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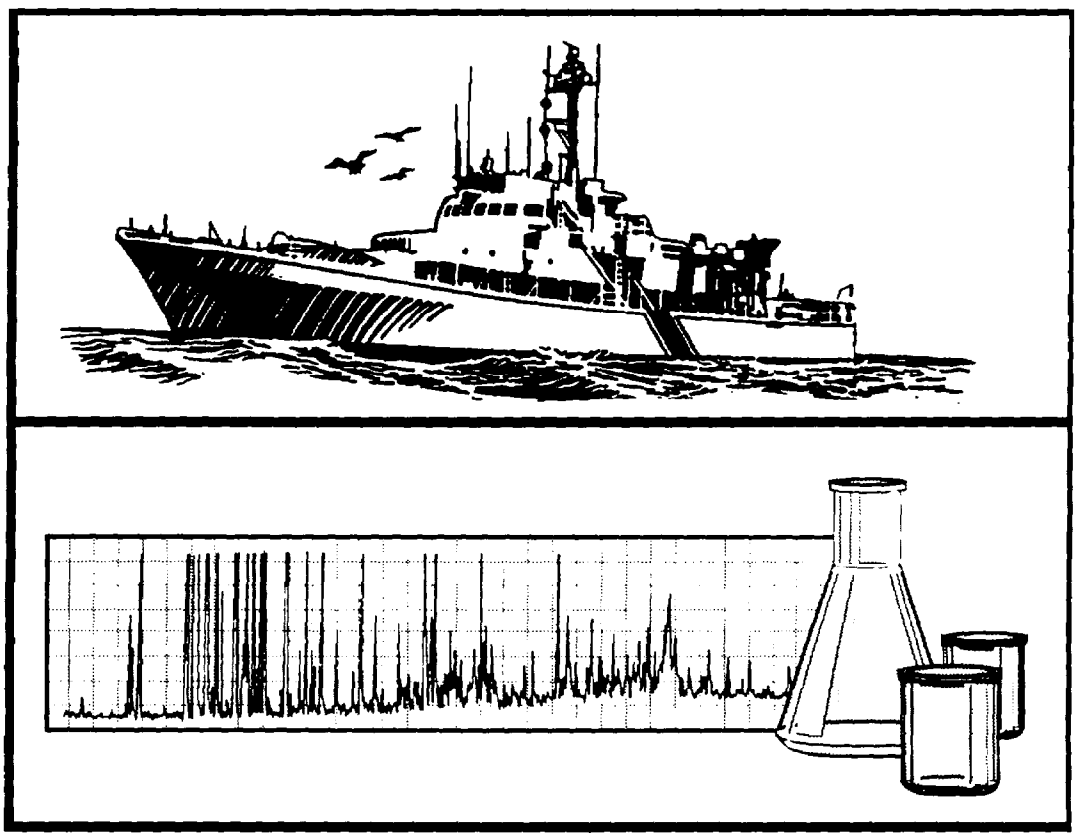
Office of Water
(4305)

EPA 823-B-95-001
April 1995

QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations

Chemical Evaluations



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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

EPA 823-B-95-001

APR 28 1995

OFFICE OF WATER

Dear Colleagues:

The U.S. Environmental Protection Agency (EPA) is pleased to transmit a copy of the document titled *QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations. Chemical Evaluations*. This document was prepared in response to regional requests for quality assurance/quality control (QA/QC) guidance associated with the testing and evaluation of proposed dredged material discharges into inland or ocean waters. The workgroup that developed this national guidance was comprised of individuals from headquarters, field offices, and research laboratories of EPA and the U.S. Army Corps of Engineers (USACE) with experience related to dredged material discharge activities.

EPA and USACE technical guidance for evaluating the potential for contaminant-related impacts associated with the discharge of dredged material into inland and ocean waters, respectively, is found in the documents "Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S.—Testing Manual (Draft)" (the *Inland Testing Manual*) (U.S. EPA and USACE 1994), and "Evaluation of Dredged Material Proposed for Ocean Disposal—Testing Manual" (the *Ocean Testing Manual*) (U.S. EPA and USACE 1991). Results of tests conducted using the testing manuals are the basis of independent evaluations made by EPA and USACE regarding the suitability of proposed dredged material for aquatic disposal.

This QA/QC guidance document serves as a companion document to the *Inland* and *Ocean Testing* manuals. The purpose of this document is as follows: 1) to provide guidance on the development of quality assurance project plans for ensuring the reliability of data gathered to evaluate dredged material proposed for discharge under the Clean Water Act or the Marine Protection Research and Sanctuaries Act, 2) to outline procedures that should be followed when sampling and analyzing sediments, water, and tissues, and 3) to provide recommended target detection limits for chemicals of concern. This document pertains largely to physical and chemical evaluations. Though it is directed primarily toward the evaluation of dredged material for aquatic disposal, it may be useful in other areas of dredged material assessment and management as well (e.g., disposal site monitoring or evaluation of alternative disposal options). The audience for this document is Federal and State agency personnel and public with an interest in the evaluation and management of

dredged material. The information provided herein is for the purpose of guidance only and does not constitute a regulatory requirement.

Requests for copies of this document (EPA document number EPA 823-B-95-001) should be sent to U.S. Environmental Protection Agency, National Center for Environmental Publications and Information, 11029 Kenwood Road, Building 5, Cincinnati, Ohio 45242.

We appreciate your continued interest in EPA's activities related to impact assessment of potentially contaminated sediments.

Sincerely,

Tudor T. Davies
Director
Office of Science
and Technology

Robert H. Wayland III
Director
Office of Wetlands,
Oceans and Watersheds

Enclosure

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United States
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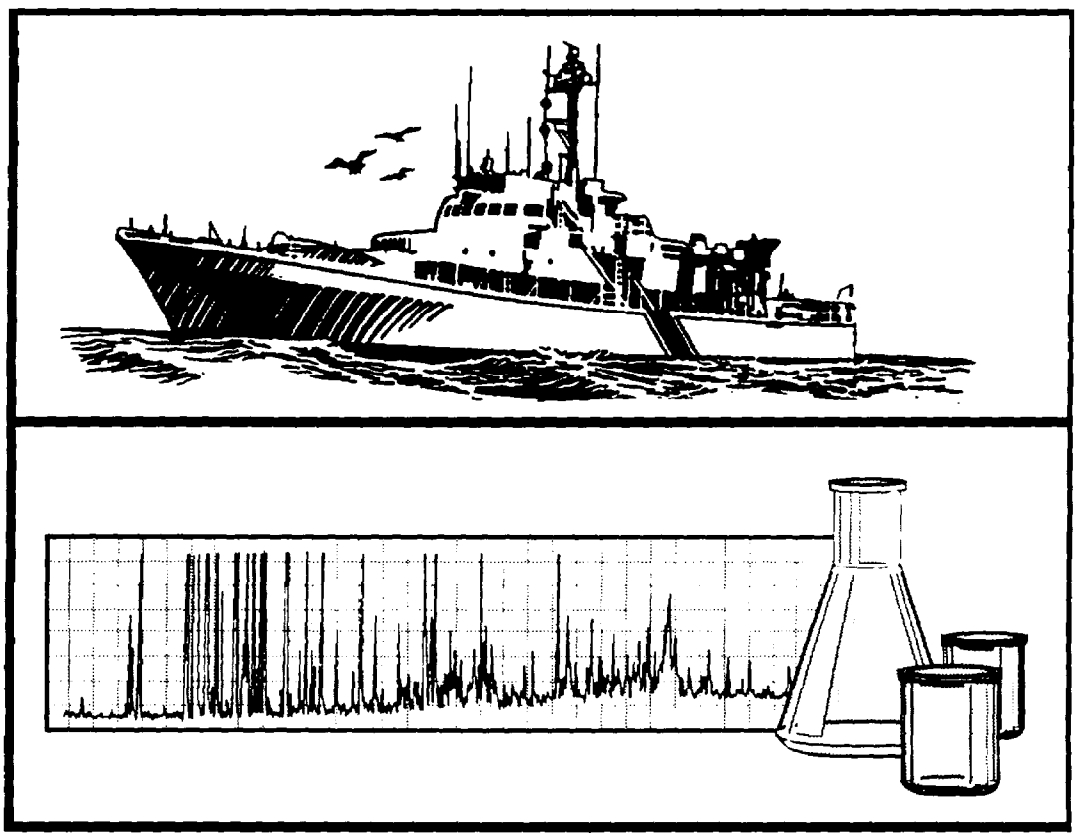

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QA/QC GUIDANCE FOR SAMPLING AND ANALYSIS OF SEDIMENTS, WATER, AND TISSUES FOR DREDGED MATERIAL EVALUATIONS

CHEMICAL EVALUATIONS

Office of Water
Office of Science and Technology
Standards and Applied Science Division
U.S. Environmental Protection Agency
Washington, DC 20460

April 1995

The polices set out in this document are not final agency action, but are intended solely as guidance. They are not intended, nor can they be relied upon, to create any rights enforceable by any party in litigation with the United States. EPA officials may decide to follow the guidance provided in this document, or to act at variance with the guidance, based on an analysis of specific site circumstances. The Agency also reserves the right to change this guidance at any time without public notice.

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ACRONYMS AND ABBREVIATIONS

AVS	acid volatile sulfide
BCF	bioconcentration factor
CLP	Contract Laboratory Program
CVAA	cold vapor atomic absorption spectrometry
CWA	Clean Water Act
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
GC/ECD	gas chromatography/electron capture detection
GC/MS	gas chromatography/mass spectrometry
GFAA	graphite furnace atomic absorption spectrometry
ICP	inductively coupled plasma-atomic emission spectrometry
MPRSA	Marine Pollution, Research, and Sanctuaries Act
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
QAMP	quality assurance management plan
QAPP	quality assurance project plan
QA/QC	quality assurance and quality control
SRM	standard reference material
TCDD	tetrachlorodibenzo-*p*-dioxin
TDL	target detection limit
TEF	toxicity equivalency factor
TOC	total organic carbon
USACE	U.S. Army Corps of Engineers

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The contributions made by many individuals are gratefully acknowledged. The work group was comprised of individuals from headquarters, field offices, and research laboratories of the U.S. Environmental Protection Agency (EPA) and the U.S. Army Corps of Engineers (USACE) with experience related to dredged material discharge activities.

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1. INTRODUCTION

This document provides programmatic and technical guidance on quality assurance and quality control (QA/QC) issues related to dredged material evaluations. The U.S. Army Corps of Engineers (USACE) and U.S. Environmental Protection Agency (EPA) share the Federal responsibility for regulating the discharge of dredged material under two major acts of Congress. The Clean Water Act (CWA) governs discharges of dredged material into "waters of the United States," including all waters landward of the baseline of the territorial sea. The Marine Protection, Research, and Sanctuaries Act (MPRSA) governs the transportation of dredged material seaward of the baseline (in ocean waters) for the purpose of disposal.

