation requirements are discussed throughout this QAPP and the associated SOPs:

- Data must be entered directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.

- Handwritten data must be recorded in ink. All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample identification (ID) and station or location ID (if applicable), name (signature or initials) of the person collecting the data, and date of data collection.

- Any changes to the original (raw data) entry must not obscure the original entry. The reason for the change must be documented, and the change must be initialed and dated by the person making the change.

- The use of pencil, correction fluid, and erasable pen is prohibited.

Any changes to raw data must be documented and approved. Changes that are anticipated up to 12 hours prior to the intended field or laboratory activities must be documented and submitted to the Project Manager for approval prior to implementation of the changes.

A.2.7.2.1 Changes and Deviations

During the conduct of this study, it may be necessary to modify the planned activities. Modifications that are anticipated prior to field or laboratory work will be reported to the Project Manager, who will assess the potential impact (e.g., those that would impact the study objectives, design, or data quality). All changes to the QAPP must be communicated to the Project QA Manager. All QAPP changes must receive the written approval of the Project QA Manager. All modifications will be described in the final report. The Project Manager and Project QA Manager will determine whether modifications are significant enough to either update the QAPP or prepare an addendum to the document.

Changes that are not anticipated prior to the planned activities are deviations and must be communicated to the Project Manager as soon as possible, documented, and submitted for approval to the Project Manager. Documentation should include an assessment of any impact that the deviation has on data quality and the corrective action. Minor deviations (e.g., those that would not impact the study objectives, design, or data quality) will be reported to and approved by the Project Manager. Major deviations (e.g., those that could impact the study objectives, design, or data quality) will additionally be reported to the Project Manager and the Project QA Manager. A discussion of major deviations and potential impact on the project objectives will be included in the final report.

A.2.7.2.2 Definition of Raw Data

Raw data are defined as any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (and verified accurate by signature) then the exact copy or exact transcript may be substituted National Environmental Laboratory Accreditation Conference (NELAC) Chapter 1 Glossary (June 2000). Raw data will be archived at each participating laboratory for 10 years from the date of the final report; reference Section A.2.7.8 for further disposition requirements.

A.2.7.3 Field Documentation and Forms

This section defines the specific records and data that must be maintained for each field activity to ensure that samples and data are traceable and defensible. Field records will be documented in bound, paginated field logbooks to provide a secure record of field activities, observations, and measurements during

sampling. All field records and documentation must comply with the documentation requirements defined in this section. Copies of all field data collection forms are provided in Attachment 1.

Field data and observations will be recorded in real time on activity-specific data forms that are bound into the logbooks. Completion of a sample collection form for each sample is the responsibility of the appropriate Research Studies Leader. The information recorded for each sample includes, as appropriate:

- Unique sample ID number and description
- Date and time of collection
- Identification of person who collected the sample
- Identification of person recording field data (if different than the collector)
- Sample location (Lat/Long or State Plane)
- Sampler type
- Sampling procedures, sample volume and receiving container
- Storage conditions from sampling to aliquotting or shipment.

A.2.7.4 Laboratory Documentation

Documentation of all laboratory activities is critical for tracking data and evaluating the success of any activity. It is expected that each laboratory maintains written policies that define documentation requirements and procedures. Laboratory documentation requirements at BDO are defined in the laboratory QA Manual and SOPs. Required documentation includes, but is not limited to, the following:

- Calibration and maintenance records for all instruments and equipment involved in the collection of environmental data.

- Preparation of calibration standards, spiking solutions, and dosing solutions such that each unique preparation can be tracked to the original (neat) material.

- Lot numbers for all standards, stock solutions, reagents, and solvents.

- All sample processing or preparation for testing such that it is traceable to sample receipt records.

- All sample analyses and results of analyses. All rejected data are accompanied by explanations of the failure and the corrective action.

- All data reduction formulas such that reported data can be reproduced from the raw data.

A.2.7.5 Contents of Data Packages

Laboratories at Stanford, UMBC, and ERDC will generate full data packages for 20% of the samples analyzed and summary data packages for 80% of the sample analyzed. BDO laboratory will generate a full data package for 100% of the samples analyzed. The full data package contains all information required for validation (Section A.5.0 discusses data validation requirements). The full data packages must contain any of the following elements that are applicable to the analysis because the data will be validated:

- Title page;
- Table of contents;

- Data package narrative (contents defined in the DoD QSM [2002] and this QAPP);
- Copies of SOPs for all analyses not performed in accordance with strict U.S. EPA methods (once);
- Final data report tables (see Section A.2.7.7 for contents);
- Analytical records:
  - Instrument tuning (GC/ECD methods);
  - Retention times (GC methods);
  - Calibration data;
  - Calibration verifications;
  - Surrogate recoveries (GC/ECD and GC methods);
  - Internal standard response and retention times;
  - All QC data required by the analytical method or the QAPP (blanks, laboratory control samples [LCS]/LCS duplicates [LCSD], matrix spike samples [MS])/MS duplicates [MSD], duplicates);
- Required supporting information:
  - Entire package of sample custody documentation, including sample receipt form;
  - Sample processing and spiking records;
  - Copies of standard preparation logs for each standard used in sample preparation and instrument calibration;
  - Run logs (see DoD QSM [2002] requirements);
  - Raw data associated with field and QC data;
  - Chromatograms;
  - Instrument calibration records and calibration results;
  - Results of all QC samples required by the QAPP; matrix spike solution compounds in concentration units;
  - Sources of control limits for surrogates and LCS; and
  - Source of LCS;
- Summary of internal standard retention times and response;
- Description of manual integration procedures; and,
- List of current MDLs for the preparation and analysis methods used for sample processing.

Summary data packages will include sample results and a QA/QC summary report. Section A.3.10 describes the data reporting requirements for this project.

A.2.7.6 Electronic Data Deliverable

All analytical data and the associated field data produced by Stanford, UMBC, ERDC, and BDO will be submitted to the Stanford database manager. Standard data reporting formats have been designed and described in project-specific SOPs such that data will be submitted in a uniform manner that meets the ESTCP DP database requirements. This process is described in Section A.3.10. Because the ESTCP DP database will be used to facilitate analytical data validation, the laboratory will be required to include QC data in the data submission. Project-specific SOPs will be provided to the lab and field team that are submitting data. If applicable, the electronic submission should include QC results. All electronic data deliverables (EDDs) must conform to Navy Environmental Data Transfer Standards (NEDTS) by being Excel 97 or Excel 2000 for Windows compatible, or as a tab-delimited text (ASCII) file.

A.2.7.7 Reports

- The ESTCP reports (Cost and Performance, Final Technical, and Verified Fact Sheet) will be prepared by the combined efforts of Stanford University, UMBC, and ERDC.
- BDO laboratory data reports must contain the following:
  - The concentration, units, MDL, RL, and data qualifier for critical data;
  - The sample collection date, extraction date (if applicable), and analysis date;
  - The Field Sample ID, Laboratory Sample ID, and the sample delivery group or analytical batch (SDG) number.
  - All required QC data including detected concentrations, spike amounts (or concentrations), percent recoveries and the appropriate calculation of precision (relative percent difference [RPD], relative standard deviation [RSD]).

A.2.7.8 Storage and Disposal

Stanford's database will be maintained in electronic and hardcopy format for 10 years following the submission of required ESTCP reports.

If critical data is obtained from the archived sample splits, BDO is responsible for maintaining electronic and hardcopy raw data, data packages, and final data that it generates for this project for 10 years after data submission. If raw data will be stored on tape or CD, then the magnetic tape storage device or other similar storage device must be capable of recording data for long-term, off-line storage. At the end of the 10-year period, BDO will contact the Navy RPM or a representative to determine if the Navy wants to take possession of the data. If directed to do so, BDO will transfer the data and electronic records associated with this investigation to the Navy. The Navy is then responsible for maintaining that data in accordance with the prescribed time requirements. The Stanford project manager will provide BDO with a complete photocopy of all field records associated with samples analyzed by BDO. BDO will archive these records as part of the project files.

Sample archiving and disposal is discussed in Section A.2.2.8.

A.3.0 STUDY DESIGN, DATA GENERATION AND ACQUISITION

This section describes the method requirements for all aspects of data measurement and acquisition: collection, handling, and analysis of samples; QC procedures and requirements; and data management. The overall purpose of this project is to demonstrate that AC sorbent mixed with sediment is a cost-effective, in situ, non-removal, management strategy for reducing the bioavailability of PCBs in offshore sediments at HPS site.

A.3.1 Sampling Process Design (Experimental Design)

The field data will be obtained by collecting samples according to the Sampling Design shown in Table A-1. Table A-4 defines the measurements associated with the primary and secondary performance criteria, respective lab samples, and laboratories responsible for analyses. Table A-5 defines the total number of samples that will be collected during the entire ESTCP DP and the intended analyses.

This project is designed to compare the effectiveness of two available large-scale mixing technologies, demonstrate that AC treatment reduces aqueous PCB availability and PCB bioaccumulation in field tests, and evaluate sediment resuspension and PCB release. To achieve these objectives, five test plots of 370 ft^2 area will be used in the field study and analyzed once before and twice after treatments occurs as shown in Table A-1. As discussed in Section 2.4.1, various treatments will be applied to four of the five plots, leaving one plot (Plot E) to serve as a control. A schematic of these five plots, labeled with respective treatments, is shown in Figure A-5. Plot C will be treated by mixing the sediment with the Aquamog rotovator, but without applying AC. Plot G will be treated by mixing with the CEI slurry injector system, but without applying AC. Plots D and F will be treated by applying a 3.4 wt.% AC and mixing it into the sediment with the Aquamog and CEI slurry injector system, respectively. The AC dose will be applied to an approximate depth of one foot, corresponding to the biologically active zone. The shapes of the Plots C and D were made to fit the radial design of the Aquamog's rotovator arm. The shapes of Plots F and G were chosen to fit the design of CEI's equipment. All of the plots were made to follow the contour line of the tides so that similar benthic communities would exist in each of the plots at the beginning of the study.

In each of the five plots, there will be five sampling locations, as shown in Figure A-5. These five sampling locations in each plot have been selected using a stratified random sampling strategy. This sampling strategy ensures that the sampling locations are spatially distributed, and meet the criterion of random sampling so that statistical tests can be applied during data analysis. To obtain the five stratified random sampling locations for a given plot, each plot was divided into five equal sub-areas containing the same number of possible sampling locations. The outside 3-foot edge of the plots was not be included in the selection process to ensure that the sampling locations are located within the actual treatment area. In each sub-area, a random sampling location was selected. The resulting randomly-selected sampling locations are shown in Figure 3-6 for each plot. These same sampling locations for the five plots will be used in all three sampling time points so that pair-wise comparisons can be made over time when appropriate.

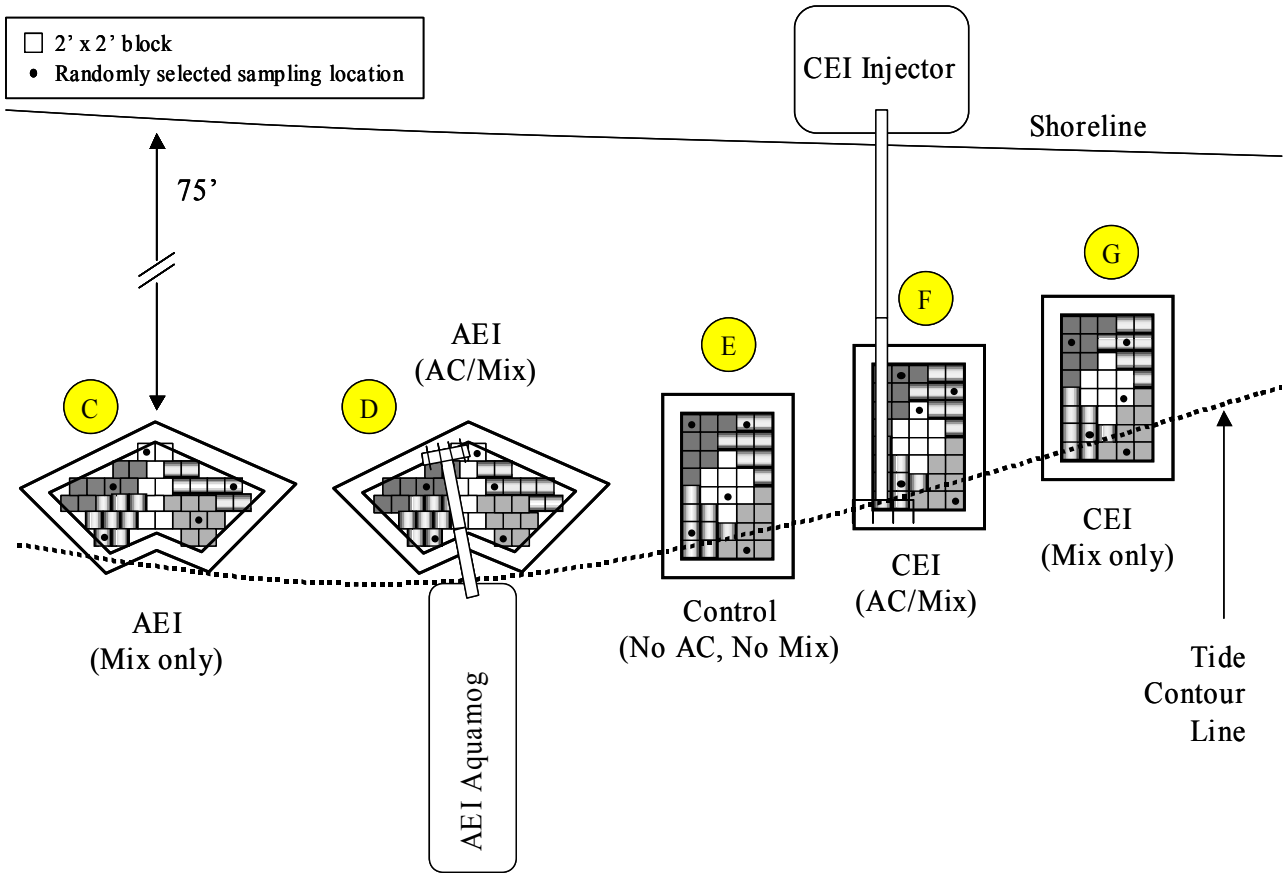

Figure A-5. Schematic of ESTCP DP Plots C, D, E, F, and G in Parcel F Demonstration Area

A.3.2 Field Sampling Methods

To perform analytical tests, field samples must be collected according to standard protocols. This section defines the field sampling methods that apply to this ESTCP DP. These protocols describe appropriate procedures to collect field samples for the purpose of (1) determining physical characteristics and (2) measuring chemical constituents. The field protocols for this study were selected to ensure that sampling procedures meet the requirements for the intended use of the data. Field sampling activities will be led by Dr. Dennis Smithenry. All general field information, including field location, field activities, type of equipment, and weather, will be recorded on the Field Daily Log Form, and maintained in a paginated and bound field logbook (see Section A.2.7.3). Field SOPs can be found in Attachment 2.

