
ANALYSIS PLAN /
QUALITY ASSURANCE PROJECT PLAN

**NAPA RIVER SALT MARSH RESTORATION
FEASIBILITY STUDY**

**SALT POND WATER AND SEDIMENT
CHARACTERIZATION**



U.S. Army Corps of Engineers
Environmental Planning Section
Materials Management Unit
San Francisco District

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1 Project Management

1.1 Purpose

This Sampling and Analysis Plan (SAP) / Quality Assurance Project Plan (QAPP) presents functions and procedures to meet the objectives of the analysis of salt pond water and sediment samples from the old Cargill Salt Ponds (Napa County, California) in support of the Napa River Salt Marsh Restoration Feasibility Study. This work will be performed by the Environmental Section, Materials Management Unit, of the U.S. Army Corps of Engineers (USACE), San Francisco District. The purpose of this investigation is to characterize the pond water and sediment to identify Contaminants of Concern (COCs) so that the restoration of this site can begin. Quality Assurance (QA) procedures designed to meet the project data quality objectives are described. The specifications herein must be followed to ensure that comparable data is produced and that data quality is consistently assessed and documented. The objectives of this document are to:

- Provide standardized references and quality specifications for all laboratory analysis, and data review procedures required for the Napa Salt Marsh Project;
- Provide guidance and criteria for selected field and analytical procedures; and
- Establish procedures for reviewing and documenting compliance with field and analytical procedures.

This SAP/QAPP is prepared to be consistent with the draft San Francisco District Public Notice Number 99-04 and EPA QA/G-5, EPA Requirements for Quality Assurance Project Plans for Environmental Operations.

1.2 Project Team and Responsibilities

1.2.1 Corps of Engineers

The USACE San Francisco District office is located at 333 Market Street, San Francisco, California, 94105. At the request of Project Manager, Scott Nicholson, the Materials Management Unit (MMU) of the Environmental Section will manage the contracting of sampling and testing for this project. The key personnel are:

<u>Title</u>	<u>Name</u>	<u>Phone</u>	<u>Fax</u>	<u>Email Address</u>
Project Leader	Yvonne Le Tellier	(415) 977-8541	977-8695	yletellier@spd.usace.army.mil
Team Leader	Frank Snitz	(415) 977-8540	977-8695	fsnitz@spd.usace.army.mil
Project Manager	Scott Nicholson	(415) 977-8706	977-8483	snicholson@spd.usace.army.mil

The Corps Project Leader is responsible for preparing and maintaining the QAPP for all work performed under contract and acts as the Quality Assurance (QA) Officer, overseeing laboratory

activities and performing inspections of laboratories as appropriate. The Project Leader is also responsible for overseeing review of the project QA/QC program.

1.2.2 Contract Laboratory

The Material Management Unit manages an Indefinite Delivery Indefinite Quantity Contract for sampling and analysis of environmental media for the San Francisco District projects involving removal and discharge, or relocation of materials. The laboratory and its subcontractors to whom this project will be contracted are:

Field Sampling Oversight:

Analytical Chemistry (subcontractor):

MEC Analytical, Inc
Project Manager: David Moore
98 Main Street, Suite 428
Tiburon, CA 94920
Phone: (415) 435-1847
Fax: (415) 435-0549
Email: moore@mecanalytical.com

Pacific Treatment Analytical Services
POC: Janis Columbo
4340 Viewridge Ave, Suite A
San Diego, CA 92123
Phone: (619) 560-7717
Fax: (619) 560-7763

Dr. David Moore is responsible for keeping the USACE Project Leader aware of all sampling and analysis problems or conditions that may affect data quality. MEC field personnel will be responsible for oversight of sample collection, processing and compositing of samples, and archiving. They will assure appropriate transport and implementation of chain-of-custody procedures. MEC Analytical will prepare the final data report as described in Section 1.7 of this document.

1.3 Project Objectives

The objectives of this water and sediment characterization project are:

- Carry out oversight of the sampling of pond water and sediment by another contractor;
- Carry out the physical and chemical testing of water and sediment to discharged;
- Evaluate the water and sediment suitability for discharge to the Napa River.

This SAP/QAPP specifies sampling and analytical protocols for the physical and chemical testing of sediment from this site. Protocols specified by this document conform to the specifications of the USEPA *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846*.

1.3.1 Regulatory Agencies

The regulatory agencies with jurisdiction over this project are:

- San Francisco Regional Water Quality Control Board (SFRWQCB)
- California Coastal Commission

1.4 Project Description

1.4.1 General Background

The project description and background information will be provided in the Sampling Plan prepared by Hydrosience Engineers, Inc.

1.4.2 Permitting

Sampling permits will be obtained as required.

1.4.3 Testing Requirements

Each water and sediment sample will be analyzed in accordance with the lists of constituents provided in Table 1 and corresponding sample locations in Figure 1. Composite samples for both water and sediment will be prepared for dioxin/furan analysis only. Chemical testing will be performed on a 14 to 21-day turnaround. Analytical testing requirements, methods, and reporting limits are outlined in Table 1 and 2. Test results will be compared with California Toxics Rule Priority Pollutant criteria.

Table 1. Chemical Analysis Method Lists

**NAPA RIVER SALT MARSH RESTORATION FEASIBILITY STUDY
SALT POND WATER AND SEDIMENT QUALITY SAMPLING PLAN**

Pond Number	No. Sampling Points
1	2
1A	2
2	4
2A	2
3	4
4	4
5	3
6	3
6A	3
7	4
7A	4
8	2
Total	37

Water Sampling Parameters

Parameter	Method1	Detection Limit (ug/L)
List No. 1 - Selected Priority Pollutants		
Arsenic	6020	20
Cadmium	6020A	0.5
Chromium (Total)	6020A	10
Copper	6020A	5
Lead	6020A	5
Mercury	7472	0.1
Nickel	6020A	5
Selenium	6020A	5
Silver	6020A	1
Zinc	6020A	20
Cyanide	9012A	5
Total PCB	8082	0.5
Chlordane	8081A	0.1
DDT	8081A	0.01
Dieldrin	8081A	0.01
List No. 2 - Additional Toxic Pollutants		
PAH	8270C	
Dioxin	1613	
Furan Compounds	1613	
Diazinon	8141A	0.05
List No. 3 - General Water Quality		
TDS	160.1	100
Turbidity	Field	0.1 NTU
TSS	160.2	10
pH	Field	0.1
Ammonia (N-NH3)	350.3	1
Nitrates (N-NO3)	300	1
Sodium Chloride	6020A SM 4500	
Hardness as CaCO3	SM 2340	
Total Coliform (MPN)	SM 9221	
TKN	SM 4500	1
BOD (5 Day)	SM 5210	1
Dissolved Oxygen	Field	
Temperature	Field	
List No. 4 - All Priority Pollutants²		

¹U.S. EPA Method unless otherwise specified.

² Priority Pollutants as identified by the National and California Toxics Rules (total of 126 constituents).

³ SW 846 Method unless otherwise specified.