EPA and USACE technical guidance for evaluating the potential for contaminant-related impacts associated with the discharge of dredged material into inland and ocean waters, respectively, is found in the documents "Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S.—Testing Manual (Draft)" (the *Inland Testing Manual*) (U.S. EPA and USACE 1994), and "Evaluation of Dredged Material Proposed for Ocean Disposal—Testing Manual" (the *Ocean Testing Manual*) (U.S. EPA and USACE 1991). Results of tests conducted using the testing manuals are the basis of independent evaluations made by EPA and USACE regarding the suitability of proposed dredged material for aquatic disposal.

This QA/QC guidance document serves as a companion document to the *Inland* and *Ocean Testing* manuals. The purpose of this document is as follows: 1) to provide guidance on the development of quality assurance project plans for ensuring the reliability of data gathered to evaluate dredged material proposed for discharge under the CWA or the MPRSA, 2) to outline procedures that should be followed when sampling and analyzing sediments, water, and tissues, and 3) to provide recommended target detection limits (TDLs) for chemicals of concern. This document pertains largely to physical and chemical evaluations. Though it is directed primarily toward the evaluation of dredged material for aquatic disposal, it may be useful in other areas of dredged material assessment and management as well (e.g., disposal site monitoring or evaluation of alternative disposal options).

QA/QC planning is necessary to ensure that the chemical and biological data generated during dredged material evaluations meet overall program and specific project needs. Establishing QA/QC procedures is fundamental to meeting project data quality criteria and to providing a basis for good decision-making. The EPA has developed a two-tiered quality management structure

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that addresses QA concerns at both the organizational level and at the technical/project level. QA management plans (known as QAMPs) identify the mission and customers of the organization, document specific roles and responsibilities of top management and employees, outline the structure for effective communications, and define how measures of effectiveness will be established. The quality standards, goals, performance specifications, and the QA/QC activities necessary to achieve them, are incorporated into project-specific QA project plans (known as QAPPs).

QA activities provide a formalized system for evaluating the technical adequacy of sample collection and laboratory analysis activities. These QA activities begin before samples are collected and continue after laboratory analyses are completed, requiring ongoing coordination and oversight. The QA program summarized in this document integrates management and technical practices into a single system to provide environmental data that are sufficient, appropriate, and of known and documented quality for dredged material evaluation.

QA project plans (QAPPs) provide a detailed plan for the activities performed at each stage of the dredged material evaluation (including appropriate sampling and analysis procedures) and outline project-specific data quality objectives that should be achieved for field observations and measurements, physical analyses, laboratory chemical analyses, and biological tests. Data quality objectives should be defined prior to initiating a project and adhered to for the duration of the project to guarantee acquisition of reliable data. This is accomplished by integrating quality control (QC) into all facets of the project, including development of the study design, implementation of sample collection and analysis, and data evaluation. QC is the routine application of procedures for determining bias and precision. QC procedures include activities such as preparation of replicate samples, spiked samples, blanks; calibration and standardization; and sample custody and recordkeeping. Audits, reviews, and compilation of complete and thorough documentation are QA activities used to verify compliance with predefined QC procedures. Through periodic reporting, these QA activities provide a means for management to track project progress and milestones, performance of measurement systems, and data quality.

A complete QA/QC effort for a dredged material testing program has two major components: a QA program implemented by the responsible governmental agency (the data user), and QC programs implemented by sampling and laboratory personnel performing the tests (the data generators). QA programs are also implemented by each field contractor and each laboratory. Typically, all field and laboratory data generators agree to adhere to the QA/QC of the data user for the contracted project as specified in the project QAPP. USEPA (1987a) provides useful guidance and may be followed on all points that are not in conflict with the guidance in this document. The guidance provided in this

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document also incorporates information contained in U.S. EPA (1984a, 1991d) and U.S. EPA and USACE (1991, 1994).

1.1 GOVERNMENT (DATA USER) PROGRAM

Because the data generated in a dredged material evaluation are used for regulatory purposes, it is important to have proper QA oversight. The USACE, working in conjunction with the appropriate EPA Region(s), should implement a QA program to ensure that all program elements and testing activities (including field and laboratory operations) in the dredged material evaluation comply with the procedures in the QA project plan or with other specified guidelines for the production of environmental data of known quality. This QA guidance document was designed with the assistance of programmatic and scientific expertise from both EPA and USACE. Other qualified sources of QA program management should be contacted as appropriate. Some specific QA considerations in contract laboratory selection are discussed by Sturgis (1990) and U.S. EPA (1991d).

The guidance in this document is intended to assist EPA and USACE dredged material managers in developing QA project plans to ensure that: 1) the data submitted with dredged material permit applications are of high quality, sufficient, and appropriate for determining if dredging and disposal should occur; and 2) the contract laboratories comply with QC specifications of the regulations and guidelines governing dredged material evaluations. This includes the development of an appropriate QA management plan.

1.2 CONTRACTOR (DATA GENERATOR) PROGRAM

Each office or laboratory participating in a dredged material evaluation is responsible for using procedures which assure that the accuracy (precision and bias), representativeness, comparability, and completeness of its data are known and documented. To ensure that this responsibility is met, each participating organization should have a project manager and a written QA management plan that describes, in specific terms, the management approach proposed to assure that each procedure under its direction complies with the criteria accepted by EPA and USACE. This plan should describe a QA policy, address the contents and application of specific QA project plans, specify training requirements, and include other elements recommended by EPA quality assurance management staff (e.g., management system reviews). All field measurements, sampling, and analytical components (physical, chemical, and biological) of the dredged material evaluation should be discussed.

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For the completion of a dredged material testing project, the project manager of each participating organization should establish a well-structured QA program that ensures the following:

- Development, implementation, and administration of appropriate QA planning documents for each study
- Inclusion of routine QC procedures for assessing data quality in all field and laboratory standard operating procedures
- Performance of sufficiently detailed audits at intervals frequent enough to ensure conformance with approved QA project plans and standard operating procedures
- Periodic evaluation of QC procedures to improve the quality of QA project plans and standard operating procedures
- Implementation of appropriate corrective actions in a timely manner.

The guidance provided in this document is intended to assist the data generator with the production of high-quality data in the field and in the laboratory (i.e., the right type and quality of information is provided to EPA and USACE to make a decision about the suitability of dredged material for aquatic disposal with the specified degree of confidence).

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2. DRAFTING A QUALITY ASSURANCE PROJECT PLAN

A formal strategy should always be developed to obtain sufficient and appropriate data of known quality for a specific dredged material testing program. When the sample collection and laboratory analysis effort is small, this strategy may be relatively straightforward. However, when the sample collection and laboratory analysis effort is significant, the assurance of data quality may require the formulation of a formal and often quite detailed QA project plan. The QA project plan is a planning and an operational document.

The QA project plan should be developed by the applicant or contractor for each dredged material evaluation, in accordance with this document. The QA project plan provides an overall plan and contains specific guidelines and procedures for the activities performed at each stage of the dredged material testing program, such as dredging site subdivision, sample collection, bioassessment procedures, chemical and physical analyses, data quality standards, data analysis, and reporting. In particular, the QA plan addresses required QC checks, performance and system audits, QA reports to management, corrective actions, and assessment of data accuracy (precision and bias)[1], representativeness, comparability, and completeness. The plan should address the quantity of data required to allow confident and justifiable conclusions and decisions.

The following information should be included in each QA project plan for dredged material evaluation unless a more abbreviated plan can be justified (see U.S. EPA 1989a):

- Introductory material, including title and signature pages, table of contents, and project description
- QA organization and responsibilities (the QA organization should be designed to operate with a degree of independence from the technical project organization to ensure appropriate oversight)

[1] Historically, "accuracy" and "precision" have often been defined as separate and distinct terms. In particular, accuracy has often been taken tc be only a measure of how different a value is from the true value (i.e., bias). However, data that have poor precision (i.e., high variability) may only have low bias *on the average* (i.e., close agreement to the true value). Therefore, recent literature (e.g., Kirchmer 1988) has defined accuracy as both the precision and bias of the data. This definition of accuracy is used throughout this guidance document.

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- QA objectives
- Standard Operating Procedures
- Sampling strategy and procedures
- Sample custody
- Calibration procedures and frequency
- Analytical procedures
- Data validation, reduction, and reporting
- Internal QC checks
- Performance and system audits
- Facilities
- Preventive maintenance
- Calculation of data quality indicators
- Corrective actions
- QA reports to management
- References.

The remaining sections of this document provide more specific information on each of these items.

2.1 *INTRODUCTORY MATERIAL*

The following sections should be included at the beginning of every QA project plan:

- Title and signature pages
- Table of contents
- Project description
- Certification.

The signature page should be signed and dated by those persons responsible for approving and implementing the QA project plan. The applicant's project manager's signature should be included even if other persons are primarily responsible for QA activities. The headings in the table of contents should match the headings in the QA project plan. A list of figures, list of tables, and list of appendices should be included in the table of contents.

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The goals and objectives of the study project should be outlined in the project description. The project description should illustrate how the project will be designed to obtain the information needed to achieve those goals. Sufficient detail and information should be included for regulatory agency decision-making.

The QA project plan should include the following certification statement signed by a duly authorized representative of the permittee:

> *I certify under penalty of law that this document and all attachments were prepared under my direction or supervision. The information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.*

2.2 QUALITY ASSURANCE ORGANIZATION AND RESPONSIBILITIES

A clear delineation of the QA organization and line of authority is essential for the development, implementation, and administration of a QA program. The relationship of the QA personnel to the overall project team and their responsibilities for implementing the QA program are identified in this section. In addition, guidance is provided for developing statements of work that address the responsibilities of contract laboratories used in the project.

2.2.1 Staffing for Quality Assurance

Organizational charts or tables should be used in the QA project plan to describe the management structure, personnel responsibilities, and the interaction among functional units. Each QA task should be fully described and the responsible individual, their respective telephone number, and the associated organization named. Names of responsible individuals should be included for the sampling team, the analytical laboratory, the data evaluation, QA/QC effort in the laboratory, and the data analysis effort. An example of a QA organization flow diagram is provided in Appendix A.

The project manager has overall responsibility for assuring the quality of data generated for a project. In most projects, actual QA activities are performed independent of the project manager. However, the project manager does ensure the implementation of any corrective actions that are called for during sampling, analysis, or data assessment. The writing of a QA project plan can usually be accomplished by one person with assistance as needed from

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technical specialists for details of methods or QC criteria. One person should also have primary responsibility for coordinating the oversight of all sampling activities, including completion of all documentation for samples sent to the laboratory. Coordinating laboratory interactions before and during sample analysis is also best performed by one person to avoid confusion. Subsequent interactions that may be necessary with the laboratory during a QA review of the data may involve the persons actually doing the review.