The sampling area will be scanned for radioactivity by Tetra Tech ECI field personnel prior to the survey. This scanning will be conducted at HPS due to the historical disposal of radium dials in the landfill in Parcel E. The scanners will notify the HSO, and Radiation Safety Officer (RSO) of any samples with greater than two sigma background readings. The HASP describes the procedures for sample segregation and disposal, decontamination, and the procedures for the release of materials for unrestricted use. The Tetra Tech ECI project HASP details the scanning procedures.

A.3.2.1 Plot Locations

GPS coordinates will be recorded in the field using a handheld GPS unit (Garmin Geko™ 201) with WAAS-enabled accuracy of ±3 m. The exact GPS coordinates will be defined with the latitude and longitude in terms of degrees and decimal minutes using WGS 84 datum. The dimensions of the plot are on a similar scale to that of the unit's accuracy, so only the center of each plot will be defined with GPS coordinates. The locations of clam tube/SPMD deployments and core samples will be marked on a scale map (with magnetic North identified) in relation to the center and corners of each plot. GPS coordinates will be recorded for water column samples taken over the plot areas. The exact GPS coordinates will define the latitude and longitude in terms of decimal degrees or degrees and decimal minutes.

A.3.2.2 Testing Material Deployment and Sampling of Environmental Media for Chemical Analysis

A.3.2.2.1 SPMD Deployment and Retrieval

As shown in Table A-1, biomimetic SPMDs will be deployed in the sediment once before and twice after AC treatment to simulate the in situ availability of PCBs to biota. The SPMDs used in this study will be 10 cm long and will contain the nonpolar lipid triolein. One SPMD will be vertically suspended inside each clam tube onto two hooks mounted on the inner wall. Each end of the SPMD has a 3-cm-long loop. These loops will be slipped onto the hooks that are 16 cm apart. The top loop of the SPMD will be located 3 cm below the sediment surface. This design will allow the SPMD to be suspended and stretched vertically, keeping it away from the clam tube wall. A total of 75 SPMDs will be deployed during the entire project. Following field collection, the SPMDs will be sent to Stanford University for PCBs analysis.

A.3.2.2.2 M. nasuta ***Tube Deployment and Retrieval***

PCB bioaccumulation in test clams will be measured using particle-feeding *M. nasuta* clams native to San Francisco Bay. The work shall use small organisms (6-g "whole clam with shell" weight, to reduce the slow internal equilibration kinetics associated with larger organisms) of standard size (to minimize size-related accumulation effects). These clams will be placed in mesh-covered PVC tubes sunk into the five plots once before and twice after AC treatment at each of the five sampling locations, according to the schedule shown in Table A-1. The clam tube will be 1.5 feet long and have a diameter of 6 inches. The five clam tubes in each plot are considered experimental replicates. The six clams will be placed per clam tube onto the sediment surface within the tube's diameter and allowed to burrow. A total of 75 clam tubes will be deployed during the entire project. After a 28-day exposure, the clams will be removed by carefully scooping out the sediment in the clam tubes. The clams then will be separated from the sediment, rinsed with site water, and placed in polyethylene containers. The organisms shall be depurated in clean sediment for 24 hours and then in seawater for 48 hours at ambient temperatures before sacrificing clams. Each clam will be shucked, and the resulting whole tissue will be placed in a separate scintillation glass vial. At ERDC each set of six (or total number surviving) clams that came from a given clam tube will be homogenized and split. Half will be shipped to BDO for archiving and while the other half will be analyzed at ERDC. The in situ tests will conform to work of others employing planktonic crustaceans, amphipods, shrimp, and oligochaete worms (e.g., Chappie and Burton, 1997).

A.3.2.2.3 Indigenous Amphipod Sample Collection

According to the schedule in Table A-1, five separate surface (0-2 cm) sediment samples shall be collected at the sampling locations in each plot as shown in Figure A-5 and placed into a separate wide-mouthed polyethylene jar with a vented lid. These jars shall be maintained at <18 °C in a cooler, and

transferred to laboratory conditions within 2h of collection where they will be sieved for *Corophium* spp.amphipods. Each sieved sediment sample shall provide at least 200 mg wet weight of amphipods.

A.3.2.2.4 Quadrat Surface Sediment Collection and Sieving

At each of the sampling locations shown in Figure A-5, surface sediment (0-10 cm) will collected from 0.25-m quadrats once before and twice after plot treatments as shown in Table A-1 and placed in separate, labeled plastic buckets prior to processing. The benthic organisms existing in these quadrat sediment samples will be sieved using a 500µm sieve, preserved in 10% formaldehyde solution in the field, and transferred to the laboratory in 500mL polyethylene jars. A total of 75 quadrats will be sieved during the entire study producing 75 benthic community samples. By comparing the macrofaunal composition that exists in the benthic community samples collected before and after treatments, the AC treatment effects upon benthic recolonization, community structure and organism growth can be determined.

A.3.2.2.5 Surface Water Sample Collection

Overlying water above the all five plots will be sampled simultaneously soon after the high tide recovers the plots before and after treatment with AC, as indicated in Table A-1. This sampling event for the five plots will be repeated after the first set of samples is obtained. A total of 40 water samples will be collected for analysis. The method is similar to the surface water sampling method used in the EPA Lake Michigan Mass Balance Study (http://www.epa.gov/glnpo/lmmb/methods/field96.pdf). The inlet of the sampling tube will be positioned and anchored 0.5 ft above the sediment surface and submerged under water during high tide. The method involves sampling up to 50 L of water per sample from the field, pumping the water through a pre-combusted glass fiber filter paper with a nominal pore size of 0.7 microns, and passing the filtered water through a pre-cleaned XAD-2 resin adsorbent column. The filter paper containing the suspended particulates and the XAD-2 resin columns containing trapped dissolved PCBs will be shipped in a cooler to the UMBC laboratory for extraction and PCB analysis.

A.3.2.2.6 Sediment Core Sample Collection

According to the schedule in Table A-1, sediment core samples will be collected to evaluate the depth and homogeneity of the treatments in the sediment and the sediment PCB concentrations. At each of the sampling locations shown in Figure A-5, 2.0-inch-diameter sediment core samples will be taken once before and twice after AC treatment for a total of 75 core samples during the entire project. Samples will be collected, capped, and returned to Stanford for processing.

A.3.2.2.7 Equipment Decontamination

Throughout sample collection activities, care will be taken to avoid sample contamination. This will be accomplished through rigorous decontamination procedures and careful sample handling procedures (Section A.3.3).

- To the extent possible, non-contaminating materials (glass, stainless steel, Teflon™) will be used for sample collection.
- Sampling equipment will be cleaned prior to use and between samples.
- All sources of contamination (airborne sources, fingers, unclean equipment) should be avoided.

To avoid cross-contamination in core samples collected for TOC and PCB analysis, a separate pre-cleaned core liner will be used to collect and contain each sample. The core sample will be capped at both ends to seal in the sediment, which will not be removed from the liner until it is opened for processing under controlled laboratory conditions (described in Section A.3.3.3.4).

A.3.2.2.8 Management and Disposal of Investigation-Derived Waste

Field sampling and sample preparation activities will be conducted such as to minimize generation of waste materials. In the field, sediment and rinse water from sampling equipment will be washed back to Parcel F. Solvent waste will not be generated in the field. All solid waste (gloves, paper towels, etc.) will be bagged or otherwise contained prior to disposal in standard refuse containers (dumpsters). In the laboratory, solvent waste will be contained in appropriately labeled containers and disposed of in compliance with state and federal waste handling regulations. Solid waste and wastewater generated during sample preparation of sediment samples at each laboratory will be managed in compliance with the organization's requirements. Sediment analytical results can be used to characterize the waste, identify the waste stream, and determine whether or not excess sediment requires management as hazardous waste. Excess sediment and archived sediment samples will be held as long as they are analytically viable (up to one year); when the samples are no longer of use to the project they will be handled as waste.

A.3.3 Sample Processing, Handling, and Custody

A.3.3.1 Sample Processing

Minimal sample processing will be conducted in the field. Sample processing will be conducted at facilities that have the appropriate clean laboratory space, experienced staff, secure sample storage, decontamination facilities, and shipping/receiving service for processing and subsampling cores.
All other samples will be processed at the laboratory that will perform the analysis. Table A-6 defines the container types, sample volumes, preservation methods, laboratory addresses and contacts, and holding times.

A.3.3.2 Field Sample Containers and Labeling

Sample containers will be labeled with waterproof, adhesive-back labels. Sample labels must provide sufficient detail to uniquely identify each sediment sample and allow tracking to field activities. Sample identification numbers will be in the format:

EAE-001

Where E is the year 2005 (F-2006, G-2007, H-2008)
AE is the Survey Number
001 is a unique, sequential number

Sample labels must include a unique sample identification number (EAE-XXX), sample type (core, clams, SPMD, filter, or XAD column), collection date, sample collector's name, container number and total number of containers (e.g., 1 of 2, 2 of 2). An example is provided below.

ESTCP DP Project
Unique Sample ID: EAE-___ _____ ___
Location ID_____
Sample Type (circle one)
Core / Clams / Amphipods / Quadrat / SPMD /filter / XAD/
Date: _____ **Time:** _____
Sample Collector:_____
Container_____of_____

A.3.3.3 Sample Handling

During sample collection and handling, field personnel will wear polyethylene or latex gloves gloves during all sampling collection activities that involve sediment. Gloves should be changed often.

Sample holding conditions and holding times are detailed in Table A-6. Holding times are calculated from the time of sample collection. Documentation must be sufficient to track sample holding, processing, and analysis times to ensure that holding times are met. Documentation of sample collection must include both date and time. The following sample handling requirements must be met for all samples:

- Samples must be held in a controlled area with limited access; and,
- Deviations from the defined storage requirements must be documented and reported with the data.

A.3.3.3.1 SPMD Sample Handling

SPMDs will be rinsed gently with site water to remove sediments attached to the outer surface, taking care not to puncture the surface. The SPMD will be placed in a glass container with a Teflon™-lined lid. SPMDs will be stored at 4°C until analysis at Stanford.

A.3.3.3.2 **M. nasuta** *Sample Handling*

Living clams shall be removed from tubes and transferred to a vented polyethylene jar that contains clean water. The clams will be transported to Stanford University and allowed to depurate in clean water for 48 hours at ambient temperatures. After depuration, each surviving clam will be shucked and each resulting clam tissue will be placed into a separate pre-cleaned 20 mL scintillation vial. The vials containing a single clam tissue will be immediately placed in a -10°C freezer. Once frozen, the samples will be shipped overnight (on dry ice in a cooler) to ERDC. At ERDC each set of six (or total number surviving) clams that came from a given clam tube will be homogenized and split. Half will be shipped to BDO for archival at -10°C; while the other half will be analyzed at ERDC. If the survival is less than three clams

per clam tube, a conference call between BDO, Stanford, and ERDC will be conducted to determine the best distribution of available clam tissue.

A.3.3.3.3 Indigenous Amphipod Sample Handling

In the laboratory, the amphipods shall be removed from the sediment using a 500µm sieve and rinsed with clean artificial seawater. Amphipods shall be depurated for 24 h using San Francisco Bay seawater receiving trickle flow aeration in a cold room facility at 15 °C. Following depuration, amphipods from each sampling location shall be removed and weighed by placing them into tarred and pre-cleaned 20 mL scintillation vials. Samples will be immediately frozen. Once frozen, samples will be shipped on dry ice to ERDC for homogenization and splitting. Half of the resulting homogenate sample will be analyzed by ERDC, while the other half will be shipped on dry ice to BDO for archival at -10°C. Analysis of the PCB concentrations in these amphipod samples will assess the AC treatment effects upon PCB bioaccumulation in a resident benthic population.

A.3.3.3.4 Benthic Community Sample Handling

Benthic community samples collected from sieved quadrats will be preserved in a 10% formaldehyde solution, stored at 4 °C temporarily , and then shipped overnight to ERDC in coolers maintained at 4 °C. Once at ERDC, these samples will be subjected to benthic community structure analyses.

A.3.3.3.5 Surface Water Sample Handling

Sampling of the water column will produce a filter paper sample and a XAD-2 resin column sample. The filter paper sample will be transferred to a glass container with a Teflon™-lined lid. The XAD-2 resin column will be tightly capped. The filter paper containing the suspended particulates and the XAD-2 resin columns containing trapped dissolved PCBs will be shipped in a cooler to the UMBC laboratory for extraction and PCB analysis.

A.3.3.3.6 Sediment Core Processing and Sample Handling

Sediment cores for chemical analysis will be capped upon collection with no further field processing. These cores will be transferred in a cooler to Stanford University at the end of each collection day. Sediment cores will be subsampled at Stanford according to the following guidelines:

- Place the core on a non-contaminating surface and remove the end caps;
- Using a core plunger, slowly push out the core onto the non-contaminating surface and take a picture of the core;
- Every two inches, gently pass a clean stainless steel knife through the core and place cross sections into pre-cleaned beakers;
- Homogenize each cross section and remove a 1-g subsample for TOC measurement. The TOC subsample will be placed into a small pre-cleaned and labeled glass vial;
- Recombine and homogenize the top three cross sections (0-6 inches) in a large glass container with a Teflon™-lined lid. From this homogenate, a) remove a 5-g subsample for sediment PCB concentration measurement and place it into a pre-cleaned and labeled beaker, b) remove a 30-g subsample for aqueous equilibrium PCB concentration measurement and place it into a pre-cleaned and labeled 4 oz. glass jar, and c) remove a 100-g subsample for PCB desorption tests and place it into a pre-cleaned and labeled 500 mL beaker. [Note: This 500 mL beaker should be used to collect all five 100-g subsamples that are taken from the five homogenized sediments

cores that come from one given plot. Homogenize the resulting 500-g sample and remove two 100-g subsamples for the desorption tests. These two 100-g subsamples should be placed into separate pre-cleaned and labeled 4 oz. glass jars.]