Sediment Sampling Parameters

Parameter	Method3
Arsenic	6020A
Cadmium	6020A
Chromium (Total)	6020A
Copper	6020A
Lead	6020A
Mercury	6020A
Nickel	6020A
Selenium	6020A
Silver	6020A
Zinc	6020A
Total PCB	8081A
Dioxin	8290
Furan Compounds	8290
Chlordane	8081A
DDT	8081A
Dieldrin	8081A
Diazinon	8081A
NPK	
Sodium Chloride	6020A 300
pH	9045C

Table 2. California Toxics Rules Priority Pollutant Analysis Methods

Constituent	Method
Metals	
Antimony	EPA 6020/7000
Arsenic	EPA 6020/7000
Beryllium	EPA 6020
Cadmium	EPA 6020
Chromium	EPA 6020
Chromium VI	EPA 7196
Copper	EPA 6020
Lead	EPA 6020
Mercury	EPA 7471
Nickel	EPA 6020
Selenium	EPA 6020/7000
Silver	EPA 6020
Thallium	EPA 6020/7000
Zinc	EPA 6020
Conventionals	
Cyanide	9010B
Asbestos	
Organics:	
Organochlorine Pesticides/PCBS	EPA 8081A/8082
Organophosphorus Pesticides	EPA 8141A
Dioxin/Furans	EPA 1613
Semivolatile Organic Compounds (full list w/ PAHs)	EPA 8270C
Volatile Organic Compounds	EPA 8260C

1.4.4 Technical Standards / Criteria

The testing protocol is based on criteria established in

1.4.5 Schedule of Work

The following schedule with milestones and submittals are proposed for this contract.

<u>Action</u>	<u>Date</u>
Notice to Proceed	22 Oct 2001
Complete Field Sampling	26 Oct 2001
Complete laboratory analysis	19 Nov 2001
Submit draft report for Corps' review	03 Dec 2001
Submit final report to Corps	10 Dec 2001

1.4.6 Quality Records / Reports

A detailed description of record maintenance and report requirements is discussed in Section 1.7 of this document.

1.5 Data Quality Objectives

1.5.1 Characteristics of Data Quality

Data quality refers to the level of uncertainty associated with a particular data set. Data quality associated with environmental measurement is a function of the sampling plan rationale and procedures used to collect the samples, as well as, the analytical methods and instrumentation used in making the measurements. Uncertainty cannot be eliminated from environmental data. However, quality assurance programs effective in measuring uncertainty in data are employed to monitor and control excursions from the desired data quality objectives. Sources of uncertainty that can be traced to the sampling component are poor sampling plan design, incorrect sample handling, faulty sample transportation, and inconsistent use of standard operating procedures. The most common sources of uncertainty that can be traced to the analytical component of the total measurement system are problems associated with calibration and contamination.

The purpose of this SAP/QAPP is to ensure that the data collected are of known and documented quality and useable for characterizing water and sediment. The procedures described are designed to obtain data quality indicators for each field procedure and analytical method. Data quality indicators include the PARCC parameters (i.e., Precision, Accuracy, Representativeness, Comparability, and Completeness). To ensure the production of good quality data, systematic checks must show that test results and field procedures remain reproducible and that the analytical methodology is actually measuring the quantity of analytes in each sample.

To generate data that will meet the project objectives, it is necessary to define the types of decisions that will be made, identify the intended use of the data, and design a data collection

program. Data Quality Objectives are defined as an integrated set of thought processes that define data quality requirements based on the intended use of the data. Data Quality Objectives are necessary in obtaining sufficient data of known defensible quality for the intended use. The DQO process will assist in determining the appropriate quantitation, detection, and reporting limits, analytical methods, and sample handling procedures.

1.5.2 Data Quality Objectives

All data that will be collected for this site will be definitive data. Definitive data measures organics and inorganics using EPA procedures and should produce data that can be used in suitability determinations or risk assessment, during implementation. The data obtained will conform to the quality control requirements specified in the following text and the tables accompanying this document.

The QA/QC evaluation of the laboratory data will determine whether the data meet the requirements of the QAPP and will include an evaluation of the laboratory data performed per the analytical methods. Specific QA measurements will be addressed to satisfy the QA objectives. These measurements include precision, accuracy, representativeness, completeness, and comparability. These will be discussed in detail in Section 2.7.

1.5.3 Project Specific Data Quality Objectives

1.5.3.1 The Problem

Water and sediment samples within the Old Cargill abandoned salt ponds along the Napa River will be collected and characterized. Hydrosience Engineers, Inc will be responsible for the sampling from the ponds and river. MEC Analytical will oversee the sampling to ensure sample integrity, proper sampling handling, and preservation, and chain of custody. Characterization of the impounded water and sediment is required to determine its suitability for discharge into the Napa River so that a salt marsh can be restored.

1.5.3.2 The Decision

- Determine the level of COPCs in water and sediment.
- Assess whether levels of contamination in water and sediment are appropriate for anticipated restoration scenario.

The results of this investigation will be used to assess the suitability of impounded water and sediment for discharge into the Napa River.

1.5.3.3 Identify Inputs

- Coordinate with Hydrosience Engineers to identify and label water and sediment sampling locations within the ponds.
- Provide one Field Manager to oversee sampling to ensure sample integrity and

- generally assist in the sampling operation.
- Analyze sediment samples for constituents of concern presented in Table 1 and 2.

1.5.3.4 Define Study Boundaries

- Spatial boundaries: Samples will be taken within the Old Cargill salt ponds, Napa Slough, Napa River, and San Pablo Bay. Sediment samples will be taken to a depth of 6 to 8 inches.
- Fiscal boundaries: Funding for this project is only available until 30 September 2002.

1.5.3.5 Develop a Decision Rule

Maximum allowable levels of contaminants of concern will be determined based on regional guidance. If levels of contamination in the sediment are less than the maximum, discharge will occur in accordance with the San Francisco Regional Water Quality Control Board's Waste Discharge Order.

1.5.3.6 Specify Limits on Decision Errors

Laboratory analysis will be used to assess the concentration of contaminants of concern in the samples. The laboratory data will be evaluated against the precision, accuracy, representativeness, completeness and comparability (PARCC) requirements as outlined in the text of the project's QAPP and which have been developed and used by San Francisco District. Possible decision errors will be considered tolerable when data meet the stated PARCC goals.

1.6 Training Requirements / Certification

Laboratory chemical data will be generated by a laboratory certified by the State of California for analyses presented in Table 5. This applies to the primary laboratory and any laboratory subcontracted by the primary laboratory to perform analysis. Laboratories must have an in-place program for data reduction, validation, and reporting as discussed in Section 1.7. The reliability and credibility of analytical laboratory results can be corroborated by the inclusion of a program of scheduled replicate analyses, analyses of standard or spiked samples, and analysis of split samples with QA laboratories for some projects. Regularly scheduled analyses of known duplicates, standards, and spiked samples are a routine aspect of data reduction, validation, and reporting procedures.