Additional QC tasks and responsibilities during sampling and analysis are often assigned to technicians who collect samples, record field data, and operate and maintain sampling and analytical equipment. These technicians perform a number of essential day-to-day activities, which include calibrating and servicing equipment, checking field measurements and laboratory results, and implementing modifications to field or laboratory procedures. These individuals should have training to perform these functions and follow established protocols and guidelines for each of these tasks.

Technical staff are responsible for the validity and integrity of the data produced. The QA staff should be responsible for ensuring that all personnel performing tasks related to data quality are appropriately qualified. Records of qualifications and training of personnel should be kept current for verification by internal QA personnel or by regulatory agency personnel.

Technical competence and experience of all contract laboratory staff should be demonstrated. Staff qualifications should be documented, and training should be provided by the laboratory to encourage staff to attain the highest levels of technical competence. Staff turnover can affect the ability of a laboratory to perform a particular analysis. The experience of current staff with projects of similar scope should be assessed during the laboratory selection process. Technical competence and other factors such as the laboratory setup (including quality and capacity of the available analytical equipment), past experience (e.g., analysis of appropriate QC check samples and review of quarterly performance evaluation analyses), or an upfront demonstration of performance can be used to influence the project manager's selection. The need to conduct a comprehensive evaluation of candidate laboratories will vary with the project and the familiarity with available laboratories.

2.2.2 Statements of Work

Statements of work are prepared for both field work and laboratory analysis. Data quality requirements and analytical methods need to be clearly and concisely communicated to either USACE personnel performing the analyses or to the laboratory selected by USACE's or the permit applicant's project manager. These specifications are best contained in a written laboratory contract. The main body of the contract should consist of general terms and

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conditions common to any legal contract. A statement of work should be appended to the contract. The statement of work should be drafted and negotiated with the laboratory prior to the start of any analyses. The statement of work should be written in clear and concise terms, providing sufficient detail and references to approved protocols for each required procedure or method to eliminate any confusion about steps in the analysis. The statement of work should define all requirements for acceptable analyses, an important consideration even when working with a familiar laboratory, and all pertinent information on the price, timing, and necessary documentation of the analyses. All available information on the range of concentrations expected and any special characteristics of the samples to be analyzed should also be contained in the statement of work. A generic statement of work for the analysis of most chemicals in the most commonly analyzed sample matrices is provided in Appendix B, and is based on the following outline:

- A summary of analyses to be performed, including:
  - A list of all variables to be analyzed for in each sample or group of samples
  - A list of all methods and target detection limits (TDLs) (see discussion in Section 2.3.2) for physical and chemical analyses and a list of test protocols for biological toxicity tests
  - The total number of samples provided for analysis and the associated laboratory QC samples, the cost of each analysis, and the total cost of the analytical service requested for each sample matrix.
- Acceptable procedures for sample delivery and storage, including:
  - The method of delivery, schedule of delivery, and person responsible for notifying the laboratory of any changes in the schedule
  - Requirements for physical storage of samples, holding times (consistent with those specified in the QA project plan), chain-of-custody, and sample logbook procedures.
- Methods to be followed for processing and analyzing samples.
- QA/QC requirements, including the data quality objectives specified in the QA project plan and appropriate warning and control limits.
- A list of products to be delivered by the laboratory, specifying the maximum time that may elapse between the submittal of samples to the laboratory and the delivery of data reports to the agency,

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organization, or industry requesting the analyses. Penalties for late delivery (and any incentives for early delivery) should be specified, as should any special requirements for supporting documentation and electronic data files. A checklist of the laboratory deliverables for analysis of organic compounds, pesticides, and polychlorinated biphenyls (PCBs) is presented in Table 1. A checklist of laboratory deliverables for analysis of metals is presented in Table 2.

- Progress notices (usually necessary only for large projects).
- Circumstances under which the laboratory should notify project personnel of problems, including, for example, when control limits or other performance criteria cannot be met, instrument malfunctions are suspected, or holding time limits have or will shortly expire.
- Written authorization for any deviations from the sampling and analysis plan should be obtained from EPA and USACE before the deviation occurs.
- Notice that scheduled and unannounced laboratory visits by the project manager or representative may be conducted.

The following additional information should also be provided in the laboratory statement of work:

- Requirements that each laboratory submit a QA manual for review and approval by the agency, organization, or industry requesting or funding the analysis. Each manual should contain a description of the laboratory organization and personnel, facilities and equipment, analytical methods, and procedures for sample custody, quality control, data handling, and results of previous laboratory audits.
- Conditions for rejection or non-analysis of samples and reanalysis of samples.
- Required storage time for records and samples prior to disposal.
- Terms for payments to the laboratory, including a requirement that the quality of data must be acceptable (pending the outcome of the QA review) before payment is made.

Including these elements in the statement of work helps to assure that responsibilities, data requirements, and expectations for performance are clear. A copy of the statement of work should be provided to the individual performing the data assessment to assist in the evaluation of data returned by the laboratory.

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TABLE 1. CHECKLIST OF LABORATORY DELIVERABLES FOR THE ANALYSIS OF ORGANIC COMPOUNDS

- ☐ A cover letter discussing analytical problems (if any) and referencing or describing the procedures and instrumentation used.
- ☐ Tabulated results, including final dilution volume of sample extracts, sample size, wet-to-dry ratios for solid samples (if requested), concentrations of compounds of interest (reported in units identified to two significant figures unless otherwise justified), and equations used to perform calculations. Concentration units should be µg/kg (dry weight) for sediment, and µg/L for water, µg/kg (wet weight) for tissue. These results should be checked for accuracy and the report signed by the laboratory manager or designee.
- ☐ Target detection limits (see discussion in Section 2.3.2 of this document), instrument detection limits, and detection limits achieved for the samples.
- ☐ Original data quantification reports for each sample.
- ☐ Method blanks associated with each sample, quantifying all compounds of interest identified in these blanks.
- ☐ A calibration data summary reporting the calibration range used. For the analysis of semivolatile organic compounds analyzed by mass spectrometry, this summary should include spectra and quantification reports for decafluorotriphenylphosphine (DFTPP) or an appropriate substitute standard. For volatile organic compounds analyzed by mass spectrometry, the summary should include spectra and quantification reports for bromofluorobenzene (BFB) or an appropriate substitute standard.
- ☐ Recovery assessments and replicate sample summaries. Laboratories should report all surrogate spike recovery data for each sample, and a statement of the range of recoveries should be included in reports using these data.
- ☐ All data qualification codes assigned by the laboratory, their description, and explanations for all departures from the analytical protocols.

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TABLE 1. (cont.)

Additional Deliverables for Volatile or Semivolatile Organic Compound Analyses[a]

- ☐ Tentatively identified compounds (if requested) and methods of quantification, along with the three library spectra that best match the spectra of the compound of interest (see Appendix C, Figure 1 for an example of a library spectrum).
- ☐ Reconstructed ion chromatograms for gas chromatography/mass spectrometry (GC/MS) analyses for each sample.
- ☐ Mass spectra of detected compounds for each sample.
- ☐ Internal standard area summary to show whether internal standard areas were stable.
- ☐ Gel permeation chromatography (GPC) chromatograms (for analyses of semivolatile compounds, if performed), recovery assessments, and replicate sample summaries. Laboratories should report all surrogate spike recovery data for each sample, and a statement of the range of recoveries should be included in reports using these data.

Additional Deliverables for Pesticide and Polychlorinated Biphenyl Analyses[a]

- ☐ Gas chromatography/electron capture detection (GC/ECD) chromatograms for quantification column and confirmation columns for each sample and for all standards analyzed.
- ☐ GPC chromatograms (if GPC was performed).
- ☐ An evaluation summary for 4,4'-DDT/endrin breakdown.
- ☐ A pesticide standard evaluation to summarize retention time shifts of internal standards or surrogate spike compounds.

[a] Many of the terms in this table are discussed more completely in Appendix C.

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TABLE 2. CHECKLIST OF LABORATORY DELIVERABLES FOR THE ANALYSIS OF METALS

☐	A cover letter discussing analytical problems (if any) and referencing or describing the digestion procedures and instrumentation used.
☐	Tabulated results for final dilution volumes of sample digestates, sample size, wet-to-dry ratios for solid samples (if requested), and concentrations of metals (reported in units identified to two significant figures unless otherwise justified). Concentration units should be µg/kg (dry weight) for sediment, µg/L for water, and µg/kg (wet weight) for tissue.[a] These results should be checked for accuracy and the report signed by the laboratory manager or designee.
☐	Target detection limits (see discussion in Section 2.3.2 of this document), instrument detection limits, and detection limits achieved for the samples.
☐	Method blanks for each batch of samples.
☐	Results for all the quality control checks and initial and continuing calibration control checks conducted by the laboratory.
☐	All data quantification codes assigned by the laboratory, their description, and explanations for all departures from the accepted analytical protocols.

[a] Most laboratories will report metals data in mg/kg for solid samples. The specification here of µg/kg is for consistency with organic chemical analyses, which are typically reported as µg/kg for solid samples. If different units are used, care should be taken to ensure that results are not confused.

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2.3 QUALITY ASSURANCE OBJECTIVES

Data quality objectives are addressed in this section of the QA project plan. Data quality objectives define performance-based goals for accuracy (precision and bias), representativeness, comparability, and completeness, as well as the required sensitivity of chemical measurements (i.e., TDLs). Accuracy is defined in terms of bias (how close the measured value is to the true value) and precision (how variable the measurements are when repeated) (see footnote at the beginning of Section 2). Data quality objectives for the dredged material program are based on the intended use of the data, technical feasibility, and consideration of cost. Therefore, data that meet all data quality objectives should be acceptable for unrestricted use in the project and should enable all project objectives to be addressed.

Numerical data quality objectives should be summarized in a table, with all data calculated and reported in units consistent with those used by other organizations reporting similar data, to allow comparability among databases. All measurements should be made so that results are representative of the medium (e.g., sediments, water, or tissue) being measured. Data quality objectives for precision and bias established for each measurement parameter should be based on prior knowledge of the measurement system employed, method validation studies, and the requirements of the specific project. Replicate tests should be performed for all test media (e.g., sediments, water, or tissue). Precision of approximately ≤ 30–50 relative percent difference between measurements (the random error of measurement) and bias of 50–150 percent of the true value (the systematic error of measurement) are adequate in many programs for making comparisons with regulatory limits. Precision may be calculated using three or more replicates to obtain the standard deviation and the derived confidence interval. Bias may be determined with standard reference material (SRM) or by spiking analyte-free samples.

These data quality objectives define the acceptability of laboratory measurements and should also include criteria for the maximum allowable time that samples or organisms can be held prior to analysis by a laboratory. An example of a data quality objectives summary for laboratory measurements is provided in Appendix A.

2.3.1 Program vs. Project Objectives

This document provides general guidance for QA activities conducted during dredged material evaluations. However, specific project needs will affect the kinds of chemical analyses that are requested by the project manager. Special project needs should be identified during preparation of the QA project plan and should be documented in this section of the plan. For example, a preliminary

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reconnaissance of a large area may only require data from simple and quick checks performed in the field. In contrast, a complete characterization of contamination in a sensitive area may require specialized laboratory methods, lower TDLS, and considerable documentation of results.