- The remainder of the core will be archived;
- Document sediment subsamples by recording the following information: Date sediments were subsampled, ID code or number for each subsample, and sample allocation information (analyses performed).

At the conclusion of the project, sediment waste will be classified as potential hazardous waste and disposed of through procedures outlined by Stanford's Environmental Health and Safety program.

A.3.3.3.7 Sample Homogenization

Sample homogenization is a critical activity and must be conducted to ensure that the homogenate and aliquots are representative of the field material. For sediment samples, the sample homogenization referenced in Section A.3.3.3.6 will be accomplished by placing the wet sediment in a clean, glass container and mixed thoroughly by hand until a homogeneous color and texture is achieved. Homogenization of tissue samples is described in Sections A.3.4.2.1 and A.3.4.4.3.

A.3.3.4 Field Sample Preservation, Packaging, and Shipment

During the sampling day, samples collected for the ESTCP DP will be preserved by placing the containers in coolers immediately after collection. At the end of the sampling day, all field samples that are to be shipped overnight will be packaged in coolers and shipped with the appropriate chain-of-custody (COC) forms as described in Section A.3.3.5. Each of these coolers will also contain a temperature cooler blank so that the receiving laboratory may verify sample temperature upon receipt. Sediment cores will be stored upright.

A.3.3.5 Chain-of-Custody Records

Sample custody records are the administrative records associated with the physical possession and/or storage history of each individual sample from the purchase and preparation of each sample container and sampling apparatus to the final analytical result and sample disposal.

Sample custody will be documented throughout collection, shipping, analysis, and disposal of the sample. Samples will not be left unattended unless properly secured. The sample custody form provides a record of the samples collected and analyses requested. If more than one cooler is sent in one shipment to the laboratory, then each cooler will contain a separate custody record for the samples in that cooler. In addition, the outside of the coolers will be marked to indicate the number of coolers in the shipment (e.g., 1 of 2, 2 of 2). All coolers must be shipped under a bill of lading that identifies the total number of coolers in the shipment. Separate tracking numbers will be assigned to each cooler. Specifically for sample archives sent to BDO, sample custody procedures will be in accordance with the BDO SOPs 6-010, *Sample Receipt, Custody, and Handling*.

Each analytical laboratory must have a formal, documented system designed to provide sufficient information to reconstruct the history of each sample, including preparation of sampling containers, sample collection and shipment, receipt, distribution, analysis, storage or disposal, and data reporting within the laboratory. Laboratory documentation must provide a record of custody for each sample (versus a sample batch) throughout processing, analysis, and disposal.

The custody form summarizes the samples collected and analyses requested. The custody form tracks sample release from the field to the initial receiving laboratory. Each sample custody form will be signed by the person relinquishing samples once that person has verified that the custody form is accurate; i.e., that all samples present in the shipping container are listed on the form, and that the sample descriptions, requested analytical methods, and sampling dates are accurate. The original sample custody forms accompany the samples; the shipper will keep a copy. Upon receipt at the sample destination, sample custody forms will be signed by the person receiving the samples once that person has verified that all samples identified on the custody forms are present in the shipping container. Any discrepancies will be noted on the form (in addition to any internal laboratory documentation policy) and the sample receiver will immediately contact the Project Manager to report missing, broken, or compromised samples.

Samples are considered to be in a person's custody if:

- The samples are in a person's actual possession;
- The samples are in a person's view after being in that person's possession;
- The samples were in a person's possession and then were locked or sealed up to prevent tampering; or,
- The samples are in a secure area.

A.3.3.6 Sample Receipt

Immediately upon receipt by a laboratory, the condition of samples must be assessed and documented. The contents of the shipping container must be checked against the information on the custody form for anomalies. If any discrepancies are noted, or if laboratory acceptance criteria or project-specific criteria are not met, the laboratory must contact the Project Manager for resolution of the problem. The discrepancy, its resolution, and the identity of the person contacted must be documented in the project file. The following conditions may cause sample data to be unusable and must be communicated to the laboratory team leader:

- The integrity of the samples is compromised (e.g., leaks, cracks, grossly contaminated container exteriors or shipping cooler interiors, obvious odors, etc.);
- The identity of the container cannot be verified;
- The proper preservation of the container cannot be established;
- Incomplete sample custody forms (e.g., the sample collector is not documented or the custody forms are not signed and dated by the person who relinquished the samples);
- The sample collector did not relinquish the samples; and,
- Required sample temperatures were not maintained during transport.

The custodian must verify that sample conditions, amounts, and containers meet the requirements for the sample and matrix (Table A-6). A unique sample identifier must be assigned to each sample container received at the laboratory, including multiple containers of the same sample.

A.3.4 Analytical Laboratory Methods

The information in this section includes the analytical methods that will be used to assess the primary and secondary performance criteria listed in Table A-4. This section is divided into four parts so that the analytical methods are grouped according to the laboratory that is responsible. To summarize briefly, the following labs are responsible for the identified analyses:

- Stanford University Laboratory (Stanford, CA): PCBs in SPMD samples, total PCB in sediments, aqueous equilibrium PCBs, and total organic carbon (TOC) in sediment cores.
- USACE-ERDC Laboratory (Vicksburg, MS): PCBs in clam tissue samples, PCBs in amphipod samples, and benthic community structure analyses.
- UMBC Laboratory (Baltimore, MD): PCBs associated with surface water sampling and sediment PCB desorption characteristics
- BDO Laboratory (Duxbury, MA): PCBs in archived clam tissue samples split and PCBs in archived amphipod sample splits.

A.3.4.1 Analytical/Testing Methods for Stanford

A.3.4.1.1. PCB Uptake in SPMDs

The biomimetic SPMDs will be custom-made by Environmental Sampling Technologies to be 10 cm long and contain 0.1 g triolein, a component of fish lipid. (inner length is 10 cm and outer length including loops is approximately 16 cm) Upon retrieval, the SPMDs will be gently washed with site water to remove sediment from the surfaces, rinsed with deionized water, placed into a glass jar, and returned to Stanford for storage in a 4 ºC cold room until they are processed. The loops of SPMDs will be cut and removed. SPMDs will be cleaned by rinsing with deionized water, swirling for 30 s in 1 M hydrochloric acid, rinsing with the series of deionized water, acetone, and isopropyl alcohol, and air-drying for approximately 30s. The SPMDs will be then submerged in about 125 ml volume of hexane and dialyzed at room temperature for 24 h. The dialysate will be removed, and dialysis with 125 ml of fresh hexane will be repeated for 8 h. Dialysates will be combined with hexane rinse, the total volume will be recorded, and aliquots will be taken for cleanup. The cleanup procedure will include two steps. First, sulfur interferences will be removed by contacting with activated copper following EPA SW846 Method 3660A. Second, organic interferences will be removed using a deactivated silica gel (3% moisture) column following EPA Method 3630C. The PCB analysis of the resulting SPMD extracts will be performed according to Section A.3.4.1.3.

A.3.4.1.2 Sediment Core Processing and Analyses

The two-inch diameter core samples with lengths of 12-14 inches will be collected, capped, returned to Stanford, and stored in a 4ºC cold room until they are processed. As discussed in Section 3.3.3.6, each core sample will be divided into two-inch-long core cross sections. After TOC subsamples are removed from each cross section, the remainder of the top three cross sections (0-6 inches) from each core will be combined. From each resulting core homogenate, three portions will be removed for further analyses. The first 5-gram portion will be used to measure sediment PCB concentrations (Stanford). The second 30-gram portion will be used to measure aqueous equilibrium PCB concentrations (Stanford). The third 100-gram portion will be used to measure PCB desorption rates (UMBC)—see Section A.3.3.3.6 for complete details on how to obtain the PCB desorption subsamples.

TOC of Sediment

To assess the depth and homogeneity of the mixed AC in the sediment, the total organic carbon (TOC) of each cross section will be measured by elemental analysis, as it has been found to be an effective indicator for the amount of AC added in the sediment. Each cross section will be homogenized by stirring manually with a stainless steel spatula, and then approximately 1 g of sediment will be subsampled for elemental analysis. These subsamples will be dried and ground using an agate mortar and pestle. Duplicate subsamples of approximately 4 mg each will be weighed into silver boats. Weighed samples will be then acidified twice in situ with 6% sulfurous acid to remove carbonate phases. These sediment samples will be analyzed for total organic carbon (TOC) using a Carlo Erba NA1500 elemental analyzer at Stanford University. For well-mixed sediment in Plots D and F, we expect an average TOC of 3.8 wt.% (original sediment TOC = 1.0 wt.%) with a small standard deviation among samples within a plot.

Sediment PCB Concentrations
Sediment samples will be extracted three times with sonication in a 50% acetone and 50% hexane mixture, following a procedure based on EPA Method 3550A. The acetone portion will be removed and exchanged with hexane by a nitrogen blowdown apparatus. Then, the extract will be concentrated using a nitrogen blowdown apparatus and cleaned using the same two-step procedure mentioned previously for the SPMD extracts. The PCB analysis of the resulting sediment extracts will be performed according to Section A.3.4.1.3.

Aqueous Equilibrium PCB Concentrations
Equilibrium distribution of PCBs between sediment and aqueous phases will be measured by placing approximately 30 g of activated carbon-treated or untreated wet sediment in 780 mL glass bottles with 31 ppt seawater and 1 g/L sodium azide (practical grade, Mallinckrodt, Paris, KY) to inhibit microbiological growth. The bottles will be capped with Teflon-lined caps, shaken, and rotated at approximately 2 rpm on a roller for 14 d, after which the sediment/water mixture will be allowed to settle and the supernatant cleared of any floating particles with a Pasteur pipette. Colloids will be removed using a flocculation procedure described previously (Ghosh et al. 2000). PCBs will be extracted from the aqueous phase with hexane. The extract will be concentrated by a rotary evaporator and followed by a nitrogen blowdown apparatus. Extract cleanup will follow the same procedures mentioned previously for the SPMD extracts. The PCB analysis of the resulting extracts will be performed according to Section A.3.4.1.3.

A.3.4.1.3 Stanford PCB Congener Analysis
PCB congener specific analysis will be performed using a modified EPA Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm ID) and a micro electron capture detector will be used for analysis. A 5-level PCB calibration table will be prepared using a known PCB mixture containing 250 µg/L of Aroclor 1232, 180 µg/L of Aroclor 1248 and 180 µg/L of Aroclor 1262 yielding a total PCB concentration of 610 µg/L. The known PCB calibration mixture has been already obtained from the EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan. Concentrations of individual PCB congeners in this mixture have been obtained from Mullin. Two internal standards will be used: PCB-30 (2,4,6-trichlorobiphenyl) and PCB-204 (2,2’,3,4,4’,5,6,6’-octachloro biphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, 92 PCB congeners or congener groups can be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks will be calibrated as a sum of congeners.

A.3.4.2 Analytical/Testing Methods for ERDC

A.3.4.2.1 Extraction of PCBs in Clam and Amphipod Samples

Sample jars containing whole *M. nasuta* clam tissues will be received frozen from Stanford with no prior homogenization. Each sample jar will contain one whole clam tissue (1-2g). These clam tissues will be grouped in sets of six (or less based on survival rate) according to the clam tubes from which they were retrieved in the field. Each set of six clams will be thawed and combined (6-12 g) into a stainless steel mortar that is set in a bath of liquid nitrogen. Using a pestle, the combined tissue sample will be thoroughly pulverized and homogenized until the tissue has the consistency of a powder. After homogenization, there should be no chunks visible or pieces of whole tissue left. At this point, a 1-g aliquot will be removed for dry weight determination and a 1-g aliquot will be removed for lipid weight determination. After removing these aliquots, the resulting homogenate (4-10g) from each sample will be split into two equal parts (2-5g). One split will be analyzed by ERDC, while the other will be immediately frozen and later shipped on dry ice to BDO for archival.

If there is 4-5g of total tissue mass in the ERDC split, ERDC may further divide their split into two parts so that they have backup sample of their own. The extraction procedure will begin by weighing 2-3g aliquots of each ERDC split into 60mL vials. 0.1mL of surrogate will be added to each sample, including QC samples, and 0.1mL of spike will be added to the appropriate samples. 1g of hydromatrix will be added and stirred into each sample. 50mL of hexane will be added to each vial with sample. The vials will be shaken to ensure sample is free flowing and has not clumped together. Vials will be placed in ultrasonic bath and sonicated overnight.

The extracted samples will be filtered through a funnel containing sodium sulfate into TurboVap tubes. The vials and funnels will be rinsed several times with hexane. The TurboVap tubes will be placed in the TurboVap and the extracts will be evaporated to approximately 1mL before subsequent cleanup.

Extract cleanup will follow EPA Method 3630C (US EPA, 1996). Solvent-rinsed chromatography columns (15 x 250 mm, Kimble/Kontes, Vineland, NJ) will be packed with a plug of glass wool, followed by 3 g deactivated silica gel (3.3 % moisture) and topped with a small amount of sodium sulfate. Columns will be pre-rinsed with 20 mL hexane. Following addition of sample extracts, columns will be eluted with 80 mL of hexane. Samples will then be concentrated on a Zymark TurboVap II to approximately 2 mL. Extracts will be transferred to clear 12 mL vials, 2 mL of concentrated sulfuric acid will be added, and the mixture will be vortexed for 30 s. The hexane layer will be transferred to another 12 mL vial and the remaining acid rinsed with a small amount of hexane that will be combined with the primary extract. Approximately 1mL of water saturated with sodium bicarbonate will be added to the vial with the extract to neutralize any traces of acid. The vial will be shaken for several seconds, and then the water will be carefully removed from the extract. A small amount of sodium sulfate will be added to remove any remaining water. The extract will be concentrated under a stream of nitrogen to less than 1mL and then transferred to a 2mL chromatography vial. The 12mL vial will be rinsed with 0.5mL of hexane which will be also added to the 2mL vial. The extract will be given a final nitrogen concentration to less than 1mL. Internal standard will be added and the extract will be adjusted to 1mL.The PCB analysis of the resulting extracts will be performed according to Section A.3.4.2.3.