1.7 Documentation and Records

1.7.1 Reporting of Results

Definitive data are produced using rigorous analytical methods, such as EPA reference methods. Analyte presence and quantitation are confirmed through extensive quality control procedures at the laboratory. Public Notice 99-4, Proposed Guidance for Sampling and Analysis Plans (Quality Assurance project Plans) for Dredging Projects within the USACE San Francisco District,

Appendix A, lists the reporting requirements that will be followed for all USACE Projects. As discussed in Appendix A, the definitive data package should include a cover sheet, table of contents, case narrative, the analytical results, sample management records, and internal laboratory QA/QC information. The laboratory data package should be organized such that the analytical results are reported on a per batch basis unless otherwise specified. The data package should have sequentially numbered pages. Testing results of physical, chemical and bioassay testing (if necessary) should include the following information:

- Cover Sheet with:
 - unique report ID number
 - name and location of laboratory (to include a point of contact, phone and facsimile numbers)
 - contract number
 - client name and address
 - project name & site location
 - statement of data authenticity and official signature of release (dated)
- Table of Contents
- Case Narrative. A case narrative should be included in each report. The case narrative should contain a table(s) summarizing samples received, providing a correlation between field sample numbers and laboratory sample numbers, and identifying which analytical test methods were performed and by which laboratories. Samples that were received but not analyzed should also be identified. Extractions or analyses that are performed out of holding times should be appropriately noted. The case narrative should define all data qualifiers or flags.
- Analytical Results. The results for each sample should contain the following information at a minimum. (Information need not be redundant if noted elsewhere in the data package).
 - Laboratory name and location (city and state)
 - Project name and unique ID number
 - Field sample ID number as written on custody form
 - Laboratory sample ID number
 - Matrix (soil, water, oil, etc.) and sample description, if necessary
 - Sample preservation
 - Date sample collected
 - Date sample received
 - Date sample extracted or prepared
 - Date sample analyzed
 - Method numbers for all preparation, cleanup, and analysis procedures
 - Batch identification
 - Analyte or parameter method reporting limits adjusted for sample-specific factors (e.g. aliquot size, dilution or concentration factors, moisture content of a soil or sediment.)
 - Method quantitation limits (low-level standard concentration)
 - Method detection limit

- Test results with correct number of significant figures
 - All confirmation data (refer to method reporting limit)
 - Any data qualifiers assigned
 - Concentration units
 - Dilution factor
 - Percent solids (all soils, sediments, sludges, are to be reported on a dry weight basis)
 - Chromatograms, as needed
 - Sample aliquot analyzed
 - Final extract volume
- **Laboratory Reporting Limits.** The laboratory may use a reporting limit (RL) expressed in terms of DL, QL, regulatory action level, or project-specific threshold limits, however, the laboratory's use of these terms must be well defined.
 - **Sample Management Records.** These types of records include the documentation accompanying the samples (i.e., Original chain-of-custody record, shipping documents, laboratory notification sheets), records generated by the laboratory which detail the condition of the samples upon receipt at the laboratory (i.e., sample cooler receipt forms, any telephone conversation records, etc.), and any records generated to document sample custody, transfer, analysis, and disposal.
 - **QA/QC Information.** The minimum data package must include internal laboratory QA/QC data with their respective acceptance criteria. The data package should also include the laboratory's method quantitation and reporting limits for project-specific parameters. The data package should correlate the method QC data with the corresponding environmental samples on a preparation batch basis, with batch numbers clearly shown. Method QC data must include all spike target concentration levels, the measured spike concentration and calculated recoveries; all measures of precision, including relative percent difference; and all control limits for bias, and precision. This would include laboratory performance information such as results for method blanks, recoveries for LCSs, RPDs for (intra- or interbatch) LCS pairs, and recoveries for QC sample surrogates; and matrix-specific information such as matrix duplicate (MD) RPDs, MS and MSD recoveries, MS/MSD RPDs, field sample surrogate recoveries, serial dilutions, and post-digestion spikes, etc. At a minimum, internal quality control samples should be analyzed and reported at rates specified in the specific methods, within USACE guidance, or as specified in the contract task order whichever is greater. Any deviations from the control limits should be noted. Also, include any data review, non-conformance, or corrective action forms within the data package.

1.7.2 Report format

Two copies of the draft report and ten copies (one camera ready and nine copies) of the Final Report shall be submitted according to the schedule outlined in Section 1.4.7. In addition an electronic version that is both Microsoft Word and Microsoft Excel compatible will be provided on compact or floppy disk.

1.7.3 Data Package Archiving and Retrieval

All project records (including raw data) shall be held for a period of at least three years following acceptance of the final report by the Corps of Engineers.

2 Measurement / Data Acquisition

2.1 Sampling Process Design (Experimental Design)

2.1.1 Scheduled Activities

Restoration of the Napa Salt Marsh is planned for FY 2003.

2.1.2 Sampling Oversight

Hydroscience Engineers is responsible for preparing the Sampling Plan, and conducting the Sampling for this project. MEC shall provide one experienced Field Manager to oversee sampling in the field to ensure sample integrity through proper sample handling, preservation, and chain of custody procedures. Samples to be collected and processed through MEC and its laboratories are presented in Table 3.

Labels will be affixed to the sleeves or sample containers bearing job designation, time, sample location, sample depth interval, sample number, date sampled, and the initials of the sampler. All samples will be placed in a cooler at 4° C for shipping to the lab. The field manager will label all samples and be responsible for care and custody of the samples until they are shipped to the lab for analysis. Samples will not be transferred from one container to another.

Table 3. Water and Sediment Sampling Stations & Analysis Requirement

SAMPLE	WATER SAMPLE	SEDIMENT SAMPLE	ANALYSIS LIST	COMPOSITE FOR DIOXIN ANALYSIS
1-A-W 1-A-S	x	x	1,2,3	YES
1-B-W 1-B-S	x	x	1,2,3	
1A-A-W 1A-A-S	x	x	1,2,3	
1A-B-W 1A-B-S	x	x	2,3,4	
2-A-W 2-A-S	x	x	1,2,3	YES
2-B-W 2-B-S	x	x	1,2,3	
2-C-W 2-C-S	x	x	1,2,3	
2-D-W 2-D-S	x	x	1,2,3	
2A-A-W 2A-A-S	x	x	1,2,3	YES
2A-B-W 2A-B-S	x	x	1,2,3	
3-A-W 3-A-S	x	x	1,2,3	YES
3-B-W 3-B-S	x	x	1,2,3	
3-C-W 3-C-S	x	x	1,2,3	
3-D-W 3-D-S	x	x	2,3,4	
4-A-W 4-A-S	x	x	1,2,3	YES
4-B-W 4-B-S	x	x	1,2,3	
4-C-W 4-C-S	x	x	1,2,3	
4-D-W 4-D-S	x	x	1,2,3	
5-A-W 5-A-S	x	x	1,2,3	YES
5-B-W 5-B-S	x	x	1,2,3	
5-C-W 5-C-S	x	x	1,2,3	
6-A-W 6-A-S	x	x	1,2,3	YES
6-B-W 6-B-S	x	x	1,2,3	
6-C-W 6-C-S	x	x	1,2,3	
6A-A-W 6A-A-S	x	x	1,2,3	YES
6A-B-W 6A-B-S	x	x	1,2,3	
6A-C-W 6A-C-S	x	x	1,2,3	
NS-A-W NS-A-S	x	x	2,3,4	

Table 3. (cont'd) Water and Sediment Sampling Stations & Analysis Requirement

SAMPLE	WATER SAMPLE	SEDIMENT SAMPLE	ANALYSIS LIST	COMPOSITE FOR DIOXIN ANALYSIS
7-A-W 7-A-S	x	x	1,2,3	YES
7-B-W 7-B-S	x	x	1,2,3	
7-C-W 7-C--S	x	x	1,2,3	
7-D-W 7-D-S	x	x	1,2,3	
7A-A-W 7A-A-S	x	x	1,2,3	YES
7A-B-W 7A-B-S	x	x	1,2,3	
7A-C-W 7A-C-S	x	x	2,3,4	
8-A-W 8-A-S	x	x	1,2,3	YES
8-B-W 8-B-S	x	x	1,2,3	
8-C-W 8-C-S	x	x	1,2,3	
NR-A-W NR-A-S	x	x	2,3,4	
SP-A-W	x	None	2,3,4	

2.1.3.1 Reference Site Sampling

No reference samples will be collected for this sampling event.