Before defining the analyses that should be performed to meet the data quality objectives established on a project-specific basis, a thorough review of all historical data associated with the site (if applicable) should be performed (see discussions in U.S. EPA and USACE 1991, 1994). A review of the historical data should be conducted in response to data needs in the testing program. A comprehensive review of all historical data should eliminate unnecessary chemical analyses and assist in focusing the collection of chemical-specific data that are needed. A more thorough discussion of how to review and use historical data is provided in Section 2.5.2.

2.3.2 Target Detection Limits for Chemicals

Different analytical methods are capable of detecting different concentrations of a chemical in a sample. In general, as the sensitivity and overall accuracy of a technique increases, so does the cost. Recommended TDLs that are judged to be feasible by a variety of methods, cost effective, and to meet the requirements for dredged material evaluations are summarized in Table 3 (at the end of Section 2.4), along with example analytical methods that are capable of meeting the TDLs. However, any method that can achieve these TDLs is acceptable, provided that the appropriate documentation of the method performance is generated for the project.

The TDL is a performance goal set between the lowest, technically feasible, detection limit for routine analytical methods and available regulatory criteria or guidelines for evaluating dredged material (see summaries in McDonald et al. [1992]; PSEP [1991]). The TDL is, therefore, equal to or greater than the lowest amount of a chemical that can be reliably detected based on the variability of the blank response of routine analytical methods (see Section 2.10.1 for discussion of method blank response). However, the reliability of a chemical measurement generally increases as the concentration increases. Analytical costs may also be lower at higher detection limits. For these reliability, feasibility, and cost reasons, the TDLs in Table 3 have been set at not less than 10 times lower than available regional or international dredged material guidelines for potential biological effects associated with sediment chemical contamination. In many cases, lower detection limits than the TDL can be obtained and may be desired for some regional programs (e.g., for carefully documenting changes in conditions at a relatively pristine site).

All data generated for dredged material evaluation should meet the TDLs in Table 3 unless a regional requirement is made or sample-specific interferences

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occur. Any sample-specific interferences should be well documented by the laboratory. If significantly higher or lower TDLs are required to meet rigorously defined data quality objectives (e.g., for human health risk assessments) for a specific project, then on a project-specific basis, modification to existing analytical procedures may be necessary. Such modifications should be documented in the QA project plan. An experienced analytical chemist should be consulted so the most appropriate method modifications can be assessed, the appropriate coordination with the analytical laboratory can be implemented, and the data quality objectives can be met. A more detailed discussion of method modifications is provided in Section 2.8.2.2.

2.4 STANDARD OPERATING PROCEDURES

Standard operating procedures are written descriptions of routine methods and should be provided for as many methods used during the dredged material evaluation as possible. A large number of field and laboratory operations can be standardized and presented as standard operating procedures. Once these procedures are specified, they can be referenced or provided in an appendix of the QA project plan. Only modifications to standard operating procedures or non-standard procedures need to be explained in the main body of the QA project plan (e.g, sampling or analytical procedures summaries discussed in Sections 2.5 and 2.8, respectively).

General types of procedures that benefit from standard operating procedures include field measurements ancillary to sample collection (e.g., depth of overlying water, sampling depth, water quality measurements or mixing model input measurements), chain-of-custody, sample handling and shipment, and routine analytical methods for chemical analyses. Standard operating procedures ensure that all persons conducting work are following the same procedures and that the procedures do not change over time. All personnel should be thoroughly familiar with the standard operating procedures before work is initiated. Deviations from standard operating procedures may affect data quality and integrity. If it is necessary to deviate from approved standard operating procedures, these deviations should be documented and approved through an appropriate chain-of-command. Personnel responsible for ensuring the standard operating procedures are adhered to should be identified in the QA project plan. Example standard operating procedures are provided in Appendix D.

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TABLE 3. ROUTINE ANALYTICAL METHODS AND TARGET DETECTION LIMITS FOR SEDIMENT, WATER, AND TISSUE (parts per billion, unless otherwise noted)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Inorganic Chemicals						
Aluminum	3050A/6010A; U.S. EPA (1993a)	50,000[c]	200.8; U.S. EPA (1993a);	1,000	202.2; 6010A/200.7	40
Antimony	3050A; 7040/7041; U.S. EPA (1993a); PSEP (1990a)	2,500	200.8; 7040/7041; U.S. EPA (1993a);	100	7041; 204.2	3
Arsenic	7061; 7060A; 3050A; U.S. EPA (1993a); PSEP (1990a); EPRI (1986)	5,000	200.8/7061; 7060A; U.S. EPA (1993a)	100	3010; 7061; 206.2; 206.3; EPRI (1986)	1
Beryllium	200.8; 7090/7091; U.S. EPA (1993a)	2,500[d]	200.8; 7090/7091; U.S. EPA (1993a)	100	7091; 210.2; 6010A/200.7; 200.8	0.2
Cadmium	3050A; 6010A; 7131A/7130; U.S. EPA (1993a); PSEP (1990a)	300	200.8; 7131A; 7130; U.S. EPA (1993a)	100	213.2; 7131A; 3010; 6010A/200.7; 200.8	1
Chromium	3050A/7191; 7190; 6010A; U.S. EPA (1993a);	5,000	200.8/7191; 7190; U.S. EPA (1993a)	100	7191; 200.8; 218.2; 3010; 6010A/200.7	1

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Cobalt	7201	100	200.8; 7201	100	219.2	4
Copper	3050A/7211; 7210; 6010A; U.S. EPA (1993a); PSEP (1990a)	5,000[c]	200.8/7211; 7210; U.S. EPA (1993a)	100	7211; 200.8; 220.1; 220.2; 3010; 6010A/200.7	1
Hexavalent chromium	--[f]	--	--[f]	--	7197; 218.5	50
Iron	3050A/7381; U.S. EPA (1993a)	50,000[d]	200.8; 7381; 6010A; U.S. EPA (1993a)	10,000	6010A/200.7; 3010; 7381; 236.2	10
Lead	3050A/7421; 7420; 6010A; U.S. EPA (1993a); PSEP (1990a)	5,000	200.8/7421; 7420; U.S. EPA (1993a)	100	7421; 239.2	1
Manganese	3050A/7461; U.S. EPA (1993a)	5,000[c]	200.8/7461; U.S. EPA (1993a)	500	6010A/200.7; 243.2; 3010	1
Mercury	7471; U.S. EPA (1993a)	200	7471; U.S. EPA (1993a)	10	7471; 245.1; 245.2	0.2
Nickel	3050A/6010A; 7521; 7520; U.S. EPA (1993a); PSEP (1990a)	5,000	200.8/6010A; 7521; 7520; U.S. EPA (1993a)	100	6010A; 7521; 249.2	1
Selenium	7741; 7740; U.S. EPA (1993a); EPRI (1986)	1,000[c]	200.8/7741; 7740; U.S. EPA (1993a)	200	7740; 7741; 270.2; 270.3; EPRI (1986)	2

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Silver	3050A/7761; 7760; U.S. EPA (1993a); PSEP (1990a)	200[e]	200.8/7761; 7760; U.S. EPA (1993a)	100	7761; 272.2	1
Thallium	7840/7841; U.S. EPA (1993a)	200[c,e]	200.8; 7840; 7841; U.S. EPA (1993a)	100	7840; 7841; 279.2	1
Tin	U.S. EPA (1993a)	500[c,e]	200.8; U.S. EPA (1993a)	100	282.2	5
Zinc	3050A/7951; 7950; U.S. EPA (1993a); PSEP (1990a)	15,000	200.8/7951; 7950; U.S. EPA (1993a)	2,000	7951; 289.2; 200.7; 3010; 6010A	1
Organotin	NCASI (1986); Uhler and Durrel (1989); Rice et al. (1987)	10	NCASI (1986); Rice et al. (1987); Uhler et al. (1989)	10	NCASI (1986); Rice et al. (1987); Uhler and Durrel (1989)	0.01

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Nonionic Organic Compounds						
LPAH Compounds						
Naphthalene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; NOAA (1989); U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a) Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Acenaphthylene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Acenaphthene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a) Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Fluorene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Phenanthrene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Anthracene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
1-Methylnaphthalene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
2-Methylnaphthalene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
HPAH Compounds						
Fluoranthene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Pyrene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Benz[a]anthracene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10

T. 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Chrysene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Benzo(b&k)fluoranthenes	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Benzo[a]pyrene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Indeno[1,2,3-c,d]pyrene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Dibenz[a,h]anthracene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Benzo[g,h,i]perylene	1625C; 3540A; 3550A/8100; 8250; 8270A; 8310; U.S. EPA (1993a)	20	1625C; 8100; 8250; 8270A; 8310; U.S. EPA (1993a); Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8250; 8270A; 8310	10
Chlorinated Benzenes						
1,3-Dichlorobenzene	1625C; 3540A; 3550A/8100; 8240A; 8250; 8260; 8270A	20	1625C; 8240A: 8250; 8270A; Sloan et al. (1993)	20	1625C; 3510A; 3520A/8100; 8240A; 8250; 8260; 8270A	10
1,4-Dichlorobenzene	1625C; 3540A; 3550A/8100; 8240A; 8250; 8260; 8270A	20	1625C: 8100; 8240A; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8240A; 8250; 8260; 8270A	10
1,2-Dichlorobenzene	1625C; 3540A; 3550A/8100; 8240A; 8250; 8260; 8270A	20	1625C; 8240A: 8250; 8270A; Sloan et al. (1993)	20	1625C; 3510A; 3520A/8100; 8240A; 8250; 8260; 8270A	10
1,2,4-Trichlorobenzene	1625C; 3540A; 3550A/8250; 8260; 8270A	10[f]	1625C; 8250; 8260; 8270A; Sloan et al. (1993)	20	1625C; 3510A; 3520A/8250; 8260; 8270A	10
Hexachlorobenzene	1625C; 3540A; 3550A/8250; 8260; 8270A	10[f]	1625C; 8250; 8260; 8270A; Sloan et al. (1993)	20	1625C; 3510A; 3520A/8250; 8260; 8270A	10

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Phthalate Esters						
Dimethyl phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8060; 8100; 8250; 8270A	10
Diethyl phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8060; 8250; 8270A	10
Di-n-butyl phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8060; 8250; 8270A	10
Butyl benzyl phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8060; 8250; 8270A	10
Bis[2-ethylhexyl]phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8060; 8250; 8270A	10