Aliquots of wet homogenized amphipod tissue (100 mg) will be weighed into certified pre-cleaned 20 mL vials. A surrogate, 2,4,5,6-tetrachloro-m-xylene, will be added to each sample to monitor method efficiency. Hexane (10 mL) will be added and each sample extracted twice for a total of 6 minutes using a Fisher Scientific Model 550 Sonic Dismembrator with microtip probe. Combined solvent layers will be transferred to a prepared silica gel column and cleaned up following EPA Method 3630C (US EPA, 1996).

A.3.4.2.2 Community Structure Analysis of Benthic Organisms from Surface Sediment Quadrats

To isolate treatment effects upon benthic recolonization, community structure, and organism growth, the benthic community samples shall be analyzed for macrofaunal composition, using a suite of appropriate

univariate and/or multivariate techniques to address both spatial and temporal differences in community structure (US EPA 1992).

A.3.4.2.3 ERDC PCB Congener Analysis

Following cleanup, extracts will be transferred to solvent-rinsed 2 mL vials, internal standards pentachloronitrobenzene and 4,4'-dibromobiphenyl (Restek, Bellafonte, PA), will be added at a final concentration of 50 ng/mL, and the final volume adjusted to 1 mL. Extracts will be analyzed following EPA Method 8082 (US EPA, 1996) using a Hewlett-Packard 5890 series II gas chromatograph equipped with electron capture detectors and dual columns using 2µl injection volume. Agilent (Wilmington, DE) DB-5MS and Supelco (Bellefonte, PA) SPB-octyl columns, both 30 m, 0.25 mm ID, 0.25-µm-film thickness, will be used to achieve separation. Initial oven temperature will be 130 ºC (2 minute hold time), ramped to 255 ºC at 1.4 ºC/minute. The temperature will be then raised to 265 ºC at a rate of 18º/minute and held for 9 minutes resulting in a total run time of 100.8 minutes. Injector and detector temperatures will be 255 and 305 ºC, respectively. The carrier gas mix will be helium (1.35 mL/minute) and 5% methane in argon (65 mL/min) gas. Data for co-eluting peaks will be presented as a sum of congeners. Only congeners with all data replicates above MDL will be included.

A.3.4.3 Analytical/Testing Methods for UMBC

A.3.4.3.1 Measurement of Aqueous and Suspended Particulate PCB Concentrations in Field Water

The XAD-2 resin and the glass fiber filters will be extracted in a soxhlet extraction system with a 50% acetone and 50% hexane. The soxhlet extraction procedure will follow EPA SW846 method 3540C. The extract will be concentrated in a Kuderna Danish evaporator and a N_2 blowdown apparatus. The PCB sample will be cleaned up from organic interferences using a deactivated silica gel column following EPA SW846 method 3630C. Sulfur interferences will be removed by contacting with activated copper following EPA SW846 method 3660B. The PCB analysis of the resulting extracts will be performed according to Section A.3.4.3.2.

A.3.4.3.2 PCB Desorption Characteristics of Field Sediments

PCB desorption characteristics of subsamples from a homogenate of sediment cores from each plot will be evaluated. The desorption tests will follow previously published methods (Ghosh et al. 2003a).

A.3.4.3.3 UMBC PCB Congener Analysis

PCB congener specific analysis will be performed using a modified EPA SW846 Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm ID) and a micro electron capture detector will be used for analysis. A 5-level PCB calibration table is prepared using a known PCB mixture containing 250 µg/L of Aroclor 1232, 180 µg/L of Aroclor 1248 and 180 µg/L of Aroclor 1262 yielding a total PCB concentration of 610 µg/L. The known PCB calibration mixture has been already obtained from the EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan. Concentrations of individual PCB congeners in this mixture have been obtained from Mullin (1994). Two internal standards are used: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2',3,4,4',5,6,6'-octachloro biphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, 92 PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks are calibrated as sum of congeners.

A.3.4.4 Analytical/Testing Methods for BDO

The analytical method chosen for BDO measurements was selected to meet the ecological benchmark and is based on the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) program. The critical data compound list of PCB congeners in Table A-7, with required reporting limits and detection limits, will be used if the archived sample splits are analyzed. Table A-8 provides a list of applicable laboratory SOPs.

A.3.4.4.1 Analysis of PCB Congeners in Archived Sample Splits

If it is determined that critical data is to be obtained from the archived tissue sample splits, BDO will perform the analysis of PCBs congeners according to low-level methods developed for the NOAA Status and Trends Program (Lauenstein and Cantillo, 1993). These procedures are detailed in BDO SOPs 5-190 and 5-128. Ideally, 30 g of sample tissue is homogenized by macerating the tissue using a tissuemizer and 75 mL of dichloromethane until a uniform slurry is attained with no visible non-uniform "chunks." This procedure is repeated once and the extracts decanted between tissumizing steps. A third extract is accomplished by adding 50 mL of dichloromethane to the tissue in the extraction vessel and shaking for 0.5 hours. The extract is purified and concentrated under nitrogen to a pre-injection volume of approximately 1.0 mL. Extracts for PCB congener analysis are solvent exchanged into hexane prior to analysis. Masses of tissue as low as 1 g can be extracted using this procedure; if less than 30 g is available then the entire sample will be extracted and the detection limits adjusted accordingly.

Laboratory analyses must be performed using instruments and columns that are capable of achieving the sensitivity and separation to achieve the reporting limits defined for PCB congeners.

- Samples are quantified using the method of internal standards.
- PCB compounds are analyzed by using a GC/ECD with a confirmatory column to qualitatively verify peak identification.
- Only PCB peaks confirmed on both columns will be considered "hits."
- Sample data will not be surrogate corrected.
- No data will be blank-corrected.

Manual integrations are also a key element of low-level organic compounds analyses and are implemented routinely for low-level GC/ECD data to separate data system baseline integration features from peaks that can be distinguished at greater than 3:1 signal:noise ratio. Manual integration:

- Will not be used preferentially for QC samples and must not be used to satisfy QC criteria requirements;
- Must be identified, and must be signed and dated by the analyst; and,
- Must be justified in each data package and in the case narratives. Due to constraints of the software acquisition software, each manually integrated value is not flagged.

Sample cleanup is a critical component of low-level organic compounds analyses; therefore, a variety of cleanup options may be employed to purify the sample extracts. Sample cleanup options are incorporated into the sample processing SOPs; all sample cleanup procedures will be documented. Sample cleanup procedures will be implemented on a batch-wide basis to ensure comparability of results and to assess cleanup effects on QC samples.

A.3.4.4.2 Tissue Lipids

If archived tissue sample splits will be analyzed, lipid concentrations will be determined for each sample. The lipid concentration of each tissue sample will be determined from the dichloromethane sample extract prepared during the PCB compounds extraction according to BDO SOP 5-190. A 10-mL aliquot of unconcentrated extract is air-dried to determine the DCM extractable lipid concentration.

A.3.4.4.3 Percent Moisture

If archived tissue sample splits will be analyzed, *percent moisture* will be determined by BDO to determine the amount of water present in sample aliquots. Percent moisture is determined by drying a well-homogenized aliquot of tissue sample. Percent moisture will be determined as the percent ratio of wet to dry weight for each analytical aliquot and applied to the data generated at each laboratory. Dry weights at BDO are performed using dry heat.

A.3.4.5 General Requirements

Each laboratory performing analyses for the ESTCP DP must comply with the training requirements defined in Sections A.2.6.1 and A.2.6.2. The BDO laboratory must also comply with the specific certification requirements defined in Sections A.2.6.3 and A.2.6.4.

A laboratory batch is defined as a group of ≤20 field samples of a similar matrix that is processed as a unit with the same reagents and solvents, simultaneously with the required QC samples, and analyzed in the same method sequence. A procedural blank must be analyzed in each analytical sequence. For the purposes of this study, all sediments are considered a "similar" matrix. Critical data will not be surrogate-corrected and no data will be blank-corrected.

Analytical failures must be assessed and corrected. In most cases an analytical failure will stop the flow of work until it is reviewed, the root cause is identified, and corrective action is implemented. Most analytical failures are associated with QC results or instrument performance. Corrective action for these areas is addressed in Section A.4.1. Any deviations from the approved methods must be documented and discussed in the report narrative.

Spent samples, solvent, and acid waste will be discarded in the appropriate waste stream according to SOPs and the sample custody requirements defined in Section A.3.3.5.

A.3.5 Quality Control Requirements

A.3.5.1 Field Quality Control

This section describes the use of cooler blanks and field duplicates in this study.

> **Cooler Blanks.** A cooler (temperature) blank will be placed in a cooler so that the temperature of each cooler can be measured accurately upon receipt at the laboratory without compromising sample integrity. Thus, the cooler blank is a surrogate sample: the cooler blank for water samples is deionized water, and the cooler blank for sediment samples is a solid matrix (e.g., soil, sodium sulfate). The container type for the cooler blank is not critical, but should be approximately the same size as the sample containers. Cooler blanks lids should be clearly labeled so that laboratory sample custodians will recognize and use them to measure temperatures upon receipt. Cooler blanks are <u>not</u> assigned a unique field sample identification number.

Field Duplicates. No field duplicates will be collected for this study. The samples collected within each plot are considered study replicates.

A.3.5.2 Analytical Laboratory Quality Control

The study design and QC samples are intended to assess the major components of total study error, which facilitates the final evaluation of whether environmental data are of sufficient quality to support the related decisions. The QC sample requirements are designed to provide measurement error information that can be used to initiate corrective actions with the goal of limiting the total measurement error.

QC samples and frequency applicable to analytical chemistry laboratories at Stanford, ERDC, UMBC, and BDO are detailed in Table A-9. The laboratory duplicate and matrix spike samples must be an authentic field sample, not one of the field duplicates. If there is insufficient tissue mass (or field sample) for a matrix spike or matrix spike duplicate, a laboratory control sample duplicate will be prepared to assess laboratory precision. Table A-10 defines the general required accuracy and precision for QC samples, along with corrective actions that must be implemented if QC criteria are not met.

All QC sample failures and associated corrective actions will be documented. If data must be reported with failing QC results, then data qualifiers will be assigned to the QC sample data. Table A-11 defines data qualifiers that will be applied by the laboratories.

A.3.5.3 Control Charts

Laboratory control charts are used to track the results of quality control on an ongoing basis. Criteria for monitoring control charts, for detecting warning or control limits, and for verifying that results fall within the acceptable limits are specified in the control chart SOPs or specific analytical procedures. Control criteria are defined in Table A-10.

Control charts for PCB congener analysis are established and maintained at BDO Duxbury using the percent recovery results of the LCS. The control chart average, warning (2σ), and control limits (3σ) must be based on at least 20 individual percent recovery values generated within a calendar year vs. a "true value" calculation using representative congeners of interest for each method (i.e., the same SOP).

A.3.6 Instrumentation/Equipment Testing, Inspection, and Maintenance

A.3.6.1 Field Equipment

Stanford University, its subcontractors, and ERDC will provide all field equipment required for the field survey, including the global positioning system (GPS), coring devices, and all supplies and consumables for the field-sampling program.

A.3.6.2 Laboratory Equipment

All analytical instruments and equipment are to be maintained according to SOPs and the manufacturers' instructions. Equipment and instrument maintenance is defined in laboratory SOPs. All routine maintenance and nonroutine repairs are to be documented in a bound logbook. The information recorded should include analyst initials, date maintenance was performed, a description of the maintenance activity, and (if the maintenance was performed in response to a specific instrument performance problem) the result of retesting to demonstrate that the instrument performance had been returned to acceptable standards prior to reuse. The return to analytical control is demonstrated by successful calibration.

A.3.7 Instrument/Equipment Calibration and Frequency

Laboratory and field equipment will be calibrated in accordance with U.S. EPA guidance or the manufacturers' recommendations. Field equipment refers to articles used for on-site monitoring and testing, whereas laboratory equipment refers to articles used in the laboratory in support of data collection (e.g., refrigerators). Laboratory instruments are units used for sample analysis (e.g., GC/ECD). Calibration procedures and frequencies are provided in this section.

A.3.7.1 Field Equipment

The location of the five plots is an important measurement for the ESTCP DP. GPS coordinates will be recorded in the field using a handheld GPS unit (Garmin Geko™ 201) with WAAS-enabled accuracy of ±3 m. The exact GPS coordinates will be defined with the latitude and longitude in terms of degrees and decimal minutes using WGS 84 datum. The dimensions of the plot are on a similar scale to that of the unit's accuracy, so only the center of each plot will be defined with GPS coordinates. The five sampling locations of each plot will be marked on a scale map (with magnetic North identified) in relation to the plot center, plot corners, and an external permanent marker. GPS coordinates will be recorded for water column samples taken over the plot areas.

The GPS unit will be calibrated by conducting a comparison measurement of a known reference position at a specific location versus the position location that is acquired by the GPS unit. The reference position is Benchmark SUAA0000-CORS established by the National Geodetic Survey, defined as 37° 25.614' Longitude (N) and 122° 10.396' Latitude (W). This position is identified with a marker that is a bolt in a metal plate. The marker is mounted on a 2 meter metal tower fixed to the roof of the Durand Building on the Stanford University campus. The calibration will be done each day prior to use. If the GPS unit fails to attain a reading within 10 m of the known reference position, then the unit will be recalibrated to this position.

Calibration information will be recorded in the field logbook. In addition, a label specifying the scheduled date of the next calibration will be attached to each piece of field equipment. If this identification is not feasible, then calibration records for the equipment will be readily available for reference.

Should any of the field equipment become inoperable, it will be removed from service and tagged to indicate that repair, recalibration, or replacement is needed. The Technology Leaders and Research Studies Leaders will be notified so that prompt service or substitute equipment can be obtained. Backup systems will be available for each instrument in use and will be calibrated prior to use in the field.