2.1.3.2 Sample Identification

Specific sample identification numbers are listed in Table 3.

Information pertaining to a particular sample is referenced by its identification number. It is recorded on the sample container, in the field log book, and on the sample chain-of-custody form. Following sample collection, the sample label is filled out in waterproof ink, and secured to the sample container with clear tape wider than the label itself. MS/MSD volumes will be indicated on the COC as well as within the sample numbering sequence. The sample number will be “parent sample number” + the suffix “MS” or “MSD”.

Each sample collected at the site will be labeled with the following information:

- Sample identification number;
- Sample location;
- Date and time of collection;
- Initials of person collecting the sample;
- Analysis requested;

- Preservation;
- Any other information pertinent to the sample

2.1.3.2 Compositing Plan

Individual water and sediment samples will be mixed thoroughly before compositing for dioxin/furan analysis only.

2.2 Sampling Methods Requirements

Sampling requirements will be addressed in the Sampling Plan prepared by Hydroscience Engineers.

2.2.2.2 Laboratory Procedures

When errors, deficiencies, or out-of-control situations exist, the QA program provides systematic procedures (called “corrective actions”) to resolve problems and restore proper functioning to the analytical system. Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the acceptable windows for precision and accuracy;
- Blanks, duplicate control samples or single control samples contain contaminants above acceptable levels;
- Undesirable trends are detected in spike recoveries or RPD between duplicates;
- There are unusual changes in detection limits;
- Deficiencies are detected by the QA department during internal or external audits or from the results of performance evaluation samples; or
- Inquiries concerning data quality are received from clients.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and so on. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, manager, or QA department for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the project records.

2.2.2.3 Sampling Equipment, Preservation and Holding Time Requirements

A complete set of sampling containers will be prepared for each sample in advance of the sampling event. Containers will be labeled with the date, sample number, project name, sampler's initials, and parameters for analysis and preserved as required. The required sample containers, preservatives, and storage requirements for each analysis are presented in Table 4.

Table 4. Sediment Sample Preservation and Holding Time

Method/Analysis	Containers Sample Size	Chemical Preservation	Temperature Preservation	Hold Time
SW-8260/VOC	stainless steel sleeve (soil)	none	cool 4°C	14 days
	3 - 40 ml VOA vials (water) ²	HCl to pH < 2		7 days
SW-8270C/ Semivolatiles	stainless steel sleeve (soil)	none	cool 4°C	14 days (s)
	2 - 1 liter ambers (water)		store away from light	7days/ 40days(w)
EPA 8081A	stainless steel sleeve (soil)	none	none	14 days (s)
EPA 8082	2 - 1 liter ambers (water) ²			7days/ 40days(w)
EPA 8141A				
EPA 6020/ 7000 metals	stainless steel sleeve (soil)	none	cool 4°C	6 mo.
	500 ml polyethylene (water)	HNO ₃ to pH < 2		
9045 pH	stainless steel sleeve (soil)	none	cool 4°C	immed.
351.3 TKN	stainless steel sleeve (soil)	none	cool 4°C	28 days
365.2 Phosphorus	stainless steel sleeve (soil)	none	cool 4°C	28 days
300 Nitrate-Nitrite	stainless steel sleeve (soil)	none	cool 4°C	28 days

Notes:

1. 7 days to sample extraction and 40 days to analysis of sample extract.

2.3 Sample Handling and Custody Requirements

2.3.1 Field Custody

Custody of samples must be maintained and documented from the time of sample collection to completion of the analyses. Each sample will be considered to be in the sampler's custody, and the sampler will be personally responsible for the care and custody of the samples until they are delivered to the courier service for delivery to the laboratory. A sample is considered to be under a person's custody if:

- The sample is in the person's physical possession;

- The sample is in view of the person after that person has taken possession;
- The sample is secured by that person so that no one can tamper with the sample;
- The sample is secured by that person in an area that is restricted to authorized personnel.

All samples will be accompanied to the laboratory by a chain-of-custody form. The chain-of-custody form contains the following information:

- Project name;
- Sample numbers;
- Sample collection point;
- Sampling date;
- Time of collection of samples (this time must match the time recorded on the sample label);
- Sample matrix description;
- Analyses requested for each sample;
- Preservation method;
- Number and type of containers used;
- Any special handling or analysis requirements.
- Signature of person collecting the samples (with date and time);
- Signature of persons involved in the chain of possession (with date and time).

The chain-of-custody record forms will be filled out with ink. When the samples are transferred from one party to another, the individuals will sign, date, and note the time on the form. A separate form will accompany each delivery of samples to the laboratory. The chain-of-custody form will be included in the cooler used for preservation and transport of the samples. The sampling personnel will retain a copy of the form.

2.3.2 Laboratory Custody

All samples received at the laboratory will be checked carefully for label identification, and complete, accurate chain-of-custody documentation. The condition of the samples will be checked, and the ambient temperature in the cooler and the temperature blank will be measured immediately after the cooler is opened. These results will be recorded on the Cooler Receipt Form. Photographs are recommended to document the condition of samples if significant out-of-control conditions are noted at the time of sample receipt.

Within one working day of sample receipt by the laboratory, an acknowledgment, chain of custody, and cooler receipt form will be faxed (or emailed) to the USACE Project Leader at the fax number provided in Section 1.2.1.

A unique laboratory identification number will be assigned through a computerized Laboratory Information Management System (LIMS), if available, that stores all identification and essential information. The LIMS system tracks the sample from storage through each step in the laboratory until the analytical process is complete and the sample is returned to the custody of

Sample Control for disposal. Access to the laboratory shall be restricted to prevent any unauthorized contact with samples, extracts, or documentation.

2.3.3 Sample Management

2.3.3.1 Shipping

Samples will be transported as soon as possible after sample collection to the primary laboratory for analysis. The following procedures are to be used when packing and transporting samples to the laboratory:

- Use waterproof metal or equivalent strength plastic ice chests or coolers;
- Place absorbent material in the bottom of the cooler;
- Package samples in individual plastic bags and place in cooler samples;
- Package wet ice or a combination of wet ice and “blue ice” in plastic bags and place bags around, among, and on top of the samples;
- Fill cooler with cushioning material;
- Put paperwork (chain-of-custody record, etc.) in a waterproof plastic bag and tape it to the inside lid of the cooler;
- Tape the cooler lid and drain shut with fiber-reinforced tape;
- Place two numbered and signed custody seals on cooler, one at the front right and one at the back left of cooler;
- Put “This Side Up” and “Fragile” labels on all sides of all coolers containing glass bottles;
- Attach completed shipping label to the top of cooler and ship following the carrier's instructions.

Sample coolers are typically shipped by overnight express carrier to the laboratory. A copy of the bill of lading (air bill) is to be retained and becomes part of the sample custody documentation. The laboratory should be notified in advance of all shipments preferably by telephone on the day of shipment and by advanced scheduling.

2.2.3.2 Project Laboratory

Project laboratories shipping addresses and points of contact are provided in Section 1.2.2 of this document.

2.4 Analytical Methods Requirements

2.4.1 Preparation of Samples / Analytical Methods

Table 5 provides a summary of preparation and analytical methods that will be used to analyze sediment samples.