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Di-n-octyl phthalate	1625C; 3540A; 3550A/8060; 8100; 8250; 8270A	50	1625C; 8060; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8100; 8060; 8250; 8270A	10
Miscellaneous Extractable Compounds						
Benzyl alcohol	1625C; 3540A; 3550A/8250; 8270A	50	1625C; 8250; 8270A	100	1625C; 3510A; 3520A/8250; 8270A	50
Benzoic acid	1625C; 3540A; 3550A/8250; 8270A	100	1625C; 8250; 8270A	100	1625C; 3510A; 3520A/8250; 8270A	50
Dibenzofuran	1625C; 3540A; 3550A/8250; 8270A	50	1625C; 8100; 8250; 8270A; Sloan et al. (1993); NOAA (1989)	20	1625C; 3510A; 3520A/8250; 8270A	10
Hexachloroethane	1625C; 3540A; 3550A/8250; 8270A	100	1625C; 8250; 8270A	40	1625C; 3510A; 3520A/8250; 8270A	50
Hexachlorobutadiene	1625C; 3540A; 3550A/8250; 8270A	20	1625C; 8250; 8270A	40	1625C; 3510A; 3520A/8250; 8270A	50

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
N-Nitrosodiphenylamine	1625C; 3540A; 3550A/8250; 8270A	20	1625C; 8250; 8270A	20	1625C; 3510A; 3520A/8250; 8270A	50
Methylethyl ketone	1624C; 3540A; 3550A/8250; 8240A; 8260; 8270A	20	1624C; 8250; 8270A	20	1624C; 3510A; 3520A/8250; 8240A; 8260; 8270A	50
Polychlorinated Dibenzofurans						
Tetrachlorinated furans	1613; 8290	0.001	8290	0.001	1613; 8290	0.00001
Pentachlorinated furans	1613; 8290	0.0025	8290	0.0025	1613; 8290	0.000025
Hexachlorinated furans	1613; 8290	0.005	8290	0.005	1613; 8290	0.00005
Heptachlorinated furans	1613; 8290	0.005	8290	0.005	1613; 8290	0.00005
Octachlorinated furans	1613; 8290	0.01	8290	0.01	1613; 8290	0.0001
Polychlorinated Dibenzo-*p*-dioxins						
2,3,7,8-TCDD	1613; 8290	0.001	8290	0.001	1613; 8290	0.00001
Other tetrachlorinated dioxins	1613; 8290	0.001	8290	0.001	1613; 8290	0.00001
Pentachlorinated dioxins	1613; 8290	0.0025	8290	0.0025	1613; 8290	0.000025
Hexachlorinated dioxins	1613; 8290	0.005	8290	0.005	1613; 8290	0.00005

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Heptachlorinated dioxins	1613; 8290	0.005	8290	0.005	1613; 8290	0.00005
Octachlorinated dioxins	1613; 8290	0.01	8290	0.01	1613; 8290	0.0001
PCBs						
PCB congeners	Sloan et al. (1993); NOAA (1989); U.S. EPA (1993a)	1	NOAA (1989); U.S. EPA (1993a)	2	NOAA (1989)	0.01
Pesticides						
Aldrin	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.04
Chlordane and derivatives	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.14
Dieldrin	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.02
4,4'-DDD	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
4,4'-DDE	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
4,4'-DDT	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
Endosulfan and derivatives	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
Endrin and derivatives	3540A; 3550A/8080; NOAA (1985)	5	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
Heptachlor and derivatives	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
γ-Hexachlorocyclohexane (lindane)	3540A; 3550A/8080; NOAA (1985)	10	8080; NOAA (1985)	10	608; 3510A; 3520A/8080	0.1
Toxaphene	3540A; 3550A/8080	50	8080	50	608; 3510A; 3520A/8080	0.5
Methoxychlor	3540A; 3550A/8080	10	8080	10	608; 3510A; 3520A/8080	0.5
Chlorbenside	3540A; 3550A/8080; NOAA (1985)	2	8080; NOAA (1985)	2	608; 3510A; 3520A/8080	0.002

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Dacthal	3540A; 3550A/8080; NOAA (1985)	2	8080; NOAA (1985)	2	608; 3510A; 3520A/8080	0.03
Total chlorinated pesticides	3540A; 3550A/8080; NOAA (1985)	20	8080; NOAA (1985)	20	608; 3510A; 3520A/8080	0.02
Malathion	3540A; 3550A/8141	5	8141	5	3510A; 3520A/8141	0.8
Parathion	3540A; 3550A/8141	6	8141	6	3510A; 3520A/8141	0.8
Volatile Organic Compounds						
Benzene	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Chloroform	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Ethylbenzene	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Toluene	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Trichloroethene	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Tetrachloroethene	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Total xylenes	1624C; 8240A; 8260	10	1624C; 8240A; 8260	10	1624C; 8240A; 8260	5
Ionizable Organic Compounds						
Phenols						
Phenol	1625C; 3540A; 3550A/8040A; 8250; 8270A; 9066	100	1625C; 8040A; 8270A	20	1625C; 3510A; 3520A/8040A; 8250; 8270A	10
2-Methylphenol	1625C; 3540A; 3550A/8040A; 8250; 8270A	50	1625C; 8040A; 8270A	20	1625C; 3510A; 3520A/8040A; 8250; 8270A	10
4-Methylphenol	1625C; 3540A; 3550A/8040A; 8250; 8270A	100	1625C; 8040A; 8270A	20	1625C; 3510A; 3520A/8040A; 8250; 8270A	10
2,4-Dimethylphenol	1625C; 3540A; 3550A/8040A; 8250; 8270A	20	1625C; 8040A; 8270A	20	1625C; 3510A; 3520A/8040A; 8250; 8270A	10
Pentachlorophenol	1625C; 3540A; 3550A/8040A; 8250; 8270A	100	1625C; 8040A; 8270A	100	1625C; 3510A; 3520A/8040A; 8250; 8270A	50
Resin Acids and Guaiacols	1625C; 3540A; 3550A; 8250; 8270A	10	--[g]	--	--	--

TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Other Analyses						
Ammonia	350.1; 350.2; Plumb (1981)	100	--	--	350.1; 350.2; 350.3	30
Cyanides	9010A; 9012	2,000	9010A; 9012	1,000	335.2	5,000
Total organic carbon	PSEP (1986); U.S. EPA (1987a, 1992b)	0.1%	--	--	9060; 415.1; APHA 5310D	0.1%
Total petroleum hydrocarbons	9070; 418.1;	5,000	418.1	100,000	418.1	100
Total recoverable petroleum hydrocarbons	418.1	5,000	--	--	418.1	500
Total phenols	8040A	1,000	8040A	10,000	420.1; 625; 8040A	50
Acid-volatile sulfides	Cutter and Oates (1987); U.S. EPA (1991a); DiToro et al. (1990)	0.1µmole/g	--	--	--	--
Total sulfides	9030; Plumb (1981)	100	--	--	376.2	100
Grain size	Plumb (1981); ASTM (1992)	1%	--	--	--	--
Total suspended solids	--	--	--	--	160.2; APHA 2510D	1.0 mg/L
Total settleable solids	--	--	--	--	160.5; APHA 2540B	0.05 ml/L

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TABLE 3. (cont.)

Chemical	Example Sediment Method[a]	Recommended Sediment TDL	Example Tissue Method[a]	Recommended Tissue TDL[b]	Example Water Method[a]	Recommended Water TDL[b]
Total solids/dry weight	160.3; Plumb (1981); PSEP (1986)	0.1%	--	--	--	--
Total volatile solids	160.4; Plumb (1981); APHA 2540E; PSEP (1986)	0.1%	--	--	--	--
Specific gravity	Plumb (1981)	0.01 mg/L	--	--	--	--
pH	9045; Plumb (1981)	0.1 pH units	--	--	Plumb (1981)	0.1 pH units
Total water content of test species	--	--	U.S. EPA (1986b, 1987a)	0.1%	--	--
Total lipid	--	--	Bligh and Dyer (1959); Folch et al. (1957)	0.1%	--	--

Note: HPAH - high molecular weight polycyclic aromatic hydrocarbon
LPAH - low molecular weight polycyclic aromatic hydrocarbon
TCDD - tetrachlorodibenzo-*p*-dioxin
TDL - The target detection limit is a performance goal set between the lowest, technically feasible, detection limit for routine analytical methods and available regulatory criteria or guidelines for evaluating dredged material. The target detection limit is, therefore, equal to or greater than the lowest amount of a chemical that can be reliably detected based on the variability of the blank response of routine analytical methods. However, the reliability of a chemical measurement generally increases as the concentration increases. Analytical costs may also be lower at higher detection limits. For these reasons, the target detection limit has been set not less than 10 times lower than available dredged material guidelines.

[a] Numbered methods are found in references as listed on following page.

[b] Determined by work group discussion; no or few effects guidelines are available for comparison.

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TABLE 3. (cont.)

[c] No sediment screening or adverse effects guidelines are available for comparison.

[d] Less than 1/10 of available sediment guidelines for screening concentrations or potential adverse effects, but still cost effective and feasible to attain with a range of routine analytical methods.

[e] TDL may restrict use of some routine analytical methods, but reflects work group consensus.

[f] Sediment TDL slightly exceeds one available sediment guideline (Washington Sediment Management Standards) at low organic carbon content (< 2 percent TOC).

[g] -- - Not applicable.

REFERENCES CONTAINING NUMBERED METHODS IN TABLE 3.

Reference	Method				
US EPA 1983	160.2	206.2	220.2	270.2	350.1
	160.3	206.3	236.2	270.3	350.2
	160.4	210.2	239.2	272.2	350.3
	160.5	213.2	243.2	279.2	376.2
	200.7	218.2	245.1	282.2	415.1
	200.8	218.5	245.2	289.2	418.1
	202.2	219.2	249.2	335.2	420.1
	204.2	220.1			
US EPA 1982	608	625			
US EPA 1989b	8290				
US EPA 1990f	1613				
US EPA 1989c	1624C	1625C			
US EPA 1986a	3010	7090	7420	7841	8270A
	3050A	7091	7421	7950	8310
	3510A	7130	7461	7951	9010A
	3520A	7131A	7471	8040A	9012
	3540A	7190	7520	8060	9030
	3550A	7191	7521	8080	9045
	6010A	7197	7740	8100	9060
	7040	7201	7741	8141	9066
	7041	7210	7760	8240A	9070
	7060A	7211	7761	8250	
	7061	7381	7840	8260	
APHA 1989	APHA 2510D	APHA 2540B	APHA 2540E	APHA 5310D	

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2.5 SAMPLING STRATEGY AND PROCEDURES

A sampling strategy should be developed to ensure that the sampling design supports the planned data use. For example, a project that was planned to characterize a specific area would have different sampling design requirements than a project that was screening for a suspected problem chemical. The sampling strategy will strongly affect the representativeness, comparability, and completeness that might be expected for field measurements. In addition, the strategy for collecting field QC samples (e.g., replicates) will assist in the determination of how well the total variability of a field measurement can be documented. Therefore, development of the sampling strategy should be closely coordinated with development of QA objectives discussed in Section 2.3.