A.3.7.2 Laboratory Equipment and Instruments

Laboratory equipment and instrument calibration procedures will be completed in accordance with the laboratory SOPs. Specific DoD requirements for general laboratory equipment are defined in Table A-12. Calibration of the GC/ECD that will be used for PCB congener analysis by all laboratories (Stanford, ERDC, UMBC, and BDO) is summarized below.

Certified calibration standards used for instrument calibration will be obtained from commercial vendors for PCB congeners. Where possible, standards will be traceable to the National Institute of Standards and Technology (NIST). Stock solutions for spiking solutions will be made from reagent-grade chemicals or as specified in the SOPs. Stock standards may also be used to make intermediate standards from which calibration standards are prepared. All analytical stock solutions will be prepared using Class-A volumetric ware. Documentation relating to the receipt, mixing, and use of standards is recorded in the laboratory logbooks or on data sheets. Specific handling and documentation requirements for the use of

standards are provided in laboratory SOPs. All new calibration or spiking solutions are analyzed against a previously accepted standard to verify that the concentrations of each parameter are within 15% of the verified stock.

- Prior to analysis, a five- or six-point quadratic calibration curve that spans the expected concentration range will be generated by GC/ECD to quantify the individual PCB congeners. The correlation coefficient for the initial calibration must be r≥0.995.

- A mid-level calibration standard will be re-analyzed every 24 hours (typically 10-12 samples). The calibration check standard concentration must be ≤25% from true check standard concentration. If this calibration check fails corrective action will be performed. Affected samples will be reanalyzed according to the criteria and procedures defined in the SOP.

- Sample quantification is performed by the method of internal standards using the recovery internal standard (RIS) compounds as the quantification internal standards. Surrogate compound recoveries are determined for the surrogate internal standard (SIS) compounds. For tissue samples, target analyte concentrations are reported on a wet weight basis.

A.3.8 Inspection/Acceptance of Supplies and Consumables

Prior to use, supplies and consumables will be inspected and tested to ensure that they conform to the required level of quality. Any defective material will be replaced before the sampling event or before analysis begins. Each laboratory must maintain an inventory of all chemicals, reagents, purchased standards solutions, and solvents. All reagents and solutions must be reagent grade or better.

Certified clean containers (I-Chem or equivalent) will be used as sample containers in the field. Prior to use in the field, the containers will be inspected. Any defective material will be replaced before the sampling event begins. Certificates of analysis provided with the containers will be retained by the laboratory or field sample custodian, depending upon whether containers are shipped from the lab or drop-shipped directly to the field by the supplier. Appropriate materials, bubble wrap, plastic bags, tape, and supplies will be available for packing samples to avoid breakage during transport.

In the laboratory, tissue samples will be homogenized and transferred to certified, clean I-Chem or equivalent glass jars (PCB congeners). Prior to use, the containers will be inspected. Any defective material will be replaced before homogenization and aliquotting begins. The laboratory sample custodian will retain certificates of analysis provided with the containers. Appropriate materials, bubble wrap, plastic bags, tape, and supplies will be available for packing samples to avoid breakage during transport.

A.3.9 Nondirect Measurements

Any critical data generated from the archived tissue sample splits will be incorporated into the body of data that have been collected at HPS in support of the FS.

A.3.10 Data Management

Data generated in support of the ESTCP DP will be tracked and reviewed by the appropriate Research Leader. Critical data generated by BDO in support of the ESTCP DP are tracked and reviewed by the BDO Chemistry Laboratory Leader. After review and validation of the field and laboratory data reports, critical data will be entered into the regional database system in place at BDO. The database will provide data for the preparation of reports and graphics. The data management process for the study has been designed to minimize loss and human error. Data flow will be automated to the extent practical.

Data management (e.g., paper flow; data tracking, data entry, etc.) and data assessment (e.g., verification, validation, and data quality assessment [DQA]) activities require adequate QC procedures to ensure that the SOPs are being followed and result in records/reports that are accurate and appropriate. QC procedures include peer review of each step and management review of a certain percentage of the data. Each laboratory must document its data management procedures in an SOP. Data verification and review is described in Section A.5.0.

A.3.10.1 Field Data

Preprinted labels (Section A.3.3.2) that include a unique sample identification number and prompt for required sample-specific information will be provided to the field team. A separate label is attached to each sample container and the sample ID recorded on the field log. This provides a unique link between the field records and each sample.

Sample collection information is hand-recorded in bound, prepaginated logbooks, then keyed into spreadsheets or project-specific applications. Data entry into the electronic format follows the sampling efforts. In addition to sample collection information, which describes where and how samples were collected, the field team may also record other information associated with the collection of a sample. Sample custody forms document the transfer of each collected sample from the field to the laboratory, and from the processing laboratory to the analytical laboratory.

A.3.10.2 Laboratory Data

Data management at the laboratory begins with the receipt of samples. Samples are logged in and assigned unique identification numbers that are used to identify samples throughout storage, processing, analysis, and reporting. Laboratory data will be reported by analytical batch (20 samples) with a unique batch ID that is clearly and directly related to the unique quality control samples that were processed and analyzed with the batch. Required QC sample type and frequency are defined in Tables A-9 and A-10. QC samples should not be reported across batches.

For critical data analysis by BDO, a Laboratory Information Management System (LIMS) houses all data for samples from the arrival of the sample in the laboratory to the final delivery of data to the client. This system is used to track samples from arrival through analysis to reporting. The LIMS software is a two-fold system. SQL Server 2000 is used as the back end of the system; all data is stored in a SQL Server 2000 database. Data is entered and manipulated on the end user level with an application developed in Microsoft® Access 2000. With the exception of the database administrator and the database developer, all access to the database is accomplished using Microsoft® Access 2000. All data and derived products will be stored on the laboratory server and burned onto compact discs (CDs).

A.3.10.3 Electronic Data Deliverables

Electronic data files are named uniquely and systematically, enabling tracking and retrieval. All instruments use the same software versions. Electronic data reside on specified servers, not individual personal computers (PCs). Raw and final data files are saved to CDs in read-only format and are stored in locked cabinets.

All laboratories generating data that will be entered into the Stanford database are required to submit data to the data manager in EDD format. The EDD must be formatted as an ASCII-ii file or a spreadsheet of the laboratory data in the SOP-specified format. Section A.2.7.6 discusses the EDD.

All critical chemical concentration data collected by BDO for the study will be entered into the BDO database and the Stanford database (PCB congeners and related field data). The EDD for BDO analytical laboratories is detailed in BDO HPS SOP 003. The EDD file is validated for format and content and imported into the databases. If an EDD is not correctly structured, as described in the SOP, then the laboratory will be required to resubmit the data file in the correct format in a timely manner. All EDDs produced by BDO will conform to the requirements of the NEDTS and SWDIV EWI #6 (U.S. Navy, 2001).

A.4.0 ASSESSMENTS/OVERSIGHT

This section presents the internal and external checks (assessments) that will be used to ensure that

- Elements of this QAPP have been correctly implemented as prescribed for all investigations conducted under the ESTCP DP;
- The quality of the data generated is adequate and satisfies the DQOs identified in QAPP; and,
- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

Assessment activities will include inspection, peer review, data audits, and DQA.

A.4.1 Assessment and Response Actions

The following subsections identify planned assessment and oversight activities to ensure that the objectives identified above are attained for field and laboratory operations. The Navy QA Officer, Project QA Manager, and/or the Project Manager may also identify additional assessment activities to be performed during the course of the study, based upon findings of the planned assessment activities described below. These individuals are authorized to stop work for cause if data quality or staff safety is threatened.

A.4.1.1 Assessment Actions

An audit evaluates the capability and performance of a measurement system or its components and identifies problems warranting correction and is performed by a person independent of the activities audited. The Project QA Manager and the QA managers at each analytical laboratory are responsible for assigning audit activities. Technical expertise and experience in auditing will be considered in selecting an auditor or audit team.

A.4.1.1.1 Assessment of Field Activities

A field audit involves an on-site visit by an auditor or audit team. A field audit is not planned for the HPS ESTCP DP.

A.4.1.1.2 Assessment of Laboratory Operations

A laboratory performance audit has been conducted by NFESC at BDO analytical laboratory. The purpose of a performance audit is to ensure that the laboratory is capable of producing data of known and acceptable quality. The laboratory audit included reviewing the laboratory's written procedures, evaluating the laboratory's historical performance, and verifying that the laboratory procedures comply with Navy QA requirements. The performance audit also includes analysis of blind performance evaluation samples provided by the Navy to measure the laboratory's performance. Navy evaluation of BDO analytical laboratory for the analysis of PCB congeners has been completed.

BDO has an internal audit program to monitor the degree of adherence to its policies, procedures, and standards. The internal audit program includes systems audits, performance evaluations, data audits, and spot assessments. Internal audits are conducted by the laboratory QA officer, who is independent of the area(s) being evaluated. The internal QA program is defined in a QA manual. QA audit assessment procedures are defined in SOPs.

The Project Manager will communicate with each analytical laboratory on a regular basis while the project samples are being analyzed. This will allow assessment of progress in meeting DQOs and Management Quality Objectives (MQOs), and the identification of any problems requiring corrective actions early in the investigative process. The Project Manager will review any identified problems and provide for the swift implementation of any outstanding corrective actions.

A.4.1.2 Response Actions

An effective QA program requires prompt and thorough correction of nonconformance conditions that can affect quality. Rapid and effective corrective action minimizes the possibility of questionable data or documentation.

Two types of corrective actions exist: immediate and long term. Immediate corrective actions include correction of documentation deficiencies or errors, repair of inaccurate instrumentation, or correction of inadequate procedures. Often, the source of the problem is obvious and can be corrected at the time it is observed. Long-term corrective actions are designed to eliminate the sources of problems. Examples of long-term corrective actions are correction of systematic errors in sampling or analysis and correction of procedures producing questionable results. Corrections can be made through additional personnel training, instrument replacement, or procedural improvements. One or more corrections may be necessary.

QA problems and corrective actions will be documented to provide a complete record of QA activities and to help identify needed long-term corrective actions. Defined responsibilities are required for scheduling, implementing, documenting, and ensuring the effectiveness of the corrective action.

A.4.1.2.1 Field Corrective Actions

Field nonconformance conditions are defined as occurrences or measurements that are either unexpected or that do not meet established acceptance criteria and which will affect data quality if corrective action is not implemented. Some examples of nonconformance conditions include incorrect use of field equipment; improper sample collection, preservation, storage, or shipment procedures; incomplete field documentation, including custody records; incorrect decontamination procedures; incorrect collection of QC samples; and unsafe field practices.

Corrective action procedures will depend on the severity of the nonconformance condition. In cases in which immediate and complete corrective action is implemented by field personnel, the corrective action will be recorded in the field log notebook. Nonconformance conditions which have a substantial impact on data quality require completion of a corrective action request form (however named). This form may be filled out by an auditor or by an individual who suspects that any aspect of data integrity is being affected by a field nonconformance issue. Each form is limited to a single nonconformance issue; if additional problems are identified, multiple forms must be used for documentation.

Copies of the corrective action request form will be distributed, as appropriate, to the Project Manager, the Project QA Manager, and the project file. The problem resolution will follow the steps listed below:

- Determine when and how the problem developed;
- Assign responsibility for problem investigation and documentation;
- Determine corrective actions to eliminate the problem;
- Design a schedule for completion of the corrective action;
- Assign responsibility for implementing the corrective action; and,
- Document and verify that the corrective action has eliminated the problem.

The report will also list completion dates for each phase of the corrective action procedure and the due date for the Project QA Manager to review and check the effectiveness of the solution. If warranted, a follow-up audit will be conducted to check that the problem has not reappeared. The follow-up review is conducted to ensure that the solution has adequately and permanently corrected the problem. The Project QA Manager can require field activities to be limited or discontinued until the corrective action is complete and the nonconformance issue has been eliminated.

A.4.1.2.2 Laboratory Corrective Action

The internal laboratory corrective action procedures and a description of nonconformance situations requiring corrective action are contained in the laboratory QA plan and SOPs.

Specifically to BDO, at a minimum, corrective action and/or notification of the Chemistry Laboratory Manager will be implemented when any of the following three conditions occurs: (1) control chart warning or control limits are exceeded, (2) method QC requirements are not met, and (3) sample holding times are exceeded. Nonconformance situations will be reported to the appropriate laboratory manager within two working days after they are identified. In addition, a corrective action report, signed by the laboratory manager and the laboratory QA Manager, will be provided to the Chemistry Laboratory Manager and the Project Manager. Corrective actions will be implemented where possible, as specified in laboratory SOPs. Where corrective action is not feasible, appropriate qualifiers will be added to data.

A.4.2 Reports to Management

When the ESTCP DP is complete, the results will be incorporated into the ESTCP DP Reports (Cost and Performance, Final Technical, and Verified Fact Sheet) that will be prepared by Stanford University, UMBC, and ERDC.

A.4.2.1 Project Progress Report

The monthly and quarterly reports for this project are the responsibility of Stanford University.

A.4.2.2 Quality Control Summary Report

A data QC summary report will be prepared by BDO and submitted with the final study report if the RPM directs BDO to remove the samples from archival and analyze them. The report will describe, for each type of analysis,

- A summary of the QC procedures used to assess data accuracy, precision, and completeness;
- A detailed report of analytical data accuracy, precision, and completeness;
- The results of performance and systems audits; and,
- The corrective actions that have occurred over the period of the report.

Particular emphasis will be placed on determining whether project quality criteria were met and whether data are of sufficient quality to support required decisions. The duration and location of storage for the complete data packages also will be defined in this report.

A.5.0 DATA VALIDATION AND USABILITY

This section of the QAPP provides a description of the data review activities that will occur after the data collection phase of the project is completed. The requirements and methods for data review, verification, and validation, as well as the process for reconciling data generated with the DQOs are described. Implementation of these methods will determine whether or not the data conform to the specified primary and secondary performance criteria, thus satisfying the project objectives**.**

A.5.1 Data Review, Validation, and Oversight

Data review includes data verification, validation, and oversight, as well as reconciliation of the data quality with user requirements. The data verification process includes the initial review of the data packages to ensure that the analyses requested have been provided. Data validation is the process of reviewing data and accepting, qualifying, or rejecting data on the basis of sound criteria using established U.S. EPA guidelines. Final technical data review of analytical data occurs after independent data validation has been completed. It provides an indication of overall trends in data quality and usability. These procedures are detailed below.