2.4.2 Physical and Chemical Analysis

This section contains brief descriptions of laboratory methods to be used for this project. Unless authorized by the USACE Project Leader, the most current promulgated method shall be used. If, during the course of a project, it becomes necessary to apply a different practical quantitation limit because of changes in instrument capabilities, the Project Leader will be notified and approval will be obtained in instances where higher practical quantitation limits result. Methodology references contain specific QC criteria associated with the particular methods. These specific requirements include calibration and QC samples, and are described in detail within the methods. Daily performance tests and demonstrations of precision and accuracy are required.

The laboratory methods identified in this document were published by the United States Environmental Protection Agency (U.S. EPA) in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846*, Third Edition (November 1986; Revision 1, July 1992; and Revision 2, November 1992, Update I, August 1993, Update II, September 1994).

2.4.2.1 Preparation Methods

Method SW-3050 - Acid Digestion for Solids, Sediments, and Sludges

Method SW-3050 applies to the preparation of sediment, sludge, and soil samples for metals analysis by Flame Atomic Absorption (FLAA), Graphite Furnace Atomic Absorption (GFAA), or Inductively Coupled Plasma Emission Spectroscopy (ICPES). A 1 gram (wet weight) sample is treated and digested in HNO₃ and hydrogen peroxide. The digestate is then refluxed with HNO₃ or HCl, depending on the type of analysis to be performed. When using HCl as the final refluxing acid, the digestate should not be boiled because antimony is volatile and easily lost. A separate sample is dried for a total solids and/or percent moisture determination.

Method SW - 3550 - Sonication Extraction

This method is designed to extract non-volatile and semi-volatile organic compounds from solid samples such as soils, sludges, and solid wastes. Approximately thirty grams of sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This powder is then solvent extracted three times using an ultrasonic extractor. The extract is separated from the sample by filtration or centrifugation. The sample extract is then ready for cleanup and/or sample analysis procedures.

Method SW - 3540 - Soxhlet Extraction

Method SW-3540 (or SW-3541 automated soxhlet extraction) is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soil and sludges. The Soxhlet extraction process ensures intimate contact between the sample matrix and the extraction solvent. Extraction is accomplished by mixing the solid sample with anhydrous sodium sulfate, placing it in an extraction thimble or between two plugs of glass wool, and extracting it for 16-24 hours with an appropriate solvent in the Soxhlet extractor. Methylene chloride is used when a

solvent is not specified. The extract is dried, concentrated, and then treated using a cleanup method, or analyzed directly by the appropriate method.

MCAWW 160.3 - Percent Moisture

Percent moisture is determined for solid samples undergoing analysis for both inorganic and organic analytes. The sample is weighed, dried at 105°C, and then re-weighed. Percent moisture is calculated as:

$$\frac{\text{Initial Weight} - \text{Dried Weight}}{\text{Initial Weight}} \times 100 = \% \text{ Moisture}$$

The moisture content is used to calculate results for soil samples on a dry weight basis using the calculation presented below.

$$\text{Result} = 100 - \% \text{ Moisture} = \% \text{ Solids}$$

All sediment results and detection limits will be reported on a dry weight basis.

2.4.2.2 Organic Methods

Method 8081A- Organochlorine Pesticides

Method 8081 is a capillary column method used to determine the concentrations of various organochlorine pesticides (Table 5), in extracts from soils and water samples. This method uses an electron capture detector (ECD) to identify the target analyte. This method can be performed as a dual column method or a single column method. Compound identification based on a single column analysis shall be confirmed on a second column, or shall be supported by at least one other qualitative technique.

Method 8082- PCBs

Method 8082 is a capillary column method used to determine the concentrations of various polychlorinated biphenyls (PCBs) as Arochlors (Table 5), in extracts from soils and water samples. This method uses an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD) to identify the target analyte. This method can be performed as a dual column method or a single column method. Compound identification based on a single column analysis shall be confirmed on a second column, or shall be supported by at least one other qualitative technique.

Method 8270C - Polynuclear Aromatic Hydrocarbons (PAH)

Method 8270 is used to determine semivolatile organic compounds in extracts prepared from a variety of matrices. The semivolatile compounds are introduced in the gas chromatograph by injection. The column is temperature programmed to separate the analytes that are then detected with a mass spectrophotometer interfaced to the gas chromatograph. Concentrations of semivolatile organic compounds are determined by this method. The compounds that can be quantified include most neutral, acidic and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivation as shape peaks from a gas chromatographic fused-silica capillary column coated with slightly polar silicone. Polynuclear aromatic compounds, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, analines, pyridines, quinolines, aromatic nitro compounds and phenols (including nitrophenols) can all be analyzed by this method (see Table 5 for analyte list). Some compounds require special treatment when being determined by this method due to oxidative losses, poor chromatographic characteristics, decomposition, etc. SW-846 should be consulted for a list of compounds requiring special treatment.

2.4.2.3 Inorganic Methods

Metals by ICP-MS - Method 6020

Mercury by Cold Vapor Extraction - Method 7471A

2.4.2.4 General Physical / Chemistry Method

Grain Size Analysis (Plumb)

Total Organic Carbon - ASTM D2579 (combustion method for TOC)

Total and Soluble Sulfides - Method 9031 and methylene blue colorometric

2.4.3 Biological Testing

Biological testing will not be performed for this project.

2.5 Quality Control Requirements

The Project Laboratories will have a QA/QC program that monitors data quality with internal QC checks. Internal QC checks are used to answer two questions:

- 1) Are laboratory operations “in control,” (i.e., operating within acceptable QC guidelines), during data generation?
- 2) What effect does the sample matrix have on the data being generated?

The first question is answered by Laboratory Performance QC. Laboratory Performance QC is based on the use of a standard, control matrix to generate precision and accuracy data that are

compared, on a daily basis, to control limits. This information, in conjunction with method blank data, is used to assess daily laboratory performance.

The second question is addressed with Matrix-Specific QC. Matrix-Specific QC is based on the use of an actual dredged material or sediment sample for precision and accuracy determinations, and commonly relies on the analysis of matrix spikes and matrix spike duplicates.

Laboratory Performance QC will be provided as a standard part of every routine analysis. A brief summary of the required QC is provided in Section 2.5.1 to 2.5.6. The type and frequency of QC samples performed by the laboratory will be according to the specified analytical method.

2.5.1 Analytical Batch

The analytical batch is defined as a preparation batch. The analytical batch will not exceed 20 samples, and is defined as a set of samples that are extracted/analyzed concurrently or sequentially. Significant gaps (greater than two hours) in the analytical sequence will result in the termination of the previous sequence and the initiation of a new analytical sequence. The practice of "holding a batch open" and performing a single set of batch QC samples for all analyses performed during that period is unacceptable.

As a minimum, the Laboratory shall analyze internal QC samples at the frequency specified in this QAPP for all analytical methods. These QC samples for each analytical batch shall include method blanks (MB), MS/MSD analyses, and laboratory control samples (LCS). Definitions for the QC samples described above are provided in Chapter One of SW-846. The matrix used for LCS analyses shall be reagent grade water for aqueous analyses and reagent sand for soil/sediment matrices.

Second column confirmation for all GC sample analyses involving identification of discrete peaks with detected concentrations will be required, as per the methods. Second column confirmation is not required for concentrations reported between the MDL and the PQL as defined by SW846.

2.5.1.1 Blanks

Two types of blanks routinely analyzed in the laboratory are method blanks and reagent blanks. Method blanks are used to assess laboratory procedures as possible sources of sample contamination. Method or preparation blanks for all samples consist of deionized water or reagent sand that is subjected to the entire analytical procedure, including extraction, distillation, digestion, etc., as appropriate for the analytical method being utilized. One method blank will be analyzed for each analytical batch (minimum of one per day or one every 12 hours for GC/MS analyses).