Specific procedures for collecting each kind of sediment, water, tissue, or biological sample are described in this section of the QA project plan. The level of detail can range from a brief summary of sampling objectives, containers, special sample handling procedures (including compositing and subsampling procedures, if appropriate), and storage/sample preservation to a complete sampling plan that provides all details necessary to implement the field program. Standard operating procedures do not require elaboration in this section of the QA project plan (see Section 2.4).

If complete sampling details are not provided in the QA project plan, then reference should be made to the sampling plan that does provide all details. The QA project plan may be an appendix of the sampling plan, or specific sampling details may be provided as an appendix of the QA project plan. For smaller projects, a single planning document may be created that combines a work plan (project rationale and schedule for each task), detailed sampling plan (how project tasks are implemented), and the QA project plan. For larger projects, the QA project plan and the detailed sampling plan may be two separate documents.

This section of the document provides basic guidance for assuring sample quality from collection to delivery to the laboratory and guidance on items to consider when designing a sampling plan. A well-designed sampling plan is essential when evaluating the potential impact of dredged material discharge on the aquatic environment. The purpose of the sampling plan is to provide a blueprint for all fieldwork by defining in detail the appropriate sampling and data collection methods (in accordance with the established QA objectives; see Section 2.3). Before any sampling is initiated, the sampling plan should meet clearly defined objectives for individual dredging projects. Factors such as the availability and content of historical data, the degree of sediment heterogeneity, the volume of sediment proposed to be dredged, the areal extent of the dredging project, the number and geographical distribution of sample collection sites, potential contaminant sources, and the procedures for collection,

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preservation, storage, and tracking of samples should be carefully considered and are necessary for adequate QA/QC of the data. The magnitude of the dredging project and its time and budgetary constraints should also be considered.

The following kinds of information should be reviewed for assistance in designing the sampling plan:

- **Geochemical and hydrodynamic data**—The grain size, specific density, water content, total organic carbon (TOC), and identification of sediment horizons are helpful in making operational decisions. Areas of high tidal currents and high wave energy tend to have sediments with larger grain sizes than do quiescent areas. Many contaminants have a greater affinity for clay and silt than for sand. Horizontal and vertical gradients may exist within the sediment. If the sediments are subject to frequent mixing by wave action, currents or prop wash, the sediments are likely to be relatively homogenous. Local groundwater quality and movement should be determined if groundwater is a potential source of contamination.

- **Quality and age of available data**—Reviewing the results of chemical analyses performed in past studies can help in selecting the appropriate contaminants of concern and in focusing plans for additional analyses. In particular, analytical costs can be reduced if historical results can substitute for new analyses. Collecting these data is only the initial step, however. Assessing their usefulness to the current project should always be performed before substantial effort is spent on incorporating historical results into a project database. If it is determined that the historical data are of questionable use for a specific project, then the determination of the most appropriate chemical analyses that will meet the project needs, including the level of effort necessary, will need to be assessed.

- **Spill data**—Evidence of a contaminant spill within or near the dredging area may be an important consideration in identifying locations for sampling.

- **Dredging history**—Knowledge of prior dredging may dramatically affect sampling plans. If the area is frequently dredged (every 1–2 years) or if the area is subject to frequent ship traffic, the sediments are likely to be relatively homogenous. Assuming that there is no major contaminant input, the sampling effort may be minimal. However, if there is information regarding possible contamination, a more extensive sampling effort may be indicated. New excavations of material unaffected by anthropogenic input may require less intensive sampling than maintenance dredging.

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An acceptable sampling plan, including QA/QC requirements, should be in place before sampling begins. Regional guidance from governmental agencies (i.e., EPA and USACE) is required for developing these project-specific sampling plans. The sampling plan should be written so that a field sampling team unfamiliar with the site would be able to gather the necessary samples and field information.

Addressing quality assurance in the sampling plan includes designating field samples to be collected and used for assessing the quality of sampling and analysis, and ensuring that quality assurance is included in standard operating procedures for field measurements. The quality of the information obtained through the testing process is impacted by the following four factors:

- Collecting representative samples
- Collecting an appropriate number of samples
- Using appropriate sampling techniques
- Protecting or preserving the samples until they are tested.

Ideally, the importance of each of these four factors will be fully understood and appropriately implemented; in practice, however, this is not always the case. There may be occasions when time or other resource constraints will limit the amount of information that should or can be gathered. When this is the case, the relative importance of each of these factors has to be carefully considered in light of the specific study purposes.

An important component of any field sampling program is a preproject meeting with all concerned personnel. As with the drafting of the QA project plan, participation by several individuals may be necessary when developing the sampling plan. Personnel involved may include management, field personnel, laboratory personnel, data management/analysis personnel, and representatives of regulatory agencies, the permit applicant, and the dredging company. To assure sampling quality, at least one individual familiar with the study area should be included in the preproject meeting. The purposes of the meeting include:

- Defining the objectives of the sampling program
- Ensuring communication among participating groups
- Ensuring agreement on methods and contingency plans.

The more explicitly the objectives of a testing program can be stated (including QA objectives), the easier it will be to design an appropriate sampling plan. A complete sampling plan will result in a level of detail such that all sampling procedures and locations are clearly defined, sample volumes are clearly established, and all logistical concerns are fully addressed.

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To ensure an adequate level of confidence in the data produced and in the comparability of the data to information collected by other sampling teams, the sampling plan should adhere to published sampling protocols and guidance. Descriptions of widely used sampling methods can be found in several EPA publications, many of which are cited in this section.

The sampling plan should include the following specific sections:

- Summary of dredging plan, including the dimensions of the dredging area, the dredging depths, side-slopes, and the volume of sediment for disposal (including overdredged material)
- Site background and existing database for the area, including identification of 1) relevant data, 2) need for additional data, and 3) areas of potential environmental concern within the confines of the dredging project
- Subdivision of dredging area into project segments, if appropriate, based on an assessment (review of historical data and past assessment work) of the level of environmental concern within the dredging area
- Sample location and sample collection frequency, including selection of methods and equipment for positioning vessels at established stations
- Sample designation system (i.e., a description of how each independently collected sample will be identified)
- Sample collection methods for all test media (e.g., sediment, water, or tissue)
- Procedures for sample handling (including container types and cleaning procedures), preservation, and storage, and (if applicable) field or shipboard analysis
- Logistical considerations and safety precautions.

The subsections that follow discuss each of these steps and provide general guidance for their conduct.

2.5.1 Review of Dredging Plan

A review of the plan for the dredging project provides a basis for determining the sampling strategy (see summary discussion in Section 2.3). The volume of material to be dredged and the method of dredging are two important factors that will help to determine the number of samples required. The number of samples required is generally a judgment that considers the cost, resolution,

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and the risk of an incorrect decision regarding the volume of material to be dredged. Knowledge of the depth, volume, and physical characteristics of the material to be dredged will help to determine the kind of sampling equipment that is required. The boundaries of the dredging area have to be known (including the toe and the top of all side-slopes) to ensure that the number and location of samples are appropriate. Sampling should generally be to below the project depth plus any overdredging.

2.5.2 Site Background and Existing Database

As previously stated, reviewing the results of chemical analyses performed in past studies can help in selecting the appropriate contaminants of concern and in focusing plans for additional analyses. The level of data quality for historical data will affect the selection of station locations. Examples of four levels of data quality that can be assigned to historical results are summarized in Table 4. Labeling each set of results with a data quality level is also a simple way to summarize the relative quality of the data set for future use. This classification provides a useful summary of data quality when making conclusions and writing up the results of the project. The example classification in Table 4 considers the following factors when determining the suitability of historical results for a particular project:

- **The analytical methods used and their associated detection limits**—Analytical methods often improve over time. For example, as late as the 1970s, concentrations of many organic compounds in sediment samples were difficult to measure routinely, accurately, or sensitively. However, as better preparation methods and more sensitive analytical techniques have been developed, the ability to distinguish these compounds from other substances and the overall sensitivity of analyses have substantially improved. Methods are now available that afford detection limits that are well within the range of documented adverse biological effects.

- **QA/QC procedures and documentation**—The usefulness of data will depend on whether appropriate QA procedures have been used during analysis and if the data have been properly validated (see Section 2.9.1) and documented. Because more rigorous methods to analyze samples and document data quality have been required by environmental scientists over the past decade, only well-documented data that have been produced by laboratories using acceptable data quality controls should be considered to have no limitations. Historical data produced by even the best laboratories often may lack complete documentation, or the documentation may be difficult to obtain. However, historical data with incomplete documentation could still be used for projects with certain objectives (e.g., screening-level studies).

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TABLE 4. LEVELS OF DATA QUALITY FOR HISTORICAL DATA

Level 1 Data are acceptable for all project uses.

The data are supported by appropriate documentation that confirms their comparability to data that will be generated in the current project.

Level 2 Data are acceptable for most project uses.

Appropriate documentation may not be available to confirm conclusions on data quality or to support legal defensibility. These data are supported by a summary of quality control information, and the environmental distribution of contamination suggested by these data is comparable to the distribution suggested by an independent analytical technique. The data are thus considered reliable and potentially comparable to data that will be produced in the project.

Level 3 Data are acceptable for reconnaissance-level analyses.

The data can be used to estimate the nature and extent of contamination. No supporting quality control information is available, but standard methods were used, and there is no reason to suspect a problem with the data based on 1) an inspection of the data, 2) their environmental distribution relative to data produced by an independent analytical technique, or 3) supporting technical reports. These data should be considered estimates and used only to provide an indication of the nature and possible extent of contamination.

Level 4 Data are not acceptable for use in the current project.

The data may have been acceptable for their original use. However, little or no supporting information is available to confirm the methods used, no quality control information is available, or there are documented reasons in technical reports that suggest the data may not be comparable to corresponding data to be collected in the current project.

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2.5.3 Subdivision of Dredging Area

Sediment characteristics may vary substantially within the limits of the area to be dredged as a result of geographical and hydrological features. Many dredging projects can be subdivided into project segments (horizontal and/or vertical) that can be treated as separate management units. A project segment is an area expected to have relatively consistent characteristics that differ substantially from the characteristics of adjacent segments. Project segments may be sampled with various intensities as warranted by the study objectives and testing results.

Any established sampling program should be sufficiently flexible to allow changes based on field observations. However, any deviations from established procedures should be documented, along with the rationale for such deviations. An alteration checklist form is generally appropriate to implement required changes. An example of such a checklist is provided in Appendix A.

2.5.4 Sample Location and Collection Frequency

The method of dredging, the volume of sediment to be removed, the areal extent of the dredging project, and the horizontal and vertical heterogeneity of the sediment are key to determining station locations and the number of samples to be collected for the total dredging project. When appropriate to testing objectives, samples may be composited prior to analysis (with attention to the discussion in Section 2.5.4.8). The appropriate number of samples and the proper use of compositing should be determined for each operation on a case-by-case basis.