A.5.1.1 Data Verification

The analytical data generated during field investigations will be assembled in packages by sample delivery group, processing batch, or analytical batch. The contents of a data package are defined in Section A.2.7.5. The analytical chemistry data packages generated by BDO will contain supporting QC data for the associated field samples and will be validated by an independent data validator (Section A.5.1.2).

Each analytical laboratory is responsible for reviewing each data package prior to release for validation. At a minimum, the following reviews must be performed:

- Peer review of the data by a qualified analyst;
- Review of the reported data and deviations by a technical supervisor or data coordinator; and,
- QA office review of 10% of the data.

Implementation of these procedures is defined in laboratory SOPs. Reviews must ensure the following:

- All data for project samples are reported accurately and completely;
- Sample analysis was conducted in accordance with required laboratory procedures and analytical methods specified in the QAPP;
- Criteria for data quality have been met or deviations are documented in the package narrative and data flags have been appropriately applied;
- Each data set is appropriately reviewed; and,
- All project requirements have been met.

A.5.1.2 Data Validation

Data validation is conducted to assess the compliance of chemistry data with the DQOs defined in the QAPP. Data are assessed for completeness and compliance with the requirements of the analytical methods. Validation is conducted on each data package to determine the adequacy of the data to meet the DQOs.

The Navy requests that any of the critical PCB congener data produced by BDO be validated through an outside data validation firm. Laboratory Data Consultants (Carlsbad, CA) is proposed as the data validation firm.

The PCB congener data that may generated by BDO uses low-level (NOAA NS&T or U.S. EPA) analytical methods that are appropriate for the assessment of ecological risk. There are no formal validation guidelines for the validation of these methods. Therefore, validation will emulate U.S. EPA guidelines (U.S. EPA, 1994a, 1994b, and 1994c), although specific validation criteria for data generated according to these methods may not exist. The U.S. EPA validation *guidelines* will be used in data validation, and the method-specific data assessment criteria defined in the laboratory SOPs and the QAPP will be used as the basis of validation.

Since HPS is a National Priorities List (NPL) site, the BDO data must be subject to a data validation strategy that involves 20% Level-IV and 80% Level-III data validation. These levels of data validation are described in Sections A.5.1.2.1 and A.5.1.2.2.

Stanford, ERDC, and UMBC laboratories will use a similar data validation strategy that will be conducted internally.

A.5.1.2.1 Level-III Data Validation

Level-III data validation assumes that reported data values are correct as reported. Data quality is assessed by verifying that the criteria defined in the QAPP (Table A-13) for critical data have been achieved.

A.5.1.2.2 Level-IV Data Validation

Level-IV data validation is based on the assessment of raw data packages, which include all data required for a full review and assessment of compound selection, integration, interference assessment, and re-quantification (e.g., spectra and chromatograms). Supporting records are also included in the package (e.g., calibration standard, instrument sequence files, and dilution factors).

Level-IV data validation includes requantification of reported QC and field sample values using the raw data files. In addition, instrument performance, calibration methods, and calibration standards are reviewed to ensure that the detection limits and data values are accurate and appropriate.

A.5.1.2.3 Results of Data Validation

During data validation, the laboratory performance is assessed against prescriptive requirements and subjective requirements. Evaluation of laboratory performance against prescriptive requirements is assessed through compliance with the method requirements and the acceptability of QC sample results that are independent of sample matrix (e.g., instrument performance checks, calibration criteria). An assessment of the subjective requirements involves identification of potential matrix effects, and consists of an evaluation of the analytical results and the results of the testing blank, duplicate, and matrix spike samples. The validator then assesses how, if at all, the matrix effect impacted the usability of the data. Best professional judgment in any area not specifically addressed by U.S. EPA guidelines will be utilized as necessary and will be described in the usability assessment portion of the data validation report.

The data validation report will include a comprehensive narrative detailing all QC exceedances and explaining qualifications of data results. Data qualification “flags” will be applied by the laboratory for data that do not meet quality criteria (Table A-10). These data qualifiers are listed and defined in Table A-11. Validation qualifiers will be applied directly to the EDD by the validator, as appropriate.

A.5.2 Data Quality Assessment Reconciliation with Planning Objectives

DQA is a data analysis and interpretation process involving scientific and statistical evaluation of data sets to determine if they are sufficient to support specific decisions. To implement the DQA process, the analyst will work closely with a multidisciplinary team, potentially including the Principal Investigator, Project Manager, Research Studies Leaders, and statistician. The overall assessment of the ESTCP DP is the responsibility of the Stanford University Principal Investigator.

Upon receipt of the laboratory analytical chemistry data, the data analyst shall assemble the data set, including field information such as sample coordinates and descriptions and associated field measurements, and review any additional reports (e.g., survey and validation reports). The DQA shall begin with exploratory data analysis, including a significant graphical component. Standard data assessment tools will be used, such as histograms, q-q plots, cumulative frequency distributions, and box plots. Because the DQA process evaluates individual data points within the context of entire data sets, it will identify both "suspect" data (probable outliers to the actual data distribution) and critical observations that could affect decisions based on these data. As necessary, "suspect" data will be submitted for "focused validation" to determine whether the "suspect" data resulted from errors in the data generation process. "Suspect" and other unusual observations will be reviewed by experts on the natural environment and the measurement process to determine if there are scientific explanations and if data can be corrected or need to be rejected. If observations are not corrected or rejected by the above process and are therefore determined to represent variability inherent in the measurement process or the environment, these data shall be retained within the data set. Any changes made to the data set shall be fully documented.

The DQA process addresses the questions "Did we get what we asked for?" and "Did we ask for what we need?" The standards which will be used to evaluate the adequacy of the study findings from the actual data received are the original DQO specifications for the HPS ESTCP DP survey design, which will be reviewed for continued relevance to the ecological risk decisions being made. To assess the adequacy of this sampling design to support the study questions, the data analyst must work with other members of the project team to determine if the number, type, and quality of samples as specified in the Demonstration Plan and QAPP and as actually collected, were appropriate. This includes: determining if the correct number and location of samples were taken; determining if the appropriate media were sampled; judging the adequacy of the sample number and locations, given the updated understanding of the problem; and determining if the understanding of the problem changed since the QAPP was prepared because of observations made by the field team.

For critical data, the BDO project manager will implement the DQA process as described in U.S. EPA guidance (U.S. EPA QA/G-9, 2000a) to determine adequacy of the critical data to support a decision. The ESTCP DP will generate data to support evaluation of remedial alternatives in the HPS Parcel F FS, as described in the DQOs. The DQA will start by determining if these critical assumptions held true, and whether the sampling design provided data of adequate quality to support the decision. The ESTCP DP Demonstration Plan describes data analysis procedures.

Assuming that the sampling design was adequate to support the decision, the evaluation of data adequacy to support that decision may terminate after the initial exploratory analysis, and the site should move forward in the decision-making process. This determination will be made based on the observed chemistry, the variability of these measurements, and a determination of the uncertainty associated with the types of comparisons that are being made with the data.

If an adequate level of confidence was achieved with the chemical constituent concentrations actually observed, this observation supports the case that data are sufficient to be incorporated into the FS.

A.6.0 REFERENCES

Battelle. 2003. "Appendix E: Source Patterns of Polychlorinated Biphenyls and Metals in Sediment Samples Collected from Area X-South Basin, Parcel F and Parcel E Shoreline."

Bucheli, T.D, and O. Gustafsson. 2001. "Ubiquitous Observations of Enhanced Solid Affinities for Aromatic Organochlorines in Field Situations: Are In Situ Dissolved Exposures Overestimated by Existing Partitioning Models?" *Environ. Toxicol. Chem., 20*: 1450-1456.

Chappie, D.J., and G.A. Burton. 1997. "Optimization of in situ bioassays with *Hyalela azteca* and *Chironomu tentans*." *Environ. Toxicol. Chem., 16*: 559-564.

DoD, see United States Department of Defense.

Ghosh, U.; Weber, A. S.; Jensen, J. N.; Smith, J. R. 2000. "Relationship between PCB Desorption Equilibrium, Kinetics, and Availability during Land Biotreatment," *Environ. Sci. Technol.*, *34*: 2542-2548.

Ghosh, U., J. Zimmerman, R.G. Luthy. 2003a. "PCB and PAH Speciation Among Particle Types in Contaminated Sediments and Effects on PAH Bioavailability." *Environ. Sci. Technol., 37*: 2209-2217.

Ghosh, U., J.R. Zimmerman, P.B. McLeod, R.G. Luthy, T.S. Bridges, and R.N. Millward. 2003b. "Microscale Association of Organic Contaminants to Sediment Particles and Implications for Risk Management." *Physiochemical Processes in Environmental Systems: Symposium in Honor of Professor Walter J. Weber, Jr. ACS Syposium Series, 43*(2).

Lauenstein, G.G., and A.Y. Cantillo (eds). 1993. "Sampling Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984 – 1992." NOAA Technical memorandum NOS ORCA 71, Silver Springs, MD.

Luthy, R.G., J.R. Zimmerman, P.B. McLeod, R.N. Zare, T. Mahajan, U. Ghosh, T S. Bridges, and R.N. Millward. 2002. *In Situ Stabilization of Persistent Organic Contaminants in Marine Sediments*. Annual Technical Report. Submitted to SERDP. December.

Luthy, R.G., J.R. Zimmerman, P.B. McLeod, R.N. Zare, T. Mahajan, U. Ghosh, T S. Bridges, and R.N. Millward. 2004. *In Situ Stabilization of Persistent Organic Contaminants in Marine Sediments*. SERDP Final Technical Report.

Millward, R.N., T.S. Bridges, J.R. Zimmerman, U. Ghosh, and R.G. Luthy. 2004. "Addition of Activated Carbon to Sediment to Reduce PCB Bioaccumulation by a Polychaete (*Neanthes arenaceodentata*) and Amphipod (*Leptocheirus plumulosus*)." *Environ. Sci. Technol. 39:* 2880-2887.

Mullin, M. 1994. "PCB Congener Quantification for Lake Michigan Mass Balance Study." EPA National Health and Environmental Effects Research Laboratory, Grosse Ile, MI.

Naval Facilities Engineering Service Center. 1999. *Navy Installation Restoration Chemical Data Quality Manual*. Special Report SP2056ENV. September.

NELAC. 2000. National Environmental Laboratory Accreditation Conference – Glossary.

NFESC, see Naval Facilities Engineering Service Center.

United States Department of Defense. 2002. *Quality Systems Manual for Environmental Laboratories. Prepared by the DoD Environmental Data Quality Workgroup*. Department of Navy, Lead Service. Final Version 2. June.

United States Environmental Protection Agency. 1992. *"Marine Benthic Community Structure Assessessment (Ch. 9)" in Sediment Classification Methods Compendium.* EPA/823/R/92/006. September.

United States Environmental Protection Agency. 1994a. *U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. EPA/540/R/94/012. February.

United States Environmental Protection Agency. 1994b. *U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. EPA/540/R/94/013. February.

United States Environmental Protection Agency. 1994c. *U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, Multi-Media, Multi-Concentration (OLMO1.0) and Low Concentration (OLC01.0)*. EPA/540/R-94/090. December.

United States Environmental Protection Agency. 2000a. *Guidance for Data Quality Assessment. Practical Methods for Data Analysis (EPA QA/G-9)*: QA00 Update. EPA/600/R-96/084. July.

United States Environmental Protection Agency. 2000b. *Guidance for the Data Quality Objectives Process (EPA QA/G-4).* EPA/600/R-96/055. August.

United States Environmental Protection Agency. 2001. *U.S. EPA Requirements for Quality Assurance Project Plans (EPA QA/R-5).* EPA/240/B-01/003. March.

U.S. EPA, see United States Environmental Protection Agency.

U.S. Navy. 2001. *Environmental Work Instruction 4EN.1.* SWDIV EWI #6.

Zimmerman, J.R., U. Ghosh, R.G. Luthy, T.S. Bridges, and R.N. Millward. 2004. "Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests." *Environ. Sci. Technol. 38:* 5458-5464.

Table A-1. Schedule of Plot Sampling and Analysis

t = Months Since Treatment	Sampling Description
	Pre-Treatment Sampling
t = -1.5	• Collect duplicate water samples in the five plots to measure aqueous and suspended particulate PCB concentrations in the water column during high tide. • Deploy clams, five replicate enclosures in the five plots. • Deploy SPMDs, five replicates in the five plots. • Take five, two-inch diameter core samples in the five plots for analysis of TOC and sediment PCB concentrations, aqueous equilibrium PCB concentrations, and PCB desorption rates. • Sieve surface sediment quadrats to collect benthic community samples • Sieve surface sediment samples to collect amphipod samples.
t = -0.5	• Remove clams for PCB congener analysis. • Remove SPMDs for PCB congener analysis.
	Mixing and AC Treatments
t = 0	• Apply various treatments to four of the five plots.
	Post-Treatment Samplings
t = 0.05	• Collect duplicate water samples in the five plots to measure aqueous and suspended particulate PCB concentrations in the water column during high tide.
t = 5	• Collect duplicate water samples in the five plots to measure aqueous and suspended particulate PCB concentrations in the water column during high tide.
t = 5.5	• Deploy clams, five replicate enclosures in the five plots. • Deploy SPMDs, five replicates in the five plots. • Take five, two-inch diameter core samples in the five plots for analysis of TOC and sediment PCB concentrations, aqueous equilibrium PCB concentrations, and PCB desorption rates. • Sieve surface sediment quadrats to collect benthic community samples • Sieve surface sediment samples to collect amphipod samples.
t = 6.5	• Remove clams for PCB congener analysis. • Remove SPMDs for PCB congener analysis.
t = 17	• Collect duplicate water samples in the five plots to measure aqueous and suspended particulate PCB concentrations in the water column during high tide.
t = 17.5	• Deploy clams, five replicate enclosures in the five plots. • Deploy SPMDs, five replicates in the five plots. • Take five, two-inch diameter core samples in the five plots for analysis of TOC and sediment PCB concentrations, aqueous equilibrium PCB concentrations, and PCB desorption rates. • Sieve surface sediment quadrats to collect benthic community samples • Sieve surface sediment samples to collect amphipod samples.
t = 18.5	• Remove clams for PCB congener analysis. • Remove SPMDs for PCB congener analysis.