As part of the standard QC program, a method blank is analyzed with every batch of samples processed. A method blank consists of reagents specific to the method that are carried through every aspect of the procedure, including preparation, clean-up, and analysis. The results of the method blank analysis are evaluated, in conjunction with other QC information, to determine the

acceptability of the data generated for that batch of samples. If the blank does not meet acceptance criteria, the source of contamination will be investigated and appropriate corrective action will be taken and documented in a nonconformance report. Investigation includes an evaluation of the data to determine the extent and effect of the contamination on the sample results. Corrective actions may include reanalysis of the blank or re-preparation and reanalysis of the blank and all associated samples. No method blank may exhibit a detected concentration greater than the reporting limit. However, exceptions may be made when the analyte is not detected in the related sample. No exceptions will be made for common laboratory contaminants.

For organic and metals analyses, method blank results are reported with each set of sample results. Sample results are not corrected for blank contamination unless required by the analytical method.

2.5.1.2 Ongoing Precision and Recovery (Laboratory Control Samples)

Laboratory Control Samples (LCS) are used as a means of evaluating the efficacy of the analytical process. As discussed above, LCS are used to generate precision and accuracy data that are compared, on a daily basis, to control limits. Laboratory control samples are subjected to the entire sample procedure, including extraction, digestion, etc., as appropriate for the analytical method utilized. They are generally introduced into an analytical batch (20 samples) immediately before extraction or analysis. LCS will be performed for both inorganic and organic laboratory methods. If results are not within control limits, all samples associated with the batch will be reanalyzed.

2.5.1.3 Matrix Spikes /Matrix spike Duplicates

A Matrix Spike (MS) is a sediment sample to which known concentrations of analytes have been added. The MS is taken through the entire analytical procedure and the recovery of the analytes is calculated. Results are expressed as percent recovery. The MS is used to evaluate the effect of the sample matrix on the accuracy of the analysis.

A Matrix Spike Duplicate (MSD) is a sediment sample that is divided into two separate aliquots, each of which is spiked with known concentrations of analytes. The two spiked aliquots are processed separately and the results compared to determine the effects of the matrix on the precision and accuracy of the analysis. Results are expressed as relative percent difference (RPD) and percent recovery (%R).

One MS and MSD is required for each organic method and metals methods per analytical batch. A test sediment sample will be used rather than a reference sample to best determine the matrix effects of the project material.

2.5.1.4 Surrogate Recoveries

Surrogates are organic compounds which are similar to the analytes of interest in chemical behavior, but which are not normally found in sediment samples. Surrogates are added to samples to monitor the effect of the matrix on the accuracy of the analysis. Results are reported in terms of percent recovery. Laboratories routinely add surrogates to samples requiring GC or

GC/MS analysis and reports these surrogate recoveries to the client. The laboratory does not control its operations based on surrogate recoveries in sediment samples. The surrogate recoveries are primarily used by the laboratory to assess matrix effects. However, obvious problems with sample preparation and analysis (e.g. evaporation to dryness, leaking septum, etc.) which can lead to poor surrogate spike recoveries must be ruled out before attributing low surrogate recoveries to matrix effects.

2.5.1.5 Calibration Standards

A calibration standard is prepared in the laboratory by dissolving a known amount of a purchased pure compound or standard mix in an appropriate matrix. The final concentration calculated from the known quantities is the true value of the standard. The results obtained from these standards are used to generate a standard curve and thereby quantify the compound in the sediment sample. A minimum of three calibration standards will be used to generate a standard curve for all analyses. For organic analyses, a five-point calibration curve is used with the lowest standard at the method reporting limit.

2.5.1.6 Reference Standards

A reference standard is prepared in the same manner as a calibration standard. A reference standard is obtained from a source independent of the source of the calibration standard. The concentration of the known quantity is the “true” value of the standard. A reference standard is not carried through the same process used for the sediment samples, but is analyzed without digestion or extraction. A reference standard result is used to validate an existing concentration calibration standard file or calibration curve. The reference standard can provide information on the accuracy of the instrumental analytical method independent of various sample matrices.

2.6 Instrument / Equipment Testing, Inspection, and Maintenance

2.6.1 Preventative Maintenance

2.6.1.1 Preventative Maintenance of Field Instruments

Most instruments designed for field use operate by solid-state circuitry. Little preventive maintenance of the instruments is required, other than cleaning. Preventive maintenance actions, with the exception of battery recharging, are documented in each instrument's log book by the equipment manager or the person conducting the maintenance in the field. Specific preventive maintenance procedures will be described in Standard Operating Procedures (SOPs).

2.6.1.2 Preventative Maintenance of Laboratory Equipment

To minimize downtime and interruption of analytical work, preventive maintenance is routinely performed on each analytical instrument. Each laboratory shall have detailed SOPs on file that describe preventive maintenance procedures and schedules. All service and maintenance will be conducted by qualified laboratory staff or under service agreement with the manufacturer or their approved agent. All repairs, adjustments, and calibrations will be documented in a maintenance notebook or data sheet that will be maintained in a permanent file. The instrument notebook will

clearly document the date, the problem description, corrective action taken, results of actions, and the name of the person performing the work.

2.6.1.3 Laboratory Equipment

All instruments and equipment that may be utilized from sample custody to sample disposition are to be listed on an inventory that includes the names, quantity, and model number. This inventory shall be documented in the Field Sampling Plan or Laboratory Quality Assurance Plan. The laboratory shall maintain a stock of spare parts and consumables for all analytical equipment. Maintenance performed on each piece of equipment is documented in the maintenance notebook. The frequency of routine procedures will vary depending on the production workload and the types of samples analyzed. The contract laboratory should operate backup instrumentation for most of its analytical equipment in the event of instrument failure.

2.6.1.4 Instrument Calibration and Tuning

All instruments and equipment used during sample analysis are operated, calibrated, and maintained according to the manufacturer's guidelines and recommendations, as well as criteria set forth in the applicable analytical methodology references. Operation, calibration, and maintenance will be performed by personnel properly trained in these procedures. Laboratory capabilities will be demonstrated initially for instrument and reagent/standards performance as well as accuracy and precision of analytical methodology.

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established reporting limits. Each instrument will be calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method presented in Section 2.4.2. The frequency of calibration and calibration verification and the concentration of calibration standards are determined by the manufacturer's guidelines and the analytical method. All samples must be bracketed by passing calibration check samples. Failure to bracket all samples with acceptable calibration checks will result in the reanalysis of affected samples.

Gas Chromatography Mass spectrometry (GC/MS)

Each day before analysis of samples, the instrument is tuned with bromofluorobenzene for volatile compounds and decafluorotriphenylphosphine for semivolatile compounds or other tune criteria, as specified by the method used. Mass spectral peaks must conform both in mass numbers and relative intensity to method specified requirements before analyses can proceed.

The instrument is then calibrated for all target compounds. An initial calibration curve is produced to define the working range to establish criteria for identification. All GC/MS instruments are calibrated at five different concentrations for analytes of interest, using the procedures outlined in SW-846. Method system performance-check compounds (SPCCs) must show a minimum mean response factor and CCCs must show a RSD less than the method specified standard for the initial calibration to be considered valid. On a daily basis, SPCCs must meet the same criteria relevant for the initial calibration and method calibration check

compounds (CCC) must show a minimum percent drift relative of the expected concentration of the CCC to be considered valid. This initial calibration is evaluated on a daily basis to ensure that the system is within calibration. If the daily standard does not meet the established criteria, the system is recalibrated.