Using pertinent available information to determine station locations within the dredging area is both cost effective and technically efficient. If a review of historical data (see Section 2.5.2) identifies possible sources of contamination, skewing the sampling effort toward those areas may be justified to thoroughly characterize those areas, but can lead to an incomplete assessment of contamination in the whole study area. In areas of unequally distributed contamination, the total sampling effort should be increased to ensure representative, but not necessarily equal, sampling of the entire site. The following factors should be among those considered when selecting sampling stations and patterns: objectives of the testing program, bathymetry, area of the dredging project, accessibility, flows (currents and tides), mixing (hydrology), sediment heterogeneity, contaminant source locations, land use activities, available personnel and facilities, and other physical characteristics of the sampling site. A discussion of locating appropriate stations, sample collection, and sample handling procedures is provided in the following sections.

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2.5.4.1 Station Locations

Station locations within the dredging area should include locations downstream from major point sources and in quiescent areas, such as turning basins, side channels, and inside channel bends, where fine-grained sediments and associated contaminants are most likely to settle. Information that should help to define the representativeness of stations within a dredging area includes:

- Clearly defined distribution of sediments to be dredged (i.e., project depth, overdredged depth, and side slopes)
- Clearly defined area to be sampled
- Correctly distributed sampling locations within each dredging area.

If sample variability is suspected within the dredging area, then multiple samples should be collected. When sediment variability is unknown, it may be necessary to conduct a preliminary survey of the dredging area to better define the final sampling program.

2.5.4.2 Sample Replication

Within a station, samples may be collected for replicate testing. Sediment testing is conducted on replicate samples, for which laboratory replicates (subsamples of a composite sample of the replicates) are generally recommended as opposed to field replicates (separate samples for each replicate). The former involves pseudo-replication but is more appropriate for dredged material evaluations where sediments will be homogenized by the dredging and discharge process. The latter involves true replication but is more appropriate for field investigations of the extent and degree of variability of sediment toxicity.

2.5.4.3 Depth Considerations

Sediment composition can vary vertically as well as horizontally. Samples should be collected over the entire dredging depth (including over-dredging), unless the sediments are known to be vertically homogenous or there are adequate data to demonstrate that contamination does not extend throughout the depth to be excavated. Separate analyses of defined sediment horizons or layers may be useful to determine the vertical distribution of contamination.

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2.5.4.4 Sampling Bias

Ideally, the composition of an area and the composition of the samples obtained from that area will be the same. However, in practice, there often are differences due to bias in the sampling program, including disproportionate intensity of sampling in different parts of the dredging area and equipment limitations.

In some cases, to minimize bias, it may be useful to develop a sampling grid. The horizontal dimensions may be subdivided into grid cells of equal size, which are numbered sequentially. Cells are then selected for sampling either randomly or in a stratified random manner. It can be important to collect more than the minimum number of samples required, especially in areas suspected of having high or highly variable contamination. In some cases extra samples may be archived (for long time periods in the case of physical characterization or chemical analyses and for short time periods in the case of biological tests) should reexamination of particular stations be warranted.

In other cases, a sampling grid may not be desirable. This is particularly the case where dredging sites are not continuous open areas, but are rather a series of separate humps, bumps, reaches, and pockets with varying depths and surface areas. In these latter cases, sample distribution is commonly biased with intent.

2.5.4.5 Level of Effort

In some cases, it may be advisable to consider varying the level of sampling effort. Dredging areas suspected or known to be contaminated may be targeted for an increased level of effort so that the boundaries and characteristics of the contamination can be identified. A weighting approach can be applied whereby specific areas are ranked in increasing order of concern, and level of concern can then be used as a factor when determining the number of samples within each area.

2.5.4.6 Number of Samples

In general, the number of samples that should be collected within each dredging area is inversely proportional to the amount of known information, and is proportional to the level of confidence that is desired in the results and the suspected level of contamination. No specific guidance can be provided, but the following factors should be considered:

- The greater the number of samples collected, the better the areal and vertical definition

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- Single measurements are inadequate to describe variability
- The means of several measurements at each station within a dredging area are generally less variable than individual measurements at each station.

2.5.4.7 Time and Funding Constraints

In all cases, the ultimate objective is to obtain sufficient information to evaluate the environmental impact of a dredged material disposal operation. The realities of time and funding constraints have to be recognized, although such do not justify inadequate environmental evaluation. Possible responses to cost constraints have been discussed by Higgins (1988). If the original sampling design does not seem to fit time or funding constraints, several options are available, all of which increase the risk of an incorrect decision. For example, the number of segments into which the project is divided can be reduced, but the total number of samples remains the same. This option results in fewer segments and maintains the power of station-to-station comparisons. This may, however, provide a poor assessment of spatial variability because of reduced stratification. Another example would be to maintain (or even increase) the number of stations sampled, and composite multiple samples from within a segment. This option results in a lower number of analyses being performed per segment, but may provide a poor assessment of spatial variability within each segment.

2.5.4.8 Sample Compositing

The objective of obtaining an accurate representation and definition of the dredging area has to be satisfied when compositing samples. Compositing provides a way to control cost while analyzing sediments from a large number of stations. Compositing results in a less detailed description of the variability within the area sampled than would individual analysis at each station. However if, for example, five analyses can be performed to characterize a project segment, the increased coverage afforded by collecting 15 individual samples and combining sets of three into five composite samples for analysis may justify the increased time and cost of collecting the extra 10 samples. Compositing can also provide the large sample volumes required for some biological tests. Composite samples represent the "average" of the characteristics of the individual samples making up the composite and are generally appropriate for logistical and other reasons; however, they are not recommended where they could serve to "dilute" a highly toxic but localized sediment "hot spot." Further, composite samples are not recommended for stations with very different grain size characteristics.

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2.5.4.9 Sample Definition

When a sediment sample is collected, a decision has to be made as to whether the entire sediment volume is to be considered as the sample or whether the sediment volume represents separate samples. For instance, based on observed stratification, the top 1 m of a core might be considered to be a separate sample from the remainder of the core. After the sediment to be considered as a sample is identified, it should be thoroughly homogenized. Samples may be split before compositing, with a portion of the original sediment archived for possible later analysis, and the remainder combined with parts of other samples. These are then thoroughly homogenized (using clean instruments until color and textural homogeneity are achieved), producing the composite sample.

2.5.5 Sample Designation System

Information on the procedures used to designate the sampling location and type of sample collected should be clearly stated in the field sampling plan. The sampling stations should be named according to the site and the type of station. Each sample should be assigned an identifier that describes the station, type of sample, and field replicate. An example sample designation format is as follows:

- The first two characters of the station name could identify the site (e.g., BH = Boston Harbor).
- The third character of the station name could identify the type of station (e.g., S = site station, P = perimeter station, or R = reference station).
- The fourth and fifth characters of the station name could consist of a sequential number (e.g., 01, 02, or 03) that would be assigned to distinguish between different stations of the same type.
- The sixth character of the station name could describe the type of sample (e.g., C = sediment for chemistry and bioassay analyses, B = bioaccumulation, or I = benthic infauna).
- The resulting sample identifier would be: BHS01C.

When field replicates are collected (i.e., for benthic samples), the replicate number should be appended to the sample identifier. All field replicates from the same station should have the same sample identifier. The sample identifier and replicate number should be linked by a dash to form a single identifier for use on sample labels. The sample date should also be recorded on the sample label.

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2.5.6 Station Positioning

The type of positioning system used during sample collection and detailed procedures for station positioning should be clearly stated in the sampling plan. No single positioning method will be appropriate for all sampling scenarios. U.S. EPA (1987b), PSEP(1990b), and USACE (1990) provide useful information on positioning systems and procedures. Guidance in these publications may be followed on all points that do not conflict with this document.

2.5.6.1 Selection of Station Positioning System

Available systems should be evaluated based on positioning requirements and project-specific constraints to select the most appropriate station positioning method for the project. Specific design and location factors that may affect station positioning include physical conditions (e.g., weather and currents) and topography of the study site, proposed equipment and analyses, minimum station separation, station reoccupation, and program-imposed constraints. U.S. EPA's (1993b) locational data policy implementation guidance calls for positioning accuracy within 25 m.

There are many methods available for navigating and positioning sampling vessels. These methods range from simple extensions of well-established onshore survey techniques using theodolites to highly sophisticated electronic positioning systems. A general discussion of a few of the station positioning methods available for dredged material evaluations is provided in the following sections. U.S. EPA (1987b), PSEP (1990b), USACE (1990), and current literature from the manufacturers of station positioning systems should be thoroughly reviewed during the selection process to choose the most appropriate project-specific positioning system.

Optical Positioning Techniques

Optical positioning requires visual sighting to determine alignment on two or more ranges, or the distances and angles between the vessel and shore targets.

Intersecting ranges can be used when a number of established landmarks permit easy selection of multiple ranges that intersect at the desired sampling point, and accuracy is not critical. One of the more traditional optical positioning systems is the theodolite system. Position of the sampling vessel can be established using theodolites by two onshore observers who simultaneously measure the angle between a reference object or shore traverse and the vessel. Using a theodolite with an accuracy of ±15 seconds for a single angle measurement at an intercept angle of approximately 45° and a

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range of 5 km, could potentially yield a positioning error of < ±1 m (Ingham 1975). Although the accuracy of this method is good under optimal conditions, its use in open waters has several disadvantages such as limited line-of-sight, limits on intersection of angles, requirement of two manned shore stations, simultaneous measurements, and target movement and path interferences (e.g., fog, heavy rain, or heat waves).

Electronic Positioning Techniques

Electronic positioning systems use the transmission of electromagnetic waves from two or more stations and a vessel transmitter to define a vessel's location. Under routine sampling conditions, which may disfavor optical positioning, and at their respective maximum ranges, electronic positioning methods have greater accuracy than optical positioning methods (U.S. EPA 1987b).

LORAN-C is one type of electronic positioning system. Based on the signal properties of received transmissions from land-based transmitters, the LORAN-C receiver can be used to locate an approximate position, with a repeatable accuracy that varies from 15 to 90 m (U.S. EPA 1987b), depending on the weather and the geometry of the receiver within the LORAN-C station network. Although the LORAN-C system is not limited by visibility or range restrictions and does not require additional personnel to monitor onshore stations (as the theodolite system does), the LORAN-C system does experience interferences in some geographic areas and is more appropriately used to reposition on a previously sampled station.

Microwave positioning systems are typically effective between 25 and 100 km offshore, depending on antenna heights and power outputs, and have accuracies of 1-3 m. Microwave systems consist of two or more slave shore stations positioned over known locations and a master receiver on the vessel. By accurately measuring the travel time of the microwaves between the two known shore points and the vessel receiver, the position of the vessel can be accurately determined. The shore stations, typically tripod-mounted antennas powered by 12-volt batteries, are very susceptible to vandalism.