Table A-2. Data Quality Objectives for Primary Quantitative Performance Criteria of ESTCP DP

STEP 1: State the Problem Sediment in HPS South Basin Parcel F (Area IX-X) is contaminated with PCBs and may pose an unacceptable risk to human health and the environment. The standard approach to addressing contaminated marine "mud flat" sediments is dredging and disposal. Mixing AC into sediments to reduce the bioavailability of PCBs is potentially an effective in situ remediation strategy. Laboratory studies have demonstrated that PCBs in sediment tend to preferentially accumulate in coal-derived and char particles where the compounds may be strongly bound (Ghosh et al., 2003a; Luthy et al., 2002; Zimmerman et al., 2004). Laboratory studies also show that mixing AC with sediment reduces PCBs concentrations in the tissue of benthic organisms (Luthy et al. 2004). A field study is required to a) compare the effectiveness, in terms of homogeneity and depth of AC application, of two available large-scale mixing technologies, b) demonstrate that AC treatment of sediment reduces PCB bioaccumulation in the field, and c) evaluate sediment resuspension and PCB release.
STEP 2: Identify the Decision **PRIMARY DECISION** 1. Will AC treatment of PCB-contaminated sediment reduce PCB bioaccumulation in the field? 2. Will large-scale field application of carbon via AEI or CEI mixing equipment adequately mix the sediments and AC? 3. Will PCB resuspension occur as a result of mixing AC into sediment?
STEP 3: Identify Inputs to the Decision 1. PCB concentrations in sediment-dwelling *M. nasuta* clams (native to San Francisco Bay) from one-month exposures in clam tubes sunk in plots once before and twice after plot treatments. 2. PCB concentrations in indigenous *Corophium spp.* amphipods collected from plots once before and twice after plot treatments. 3. Total Organic Carbon (TOC) measurements in cross-sections of core samples taken from test plots once before and twice after plot treatments. 4. Dissolved and particulate PCBs in water column above test plots once before and thrice after plot treatments.
STEP 4: Define the Study Boundaries • The study area is approximately 100 ft offshore in Area X off the mid-eastern South Basin shoreline. Five 370 ft^2 test plots will be located in the study area, all equidistant from the shoreline. • The vertical limit of the study area will be a depth of 1.5 ft. • The plot treatments and field sampling schedule are constrained by the low tide schedule.
STEP 5: Develop a Decision Rule **PRIMARY DECISION RULE (Sampling design quantitatively focuses on this decision rule)** 1. If the PCB tissue concentrations for AC-treated (Plots D and F) are significantly lower when compared to control plots (Plots C, E, and G) using an appropriate statistical method, then these results indicate that AC treatment reduces PCB bioaccumulation in the field. 2. The average of the TOC values of all the sediment core cross sections analyzed from one plot (after a homogenous 3.4 wt.% AC dose in either Plots D or F) should be 3.8 wt.%, given an initial TOC of 1.0 wt.%. If the average of the TOC values of all the sediment core cross sections analyzed from one plot is 3.8 ± 2.5 wt.% (given an initial TOC of 1.0 wt.%), then the mixing afforded by the AC application was "good." Qualitative statements about the AC mixing will be based on the magnitude of the standard deviation (SD) as follows: SD = 0.0 – 1.5 wt.%, excellent mixing; SD = 1.6 – 2.5 wt.%, good mixing; SD = 2.6 – 3.6 wt.%, fair mixing; SD > 3.6 wt.%, poor mixing. 3. If there are no significant differences in the water column PCB concentrations before and after AC treatment, then sediment-bound PCBs are not resuspended due to AC application.
STEP 6: Evaluate Decision Errors Insufficient PCB bioaccumulation data could result in incorrect conclusions being drawn concerning the efficacy of AC treatment. An insufficient number of TOC samples could result in a large standard deviation across sediment cores in a given test plot, which in turn would suggest that the AC application was not homogeneous. Uncertainty in the water column PCB concentrations before and after plot treatments could result in an over- or under-estimation of the resuspension of PCBs due to treatments of the sediment. Duplicate samples during slack tide will be taken to minimize this error.

Table A-2. Data Quality Objectives for Primary Quantitative Performance Criteria of ESTCP DP (continued)

STEP 7: Optimize the Design for Obtaining Data

PCB Bioaccumulation in Test Clams
PCB bioaccumulation will be measured using *Macoma nasuta* clams that are particle-feeding organisms native to San Francisco Bay. Six clams will be deployed into each of the five mesh-covered clam tubes that are sunk into the five random sampling locations of each plot as shown in Figure A-5. At three intervals during the study (1 month pre-treatment, 6 months post-treatment, and 18 months post-treatment), we will deploy clams and characterize their survival and 28-day PCB bioaccumulation. To measure PCB bioaccumulation, living clams shall be removed from tubes and transferred to a vented polyethylene jar that contains clean water. The clams will be transported to Stanford University and allowed to depurate in clean water for 48 hours at ambient temperatures. After depuration, each surviving clam will be shucked and each resulting clam tissue will be placed into a separate pre-cleaned 20 mL scintillation vial. The vials containing a single clam tissue will be immediately placed in a -10°C freezer. Once frozen, the samples will be shipped overnight (on dry ice in a cooler) to ERDC. At ERDC each set of six (or total number surviving) clams that came from a given clam tube will be homogenized and split. Half will be shipped to BDO for archival at -10°C; while the other half will be analyzed at ERDC. the clams will be removed from the field after exposure and depurated in clean sediment for 48 hr. The clams will then be subjected to PCB congener, moisture and lipid analyses.

PCB Bioaccumulation in Indigenous Amphipods
PCB bioaccumulation will be measured in indigenous benthic biota. At each the three sampling time points, five separate surface (0-2 cm) sediment samples shall be collected at the five random sampling locations in each plot as shown in Figure A-5, and placed into a separate wide-mouthed polyethylene jar with a vented lid. These jars shall be maintained at <18 °C in a cooler, and transferred to laboratory conditions within 2h of collection where they will be sieved for *Corophium* spp.amphipods. Each sieved sediment sample shall provide at least 200 mg wet weight of amphipods. In the laboratory, the amphipods shall be removed from the sediment using a 500µm sieve and rinsed with clean artificial seawater. Amphipods shall be depurated for 24 h using San Francisco Bay seawater receiving trickle flow aeration in a cold room facility at 15 °C. Following depuration, amphipods from each sampling location shall be removed and weighed by placing them into tarred and pre-cleaned 20 mL scintillation vials. Samples will be immediately frozen. Once frozen, samples will be shipped on dry ice to ERDC for homogenization and splitting. Half of the resulting homogenate sample will be analyzed by ERDC, while the other half will be shipped on dry ice to BDO for archival at -10°C. Analysis of the PCB concentrations in these amphipod samples will assess the AC treatment effects upon PCB bioaccumulation in a resident benthic population.

Depth and Homogeneity of the Mixed AC
In each plot, 2.0-inch-diameter sediment core samples will be collected at five randomly distributed sampling locations once before and twice after plot treatments. Each of the core samples collected will be one foot in length (minimum) and divided into 2-inch-long core cross sections. A direct correlation exists between measured TOC and the amount of AC added in sediment, so TOC analysis will be performed on a subsample of each core section to evaluate the degree of AC mixing into sediment.

Resuspension of PCBs
Duplicate samples of the overlying water above the five plots during high tide once before and thrice after plot treatments will take place to measure the dissolved and particulate PCB concentrations. A total of 40 water samples will be collected 0.5 foot above the sediment surface for. Sample collection involves pumping water through a pre-combusted glass fiber filter with a nominal pore size of 0.7 microns in a stainless steel filter holder to trap suspended particles; this will be followed by passing the filtered water through a XAD-2 resin trap in a glass column.

Table A-3. Data Quality Objectives for Secondary Quant. Performance Criteria of ESTCP DP

STEP 1: State the Problem Experiments that add additional support to the primary quantitative data quality objectives/performance criteria listed in Table A-2 are required to fully assess the AC treatment technology. These experiments are needed to: 1) validate that the AC treatment reduces aqueous PCB availability in the field (biomimetic semi-permeable membrane devices (SPMDs), aqueous equilibrium studies, and desorption studies), 2) assess AC treatment effects on benthic recolonization, community structure, and organism growth, and 3) assess the stability of the AC/sediment mix.
STEP 2: Identify the Decision **PRIMARY DECISION** 1. Will AC treatment reduce aqueous PCB availability in field sediment? 2. Will AC treatment affect the indigenous benthic community? 3. Will the AC/sediment mix remain stable over time?
STEP 3: Identify Inputs to the Decision 1. a. Aqueous PCB measurements in equilibrium with sediment subsamples taken from plot cores once before and twice after plot treatments. b. PCB desorption rates for sediment subsamples taken from plot cores once before and twice after plot treatments. c. PCB uptake into SPMDs placed into plots once before and twice after plot treatments. d. PCB congeners in a homogenate of the entire sediment core taken from test plots before and after AC treatment. 2. Community structure analyses of benthic organisms found in each of the sieved quadrats taken once before and twice after plot treatments. 3. Total Organic Carbon (TOC) values measured for sediment cores from Plots D and F taken after six and eighteen months will compared to evaluate if there are any significant differences in the amount of AC in these plots between the two sampling time points.
STEP 4: Define the Study Boundaries 1. The study area is approximately 100 ft offshore in Area X off the mid-eastern South Basin shoreline. Five 370 ft^2 test plots will be located in the study area, all equidistant from the shoreline. 2. The vertical limit of the study area will be a depth of 1.5 ft. 3. The plot treatments and field sampling schedule are constrained by the low tide schedule.
STEP 5: Develop a Decision Rule **PRIMARY DECISION RULE (Sampling design quantitatively focuses on this decision rule)** 1. a. If the aqueous equilibrium PCB concentrations for the AC-treated plots (Plots D and F) are significantly lower when compared to control plots (Plots C, E, and G) using an appropriate statistical method, then these results indicate that AC treatment reduces aqueous PCB availability in field sediment. b. If the PCB desorption rates for the AC-treated plots (Plots D and F) are significantly lower when compared to control plots (Plots C, E, and G) using an appropriate statistical method, then these results indicate that AC treatment reduces the PCB desorption rate from field sediments. c. If the SPMD PCB uptake data for AC-treated plots (Plots D and F) are significantly lower when compared to control plots (Plots C, E, and G) using an appropriate statistical method, then these results indicate that AC treatment reduces PCB uptake into a biomimetic device. 2. If metrics of benthic community structure (e.g., total taxa richness, total abundance, relative amphipod abundance, and various multi-metric indices) of AC-treated plots (Plots D and F) are not statistically significantly reduced compared to that of the control plots (Plots C, E and G) then the AC application does not affect the benthic community structure. However, if a statistically significant difference (increase or decrease) does exist between treated and control plots in any metric of biological integrity, then the analysis of the community structure will be used to calculate the treatment effects on benthic recolonization. Determination of statistical differences in measures of biological integrity will be performed by one-way analysis of variance. 3. If there are no significant differences (by appropriate statistical test) between the six-month and eighteen-month TOC values measured in cross sections of sediment cores taken from Plots D and F, then the AC/sediment mix is stable in the timeframe of the study.

Table A-3. Data Quality Objectives for Secondary Quant. Performance Criteria of ESTCP DP (continued)

STEP 6: Evaluate Decision Errors Just the mixing of sediments in Plots C, D, F, and G will have a large impact on the community structure. Quadrats to assess community structure will be taken six and eighteen months after the treatments occur to give the benthic community time to reestablish itself. If this time period is insufficient, then it will be difficult to decide if it was the mixing or actual AC that affected the community structures.
STEP 7: Optimize the Design for Obtaining Data ***Sediment PCB and Aqueous Equilibrium PCB Concentrations*** Subsamples from the total of 75 cores will be analyzed for total PCB sediment concentrations and aqueous equilibrium concentration of PCBs. ***Sediment PCBs Desorption Characteristics*** Subsamples from two sediment cores per plot (taken once before and twice after treatments) will be analyzed to evaluate PCB desorption characteristics. The desorption tests on the sediment core subsamples will follow previously published methods (Ghosh et al., 2000) These analyses will allow us to assess the change in PCB availability for desorption to the aqueous phase after treatment. ***Benthic Community Structure Analyses*** Surface sediment (0-10 cm) will collected from five randomly selected 0.25-m quadrats per plot once before and twice after plot treatments. The benthic organisms existing in these quadrat sediment samples will be sieved using a 500µm sieve, preserved in 10% formaldehyde solution in the field, and transferred to the laboratory in 500mL polyethylene jars. A total of 75 quadrats will be sieved during the entire study producing 75 benthic community samples. By comparing the macrofaunal composition that exists in the benthic community samples collected before and after treatments, the AC treatment effects upon benthic recolonization, community structure and organism growth can be determined. ***PCB Uptake into SPMDs*** Five semi-permeable membrane devices (SPMDs) will be deployed inside of the clam tubes in each plot once before and twice after plot treatments. A total of 75 SPMDs will be deployed during the entire project. Measurement of PCB uptake into these devices will simulate the in situ bioavailability of PCBs to biota. The SPMDs will be vertically oriented 3 cm below the sediment surface inside each clam tube. The SPMDs will be contacted with sediment for one month before removal, processing, and analysis. ***Depth and Homogeneity of the Mixed AC*** In each plot, 2.0-inch-diameter sediment core samples will be collected at five randomly distributed sampling locations once before and twice after plot treatments. Each of the core samples collected will be one foot in length (minimum) and divided into 2-inch-long core cross sections. A direct correlation exists between measured TOC and the amount of AC added in sediment, so TOC analysis will be performed on a subsample of each core section to evaluate the degree of AC mixing into sediment. ***Stability of AC/Sediment Mix*** Total Organic Carbon (TOC) values measured for sediment cores from Plots D and F taken after six and eighteen months will compared to evaluate if there are any significant differences in the amount of AC in these plots between the two sampling time points.