Following a successful tune, the initial five-point calibration is verified by a single mid-range concentration standard. The SPCCs and CCCs are used to check response factors for adequacy and consistency against required limits before analyses can proceed. This initial calibration can be utilized as long as the daily calibration remains valid.

Gas Chromatography (GC)

The field of chromatography involves a variety of instrumentation and detection systems. While calibration standards and acceptance criteria vary depending on the type of system and analytical methodology required for a specific analysis, the general principles of calibration apply uniformly. As outlined in SW-846 procedures, each chromatographic system is calibrated prior to performance of analyses using five concentrations by external standard technique for all columns. The lowest calibration standard shall be equal to or slightly below the reporting limit, and the others corresponding to the expected range of concentrations or defining the working range of the detector. This is done on each quantitation column and each instrument at the beginning of the contract period and each time a new column is installed. The results are used to determine a calibration curve and response factors for each analyte. Initial calibration consists of determining the working range, establishing limits of detection, and establishing retention time windows. The calibration is checked on a daily basis to ensure that the system remains within specifications.

Continuing calibration standards are analyzed to check the linearity of the initial calibration curve at the beginning and end of each analytical run. Calibration checks are also performed for overall system performance and for retention time shifts, as specified in SW-846. Individual and standard mixes are analyzed to establish response factors and absolute retention time. The response factors and retention times are verified throughout the analytical run and at the end of the analytical sequence. Each analyte must be within its retention time window, or corrective action will be taken by the analyst. For GC analyses conducted on this project, the response factor must agree with the factor determined during the initial 5-point calibration within $\pm 15\%$ for quantitation analysis utilizing SW-846 methodology.

Inductively Coupled Argon Plasma Atomic Emission Spectroscopy (ICP) Metals

Each ICP is calibrated before any analyses being performed using criteria prescribed in SW846. The calibration is then verified using standards from an independent source. The working range of the instrument is established once every quarter using a linear range verification check standard. The linear range is verified at the time of the analysis using the highest mixed calibration standard, which must be within $\pm 5\%$ of its true value. No values are reported above this upper concentration value without dilution.

A calibration curve is established daily by analyzing a minimum of three standards and one calibration blank. The calibration is monitored throughout the day by analyzing a Continuing Calibration Blank and a Continuing Calibration Verification standard. Calibration blanks are analyzed after all calibration check standards and must be within three standard deviations of the mean blank value and less than one-half the reporting limit. Continuing calibration checks after every 10 samples using a mid-range calibration check standard must be within $\pm 10\%$ of the expected value. If the verification standard does not meet established criteria, corrective action must be performed.

An interelement check standard is analyzed at the beginning and end of each analytical run, to verify that interelement and background correction factors have remained constant. Results outside of the established criteria trigger reanalysis of samples.

2.6.1.5 Corrective Action

The Field Manager is responsible for initiating corrective action and for implementation of all corrective actions with respect to the field sampling operations. The laboratory QA Director in consultation with the Project Leader is responsible for implementing corrective actions in the laboratory. It is their combined responsibility to see that all analytical and sampling procedures are followed as specified and that the data generated meet the acceptance criteria.

Corrective actions for the laboratory may include, but are not limited to:

- Reanalyzing samples;
- Correcting laboratory procedures;
- Recalibrating instruments using freshly prepared standards;
- Replacing solvents or other reagents that give unacceptable blank values;
- Training laboratory personnel in correct sample preparation and analysis procedures;
- Accepting data with an acknowledged level of uncertainty.

Whenever corrective action is deemed necessary, the Laboratory Director will ensure that the following steps are taken:

- The problem is defined;
- The cause of the problem is investigated and determined;
- Appropriate corrective action is determined and
- Corrective action is implemented and its effectiveness verified.

2.6.1.6 Documentation

All calibration information, instrument maintenance and repair is recorded by the laboratory on appropriate forms developed for SW-846 procedures. Out-of-control analyses are generally described on a QA/QC discrepancy form and submitted to the laboratory supervisor for corrective action. Copies are distributed to the laboratory QA coordinator and laboratory director for approval, and to the case file. The calibration information is filed with the raw data in the reports area.

2.6.2 Inspection/Acceptance Requirements for Supplies and Consumables

2.6.2.1 Standards and Reagent Preparation

A critical element in the generation of quality data is the purity/quality and traceability of the standard solutions and reagents used in the analytical operations. The preparation and maintenance of standards and reagents will be performed per the specified analytical methods presented in Table 5. The laboratory shall continually monitor the quality of reagents and standard solutions through a series of well-documented standard operating procedures (SOPs). In general, SOPs for standards preparation should incorporate the following items:

- Documentation and labeling of date received, lot number, date opened, and expiration date;
- Documentation of traceability;
- Preparation, storage, and labeling of stock and working solutions; and
- Establishing and documenting expiration dates and disposal of unusable standards.

Primary reference standards and standard solutions used by the laboratory are to be obtained from the National Institute of Standards and Technology, or other reliable commercial sources to ensure the highest purity possible. All standards and standard solutions shall be catalogued to identify the supplier, lot number, purity/concentration, receipt/preparation date, preparer's name, method of preparation, expiration date, and all other pertinent information included in the specific SOP.

Standard solutions and reagents are validated before use. Validation procedures can range from a check for chromatographic purity to verification of the concentration of the standard using a standard prepared at a different time, concentration, or source. Reagents are examined for purity by subjecting an aliquot or subsample to the analytical method in which it will be used; for example, every lot of dichloromethane (for organic extractables) is analyzed for undesirable contaminants prior to use in the laboratory. Stock and working standards are checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change in concentration. Care is to be exercised in the proper storage and handling of standard solutions, and all containers are labeled as to compound, concentration, solvent, expiration date, and preparation data (initials of prepare / date of preparation).

2.6.2.2 Receipt and Traceability

Small amounts of standards are received on an as-needed basis. These standards are stored according to the supplier's specifications, with the lot number or supplier's identification number, the date that the standard was received, and the expiration date of the standard written on the standard storage container. This procedure references the standards to specific lots from suppliers.

2.7 Data Acquisition Requirements (Non-Direct Measurements)

The effectiveness of a QA program is measured by the quality of data generated by the laboratory. Data quality is judged in terms of its PARCC parameters as presented in Section 1.5. These terms are described below.

2.7.1 Precision

Precision is a measure of the reproducibility of analyses under a given set of conditions. Precision can be assessed by replicate measurements of duplicate control samples, reference materials, or sediment samples. The routine comparison of precision is measured by the RPD between duplicate control sample measurements with control limits established at plus three standard deviations from the mean RPD of historical duplicate control sample data. The overall precision of a sampling event has a sampling and an analytical component. The following QC data will be collected to determine sampling and analytical precision:

- Matrix spikes and matrix spike duplicates (MS/MSD), measure the precision of the analytical process for metals and organic analyses. MS/MSD samples are run on each batch of samples up to a maximum of 20.
- Laboratory duplicates will be performed for every inorganic analytical batch. The maximum size of each batch will be 20 samples.

Precision is frequently determined by comparison of replicates. The standard deviation of “n” measurements of “x” is commonly used to estimate precision. Standard deviation is calculated as follows:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

Where a quantity “x” (e.g., a concentration) is measured “n” times.