Table A-4. Primary and Secondary Quantitative Performance Criteria Measurements for the ESTCP DP

Performance Criteria	Primary/ Secondary	Associated Lab Sample	Lab Analysis	Lab Responsible for Analysis
PCB bioaccumulation in test organisms	Primary	Clam tissue	Low-level PCB congeners, lipids, dry weight	ERDC/BDO[1]
PCB bioaccumulation in indigenous organisms	Primary	Amphipod tissue	Low-level PCB congeners, lipids, dry weight	ERDC/BDO[1]
AC application	Primary	Sediment	TOC	Stanford
PCB Resuspension	Primary	XAD resin, filter	PCB congener	UMBC
AC/Sediment Stability	Secondary	Sediment	TOC	Stanford
Effects of AC treatment on indigenous benthic community	Secondary	Benthic community	Benthic community structure	ERDC
PCB Uptake into SPMDs	Secondary	SPMD	PCB congener	Stanford
Aqueous equilibrium PCB concentrations	Secondary	Water	PCB congener	Stanford
PCB Desorption Rates	Secondary	Sediment	PCB congener	UMBC

[1]Only data generated by a Navy-certified laboratory (BDO) on archived tissue sample splits can be used for decision-making at Hunters Point.

Table A-5. Total Number of Samples and Intended Analyses for the ESTCP DP

Field Sample Type	Sample Analyses	Sample Amount	Total Number Collected During Entire Project
Clam Tissue	PCB concentration	composite of 6 clams	75 (each composite will be split between ERDC and BDO)
Amphipod	PCB concentration	mininum 200 mg composite	75 (each composite will be split between ERDC and BDO)
SPMD	PCB uptake	Each	75
Sieved Quadrat	Benthic Community	Each	75
Sediment Core	TOC	1 g	450
Sediment Core	Sediment PCB concentration	5 g	75
Sediment Core	Aqueous Equilibrium PCBs	30 g	75
Sediment Core	PCB desorption characteristics	100 g	30
Overlying Water	Dissolved PCBs	XAD column	40
Overlying Water	Particulate PCBs	Filter	40

Table A-6. Container, Sample Size, Preservation, and Shipping Information for the ESTCP DP

Sample Type	Sample Container Number, Type, Size	Min. Sample Size	Sample Preser-vation	Holding Time[(a)]	Receiving Laboratory and Sample Custodian
Clams	500 mL vented polyethylene jar	One clam	In cooler with ice, but no direct ice-clam contact.	24 h from collection to depuration	Stanford University Dept. Civil & Environmental Engineering, B-55 Stanford, CA 94305 Attn: Dennis Smithenry (650) 723-8574
Depurated Shucked Whole Clam Tissues for Splitting and Analysis	20 mL pre-cleaned scintillation vial	One whole clam tissue	Frozen (-10°C)	1 yr/40 d	U.S. Army Engineer Research and Development Center (ERDC) 3909 Halls Ferry Rd. Vicksburg, MS 39180-6199 Attn: Todd Bridges (601) 634-3626
Depurated Shucked Whole Clam Tissues for Archive	20 mL pre-cleaned scintillation vial	2 g homo-genate	Frozen (-10°C)	1 yr/40 d	Battelle 397 Washington Street Duxbury, MA 02332 Attn: Carole P-McCarthy (781) 952-5232
SPMDs	Original sample containers from supplier or 4 oz. pre-cleaned wide mouth glass	1	4°±2°C	1 yr/40 d (once ampoule is open)[(b)]	Stanford University
Sediment Cores	2-inch diameter butyrate core tube (1.5 ft. long)	12 inches	4°±2°C	TOC (1 yr) PCBs (1 yr/40d)	Stanford University
Benthic Community Samples	in 4% formaldehye solution in 500 mL polyethylene jars	N/A	4°±2°C	3 yr/(N/A)	ERDC
Amphipod Sample for Splitting and Analysis	20 mL pre-cleaned scintillation vial	200 mg	Frozen (-10°C)	1 yr/40 d	ERDC
Amphipod Sample for Archive	20 mL pre-cleaned scintillation vial	100 mg homo-genate	Frozen (-10°C)	1 yr/40 d	Battelle
Surface Water Samples—Filter Papers	8 oz. pre-cleaned wide mouth glass	One	4°±2°C	1 yr/40 d	University of Maryland Baltimore County 1000 Hilltop Circle Baltimore, MD 21250 Attn: Upal Ghosh 410-455-8665
Surface Water Samples—XAD Resin Columns	50mm x 300mm Glass Column Capped after Collection	400 mL XAD	4°±2°C	1 yr/40 d	University of Maryland

(a) Holding time: yr = year; d = day; h = hour; x/y = days from collection to extraction/days from extraction to analysis.

(b) SPMD samples can be stored for an undetermined period of time. Once SPMDs have undergone dialysis, the hexane extracts sealed in ampoules can also be stored under refrigeration for an undetermined period of time. (Personal communication, Terri Spencer, EST Laboratory, 2004).

Table A-7. PCB Congeners, Detection Limits, Reporting Limits, and Benchmarks for *M. nasuta* and *Corophium spp*. (All concentrations are ng/g wet weight.)

PCB Congeners	Method Detection Limit	Reporting Limit	Benchmark
Cl2(8)	0.32	0.22	NA
Cl3(18)	0.03	0.22	NA
Cl3(28)	0.04	0.22	NA
Cl4(44)	0.03	0.22	NA
Cl4(52)	0.02	0.22	NA
Cl4(66)	0.03	0.22	NA
Cl5(101)	0.02	0.22	NA
Cl5(105)	0.04	0.22	NA
Cl5(118)	0.04	0.22	NA
Cl6(128)	0.09	0.22	NA
Cl6(138)	0.04	0.22	NA
Cl6(153)	0.07	0.22	NA
Cl7(170)	0.04	0.22	NA
Cl7(180)	0.04	0.22	NA
Cl7(187)	0.04	0.22	NA
Cl8(195)	0.04	0.22	NA
Cl9(206)	0.03	0.22	NA
Cl10(209)	0.04	0.22	NA
Total PCBs	NA	NA	13.8[(a)]

(a) Battelle developed reference threshold concentrations for PCBs in San Francisco Bay as part of the validation study (Battelle, 2003). The 90th percentile value for total PCBs was approximately 69 µg/kg dry wt. This value represents a "background" concentration for PCBs in invertebrate tissues in the bay. This value is converted to wet weight using the conversion factor of 80% moisture for clam tissue and used as the benchmark for the ESTCP DP.

NA = not available.

Table A-8. BDO Standard Operating Procedures for the Critical Data Collection from Archived Tissue Sample Splits

Battelle Duxbury Operations	
3-116	Operation and Maintenance of Gas Chromatographs
5-128	Identification and Quantification of Polychlorinated Biphenyls (By Congener and Aroclor) and Chlorinated Pesticides by Gas Chromatography/Electron Capture Detection
5-190	Tissue Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis
BDO HPS SOP 003	Navy Program Electronic Data Interchange Standards For Analytical Laboratories

Table A-9. Definitions, Requirements, and Frequency for Quality Control Samples

QC Sample	Definition	Frequency
FIELD QUALITY CONTROL		
Equipment Blank (EB)	An equipment blank is a sample of contaminant-free medium (typically reagent-grade water) that has been passed through or over the sampling equipment used to collect field samples.	None
LABORATORY QUALITY CONTROL (on any sample with the exception of a field duplicate)		
Method or Procedural Blank (MB)	A combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. Monitors purity of reagents and laboratory contamination. Matrices: Water (MilliQ); soil or sediment (sodium sulfate). A processing batch MB must be analyzed with each sequence.	1/sample batch[(a)]
Laboratory Control Sample (LCS)	A LCS sample is a matrix-specific sample that is prepared with each processing batch. It is spiked with the analytes of interest and processed identically to the field samples. Matrices are the same as those used for the procedural blank.	1/sample batch
Laboratory Control Sample Duplicate (LCSD)	A second laboratory control sample prepared as described above if there is insufficient tissue mass to perform a matrix spike duplicate.	1/sample batch *if no MSD.*
Matrix Spike (MS)	A field sample spiked with the analytes of interest at 10X the MDL, processed concurrently with the field samples; monitors effectiveness of method on sample matrix; performed in duplicate for sediments.	1/sample batch *if sufficient tissue mass.*
Matrix Spike Duplicate (MSD)	Second aliquot of a field sample processed and analyzed to monitor precision; each sample set should contain a duplicate. The duplicate may be a second matrix spike sample.	1/sample batch *if sufficient tissue mass.*
Surrogate Internal Standards (SIS)	All field and QC samples are spiked with a known amount of surrogates just prior to extraction; recoveries are calculated to quantify extraction efficiency.	Each organic compounds sample
Reagent or Solvent Purity Checks	All reagents are lot-checked prior to use.	Per lot purchase

(a) A batch is defined as 20 field samples processed simultaneously and sharing the same QC samples.

Table A-10. Measurement Quality Criteria for Measurements of PCB Congeners

QC Parameter	Acceptance Criteria	Corrective Action
	Accuracy	
Field(Equipment) Blank	<RL	Review data and assess results for evidence of field-related contamination. Flag all data that are >RL.
Instrument Solvent Blank	< lowest calibration standard	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
Method (Procedural) Blank	<RL	Evaluate batch for corrective action if Blank > RL and sample concentration < 5 times the detected blank. Perform corrective action as above and re-process (extract, digest) sample batch. If batch cannot be re-processed; "B" flag all data that are < 5 times the blank.
•*Matrix Spike*	40 - 120% recovery **Concentration in spike must be >5 × background levels to be used for data quality assessment**	Review data to assess impact of matrix. If other QC data are acceptable and no spiking error occurred, then flag associated data. If QC data are not affected by matrix failure or spiking errors occurred, then re-process MS. If not possible, then notify client and flag associated data.
•*Surrogate Spike (SIS)*	40 - 120% recovery	Review data. Discuss with Laboratory Manager (LM). Reanalyze, re-extract, and/or document corrective action and deviations.
•*Laboratory Control Sample (LCS)*	40 - 120% recovery	Perform corrective action. Re-analyze and/or re-process sample batch. Batch data associated with failed LCS (LCS data outside control limits) cannot be reported. If batch cannot be re-processed: notify client, flag data, discuss impact in report narrative.
Precision: *MS/MSD*	<30% RPD **Concentration detected must be >5 times RL to be used for data quality assessment**.	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated data. If QC data are not affected by matrix failure, then re-process duplicate. If not possible, then notify client and flag associated data.

Table A-11. Navy Environmental Data Transfer Standard (NEDTS) Data Qualifiers for PCB Congener Analysis

	Data Qualifiers
B	Blank contamination: The analyte was detected above the reporting limit in an associated blank. For this study, blank contamination indicates that the analyte was found in both a sample and the associated blank. The "B" will be reported on the result associated with the field samples, not the blank.
D	Dilution run. Initial run outside linear calibration range of instrument
E	Estimate, result outside linear calibration range of instrument.
J	Estimated value (Compared to the sample-specific reporting limit)
R	Rejected
U	The value was less than the or the analyte was not detected (The sample-specific MDL is inserted)
X	Indicates manual modification of result or U.S. EPA qualifier
	Quality Control Qualifiers
N	Spiked sample recovery not within control limits
*	Duplicate analysis not within control limits

Table A-12. Calibration Procedures for Laboratory Equipment [(a)]

Equipment	Frequency of Check	Acceptance Criteria	Reference
Chemistry Laboratory Equipment			
Balance calibration check	Daily or before use with two weights that bracket target weight(s) and Annual calibration with NIST standards by certified technician	1% performance criterion to top-loading balances, and 0.1% to analytical balances. (Expanded criteria from 0.1 to 1% for top-loaders, for no standard existed for this balance type.)	ASTM E 898, Standard Practice for the Evaluation of Single-Pan Mechanical Balances, E 319, Standard Practice for the valuation of Single-Pan Mechanical Balances, and D 5522, Standard Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock, and Contained Fluid
Refrigerator/ Freezer temperature Monitoring	Daily	Refrigerators: 4 ± 2 °C, Freezers: -10 to -20°C (This ASTM standard does not address freezers, but SW-846 has noted this freezer range in some methods)	ASTM D 5522, Standard Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock, and Contained Fluid
Thermometer calibration check	Mercury - annually Electronic, spirit, or other glass thermometers - quarterly at two temperatures that bracket target temperature(s) against an NIST traceable thermometer	Appropriate correction factors applied	ASTM Methods E 77, Standard Test Method for Inspection and Verification of Thermometers, and D 5522, Standard Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock, and Contained Fluid
Variable volume pipettes (i.e., Eppendorf)	Monthly	3% of known of true value.	ASTM E 542, Standard Practice for Calibration o f Volumetric Apparatus, and E 969, Standard Specification for Volumetric (Transfer) Pipettes.
Nonvolumetric glassware/ labware verification (Applicable only when used for measuring volumes)	By lot at the time of purchase	3% of known or true value. (Standard tolerance does not exist – Class B volumetric flasks criteria vary between 0.8 to 0.05% for 5 mL to 2,000 mL, respectively – set at 3% to maintain consistency with pipette tolerance designation)	ASTM E 542, Standard Practice for Calibration of Volumetric Ware
Drying ovens	Before and after use	Compliance with method-specific requirements	ASTM D 5522, Standard Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock, and Contained Fluid

(a) Summary of Navy IRCDQM Equipment Calibration Requirements and related references. Toxicology information is defined by the laboratory and is not covered in the IRCDQM.

ASTM = American Society for Testing and Materials.

Table A-13. Level III Data Validation Assessment Parameters

Criteria	PCBs (GC)
Holding times	X
Instrument tunes	
Initial and continuing calibrations	X
Blanks	X (5X/10X rule)
LCS/ Laboratory set limits	
Surrogates	X
MS/MSD	X
Duplicates	
Internal standard area performance	
Target compound retention times	X
Instrument performance	X
Interference with compound quantification	X