The relative standard deviation (RSD), which expresses standard deviation as a percentage of the mean, is generally useful in the comparison of three or more replicates (although it may be

$$RSD = 100 (s/\bar{x})$$

applied in the case of n = 2).

Where: RSD = relative standard deviation
 s = standard deviation
 x = mean

In the case of duplicates, the RPD between the two samples may be used to estimate precision.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where: RPD = relative percent difference
 D_1 = first sample value
 D_2 = second sample value (duplicate)

Note: If the laboratory determines that failure to meet QC criteria for accuracy or precision is a result of objectively verifiable matrix effects, no further re-extractions will be required. However, the narrative must contain an explicit description of the laboratory's rationale in this regard with reference to objectively verifiable features of raw data. The sufficiency of the laboratory's explanation will be determined by the USACE Project Leader or an appointed representative.

2.7.2 Accuracy

Accuracy is a determination of how close the measurement is to the true value. Accuracy can be assessed using laboratory control samples, standard reference materials, or spiked environmental samples. Unless specified otherwise in special contracts, the laboratory shall monitor accuracy by comparing laboratory control sample results with control limits established at plus or minus three standard deviation units from the mean of historical laboratory control sample results. The accuracy of the data submitted for this project will be assessed in the following manner:

- Accuracy for each sample will be checked by calculating surrogate percent recoveries, as applicable.
- The percent recovery of matrix spikes, matrix spike duplicates, and/or laboratory control samples will be calculated.
- The level of target compounds that are found (if any) in laboratory method blanks will be checked. If a target compound is found above the practical quantitation limit (PQL) in the method blank corresponding to a batch of samples and the same target compound is found in a sample, the data will not be background subtracted but will be flagged to indicate the result in the blank.

Accuracy is presented as percent recovery. Since accuracy is often determined from spiked samples, laboratories commonly report accuracy as:

$$\% \text{ Recovery} = \frac{R}{S} * 100$$

Where: S = spiked concentration
 R = reported concentration

Note: If the laboratory determines that failure to meet QC criteria for accuracy or precision is a result of objectively verifiable matrix effects, no further re-extractions will be required. However, the narrative must contain an explicit description of the laboratory's rationale in this regard with reference to objectively verifiable features of raw data. The sufficiency of the laboratory's explanation will be determined by the USACE Project Leader.

2.7.3 Representativeness

Representativeness is a qualitative parameter that reflects the extent to which a given sample is characteristic of a given population at a specific location or under a given environmental condition. Representativeness is best satisfied by making certain that sampling locations are selected properly, a sufficient number of samples are collected, and an appropriate sampling technique is employed. Variations at a sampling point will be evaluated based on the results of field duplicates. Some samples may require analysis of multiple phases to obtain representative results. Analytical data should represent the sample analyzed regardless of the heterogeneity of the original sample matrix. Sample representativeness will also be evaluated based on results from method blanks and trip blanks.

2.7.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under normal conditions. To be considered complete, the data set must contain all analytical results and data specified for the project. In addition, all data are compared to project requirements to ensure that specifications were met. Completeness is evaluated by comparing the project objectives to the quality and quantity of the data collected to determine if any deficiencies exist. Missing data can result from any number of circumstances ranging from sample acquisition and accessibility problems to sample breakage and rejection of analytical data because of quality control deficiencies. Completeness will be quantitatively assessed as the percent of controlled QC parameters that are within limits. The requirement for completeness for all QC parameters except holding times will be 90%. The requirement for holding times will be 100%. Any deviations are reported in the report narrative.

The percent completeness for each set of samples can be calculated as follows:

$$\text{Completeness} = \frac{\text{valid data obtained}}{\text{total data planned}} \times 100\%$$

2.7.5 Comparability

Comparability expresses the confidence with which one data set can be compared to another data set measuring the same property. To ensure comparability, field procedures will be standardized and field operations will adhere to standard operating procedures. Laboratory data comparability will be assured by use of established and approved analytical methods, consistency in the basis of analysis (wet weight, volume, etc.), and consistency in reporting units (ppm, ppb, etc.). Analysis of standard reference materials will follow USEPA or other standard analytical methods, which utilize standard units of measurement, methods of analysis, and reporting format.

2.7.6 Sensitivity (Reporting Limits)

Assuring the validity of quantitative measurements at low concentrations is an extremely difficult technical problem. With regulatory action levels being pushed lower and lower, the validity of any given measurement becomes even more important. The consequences of false positive or false negative data can be significant. The laboratory shall report results below the reporting limit (RL) as “Not Detected” because, by definition, the reliability of the data at that level is questionable. Organic data will be reported below the quantitation limit (PQL) with the data flagged accordingly.

If dilution to bring the reported concentration of a single compound of interest within the linear range of the calibration, results in non-detect values for all other analytes with detected concentrations in the initial sample analysis, the results of the original run and the dilution will be reported with appropriate notations in the narrative of the report. Matrix effects (i.e., highly contaminated samples requiring dilution for analysis, dilution to bring detected levels within the range of calibration, and matrix interference requiring elevation of detection limits) will be considered in assessing compliance with the requirements for sensitivity

3 Assessment and Oversight

3.1 Assessment and Response Action

All analytical data generated within the laboratories shall be reviewed prior to report generation to assure the validity of the reported data. The data validation process consists of data generation, reduction, and three levels of documented review. In each stage, the review process will be documented by the signature of the reviewer and the date reviewed.

The analyst who generates the analytical data will have the prime responsibility for the correctness and completeness of the data. All data will be generated and reduced following protocols specified in laboratory SOPs. Each analyst will review the quality of his or her work based on an established set of guidelines outlined in the SOPs. The analyst will review the data package to ensure that:

- The correct samples were analyzed and reported in appropriate units;
- Preservation and holding time requirements were met;
- Sample preparation information is correct and complete;
- Appropriate SOPs have been followed;
- Analytical results are correct and complete;
- QC samples are within established control limits;
- Blanks are within appropriate QC limits;
- Special sample preparation and analytical requirements have been met; and
- Documentation is complete (e.g., all anomalies in the preparation and analysis have been documented, nonconformance reports are complete; holding times are documented, etc.).

The data reduction and validation steps shall be documented, signed and dated by the analyst. The analyst will then pass the data package to an independent reviewer, who will perform an independent review of the data package. This review is also to be conducted according to an established set of guidelines structured to ensure that:

- Calibration data are scientifically sound, appropriate to the method, and completely documented;
- QC samples are within established guidelines;
- Qualitative identification of sample components is correct;
- Quantitative results are correct;
- Documentation is complete and correct (e.g., anomalies in the preparation and analysis have been documented; nonconformance reports are complete; holding times are documented, etc.);
- The data are ready for incorporation into the final report; and the data package is complete and ready for data archive.

The review is to be structured so that all calibration data and QC sample results are reviewed and all of the analytical results from 10% of the samples are checked back to the bench sheet. If no problems are found with the data package, the review is complete. If any problems are found with the data package, an additional 10% of the samples will be checked to the bench sheet. This process will continue until no errors are found or until the data package has been reviewed in its entirety.

Data reviews shall be documented and the signature of the reviewer and the date of review recorded. The reviewed data are then approved for release and a final report is prepared. Before the report is released to the client, the data are reviewed for completeness to ensure that the data meet the overall objectives of the project. This review is typically done by the Program Administrator.

Each step of this review process involves evaluation of data quality based on both the results of the QC data and the professional judgement of those conducting the review. This application of technical knowledge and experience to the evaluation of the data is essential in ensuring that data of known quality are generated consistently.