The global positioning system (GPS) is another electronic system that can determine station positions by receiving digital codes from three or more satellite systems, computing time and distance, and then calculating an earth-based position. Two levels of positioning accuracy are achievable with the GPS system. The positional accuracy of standard GPS is approximately 50–100 m (U.S. EPA 1987b). The accuracy can be improved to between 0.5–5 m by differential GPS (U.S. EPA 1987b). In differential GPS, two receivers are used. The master receiver is placed on a known location. It's location is computed based on satellite data, and a correction is applied to account for the errors in

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position from the satellites. This correction is then sent via radio link or satellite to vessel-mounted receivers.

Hybrid Positioning Techniques

A number of hybrid positioning systems combine positional data from various sources to obtain fixes. Such systems usually involve the intersection of a visual line-of-position with an electronic line-of-position. Of particular interest to coastal monitoring programs are dynamic positioning systems that require only a single shore station and that use the simultaneous measurement of angle from a known direction and range to the survey vessel. These range-azimuth systems are characterized by their operating medium (optional, microwave, laser) and/or procedure (i.e. manual or automatic tracking).

2.5.6.2 Physical Conditions at the Study Site

The ability of a positioning method to achieve its highest projected accuracy depends, in part, on site-specific conditions. Weather, currents and other physical factors may reduce the achievable accuracy of a positioning method. For example, the relative drift of the sampling equipment away from the boat under strong currents or winds can increase with depth. Resulting positioning errors in sample location (as opposed to boat location) may exceed acceptable limits for the study if effects of site location on positioning accuracy are not considered during design of the sampling program.

2.5.6.3 Quality Assurance Considerations

Once the positioning method has been selected for the specific dredged material evaluation, the proper setup, calibration, and operational procedures must be followed to achieve the intended accuracy. At least one member of the field crew should be familiar with the selected positioning method.

Recordkeeping requirements should be established to ensure that station locations are accurately occupied and that adequate documentation is available. Adequate information to ensure consistent positioning and to allow reoccupation of stations for replicate sample collection or time-series monitoring should be kept in a field logbook. Entries should be initialed by the person entering the data. Required entries into the field logbook include the following:

- **Initial Survey Description**—The positioning method and equipment used, all changes or modifications to standard methods, names of persons who set up and operate the station positioning equipment, location of on-board equipment and the reference point (e.g., antennae, sighting position), the type of map used for

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positioning and its identification number or scale should be recorded in the field logbook. In addition, a complete copy of the survey notes (if appropriate) should be included in the field logbook.

- **Day Log Entries**—The same information that is included in the initial survey description is also recorded on a daily basis in the day log. In addition, all problems or irregularities, any weather or physical conditions that may affect achievable accuracy, and all calibration data should be recorded in the day log.

- **Station Log Entries**—Each station location should be recorded in the coordinates or readings of the method used for positioning in sufficient detail to allow reoccupation of the station in the future. The positioning information should be recorded at the time of sample collection (versus time of equipment deployment) and for every reoccupation of that station, even during consecutive replicate sampling. In addition, supplemental positioning information that would define the station location or help subsequent relocation (e.g., anchored, tied to northwest corner of pier, buoy) should be recorded. If photographs are to be used for *a posteriori* plotting of stations, the roll and frame numbers should be recorded. Depth, time (tidal height) ship heading, and wire angle estimation should also be recorded for each occupation of a station.

Sampling reports should include the type of positioning method used during data collection. Any specific problems (e.g., wind, currents, waves, visibility, electronic interferences) that resulted in positioning problems and those stations affected should be identified in the sampling report. Estimates of the accuracy achieved for station positioning should be included. Station locations should be reported in appropriate units (e.g., latitude and longitude to the nearest second). Coordinates do not need to be reported for each replicate collected; a single set of coordinates for the station is sufficient. Depth corrected to mean lower low water should also be supplied for each station.

2.5.7 Sample Collection Methods

Detailed procedures for performing all sampling and equipment decontamination should be clearly stated in the sampling plan and can be included as standard operating procedures (see Appendix D). Sample collection requires an experienced crew, an adequate vessel equipped with navigational and supporting equipment appropriate to the site and the study, and noncontaminating sampling apparatus capable of obtaining relatively undisturbed and representative samples. To assure sampling quality, at least one individual familiar with the study area should be present during the

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sampling activities. Sampling effort for a proposed dredging project is primarily oriented toward collection of sediment samples for physical and chemical characterization and for biological tests. Collection of water samples is also required to evaluate potential water column impact. Collection of organisms near the disposal site might be necessary if there is a need to characterize indigenous populations or to assess concentrations of contaminants in tissues. Organisms for use in toxicity and bioaccumulation tests may also be field-collected.

In general, a hierarchy for sample collection should be established to prevent contamination from the previous sample, especially when using the same sampling apparatus to collect samples for different analyses. Where possible, the known or expected least contaminated stations should be sampled first. At a station where water and sediment are to be collected, water samples should be collected prior to sediment samples. The vessel should ideally be positioned downwind or downcurrent of the sampling device. When lowering and retrieving sampling devices, care should be taken to avoid visible surface slicks and the vessel's exhaust. The deck and sample handling area should be kept clean to help reduce the possibility of contamination.

2.5.7.1 Sediment Sample Collection

Mudroch and MacKnight (1991) provide useful reference information for sediment sampling techniques. Higgins and Lee (1987) provide a perspective on sediment collection as commonly practiced by USACE. ASTM (1991b) and Burton (1991) provide guidelines for collecting sediments for toxicological testing. Guidance provided in these publications may be followed on all points that do not conflict with this document.

Care should be taken to avoid contamination of sediment samples during collection and handling. A detailed procedure for handling sampling equipment and sample containers should be clearly stated in the sampling plan associated with a specific project; this may be accomplished by using standard operating procedures. For example, samples designated for trace metal analysis should not come into contact with metal surfaces (except stainless steel, unless specifically prohibited for a project), and samples designated for organic analysis should not come into contact with plastic surfaces.

A coring device is recommended whenever sampling to depth is required. The choice of corer design depends on factors such as the objectives of the sampling program, sediment volumes required for testing, sediment characteristics, water depth, sediment depth, and currents or tides. A gravity corer may be limited to cores of 1–2 m in depth, depending on sediment grain size, degree of sediment compaction, and velocity of the drop. For penetration greater than 2 m, a vibratory corer or a piston corer is generally preferable. These types of coring devices are generally limited to soft, unconsolidated sediments. A split-spoon core may be used for more compacted sediment. The length of core that can be collected is usually limited to 10 core diameters in sand substrate and 20 core diameters in clay substrate. Longer cores can

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be obtained, but substantial sample disturbance results from internal friction between the sample and the core liner.

Gravity corers can cause compaction of the vertical structure of sediment samples, if they freefall into the sediment. Therefore, if the vertical stratification in a core sample is of interest, a piston corer or vibra corer should be used. The piston corer uses both gravity and hydrostatic pressure. As the cutting edge penetrates the sediments, an internal piston remains at the level of the sediment/water interface, preventing sediment compression and overcoming internal friction. The vibra corer is a more complex piece of equipment but is capable of obtaining 3- to 7-m cores in a wide range of sediment types by vibrating a large diameter core barrel through the sediment column with little compaction. If the samples will not be sectioned prior to analysis, compaction is not a problem, and noncontaminating gravity (freefall) corers may be the simplest alternative.

Corers are the samplers of preference in most cases because of the variation in contamination with depth that can occur in sediment deposits. Substantial variation with depth is less likely in shallow channel areas without major direct contaminant inputs that have frequent ship traffic and from which sediments are dredged at short intervals. Generally, in these situations, bottom sediments are frequently resuspended and mixed by ship scour and turbulence, effectively preventing stratification. In such cases, surface grab samples can be representative of the mixed sediment column, and corers should be necessary only if excavation of infrequently disturbed sediments below the mixed layer is planned. Grab samplers are also appropriate for collecting surficial samples of reference or control sediments.

Grab samplers and gravity corers can either be Teflon®-coated or be made of stainless steel to prevent potential contamination of trace metal samples. The sampling device should at least be rinsed with clean water between samples. More thorough cleaning will be required for certain analyses; for instance, analyses performed for chlorinated dioxins require that all equipment and sample containers be scrupulously cleaned with pesticide-grade solvents or better because of the low detection limits required for these compounds. It is recommended that a detailed standard operating procedure specifying all decontamination procedures be included in the project sampling plan.

2.5.7.2 Water Sample Collection

If water samples are necessary, they should be collected with either a noncontaminating pump or a discrete water sampler. When sampling with a pump, the potential for contamination can be minimized by using a peristaltic or a magnetically coupled impeller-design pump. These kinds of pumps provide barriers between the sample and the surfaces of the pump (e.g., motor or fan)

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that would cause contamination. The system should be flushed with the equivalent of 10 times the volume of the collection tubing. Also, any components within several meters of the sample intake should be noncontaminating (i.e., sheathed in polypropylene or epoxy-coated or made of Teflon®). Potential sample contamination must be avoided, including vessel emissions and other sampling apparatus.

A discrete water sampler should be of the close/open/close type so that only the target water sample comes into contact with internal sampler surfaces. Water samplers should be made of stainless steel or acrylic plastic. Seals should be Teflon®-coated whenever possible. Water sampling devices should be acid-rinsed (1:1 nitric acid) prior to use for collection of trace-metal samples, and solvent-rinsed (assuming the sampler material is compatible) prior to collection of samples for organic analyses.

2.5.7.3 Organism Collection

Collection methods for benthic organisms may be species-specific and can include, but are not limited to, bottom trawling, grabs, or cores. If organisms are to be maintained alive, they should be transferred immediately to containers with clean, well-oxygenated water, and sediment, as appropriate. Care must be taken to prevent organisms from coming into contact with natural predators and potentially contaminated areas or fuels, oils, natural rubber, trace metals, or other contaminants (U.S. EPA 1990a, 1992a).

2.5.8 Sample Handling, Preservation, and Storage

Detailed procedures for sampling handling, preservation, and storage should be part of the project-specific protocols and standard operating procedures specified for each sampling operation and included in the sampling plan. Samples are subject to chemical, biological, and physical changes as soon as they are collected. Sample handling, preservation, and storage techniques have to be designed to minimize any changes in composition of the sample by retarding chemical and/or biological activity and by avoiding contamination. Collection methods, volume requirements, container specifications, preservation techniques, storage conditions, and holding times (from the time of sample collection) for sediment, water, and tissue samples are discussed below and summarized in Table 5. Exceedance of the holding times presented in Table 5 would not necessarily result in qualification of the data during data validation. However, technical reasons justifying acceptance of data that exceed the holding time should be provided on a compound class basis.

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TABLE 5. SUMMARY OF RECOMMENDED PROCEDURES FOR SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Analyses	Collection Method[a]	Sample Volume[b]	Container[c]	Preservation Technique	Storage Conditions	Holding Times[d]
Sediment						
Chemical/Physical Analyses						
Metals	Grab/corer	100 g	Precleaned polyethylene jar[e]	Dry ice[e] or freezer storage for extended storages; otherwise refrigerate	≤ 4°C	Hg - 28 days Others - 6 months[f]
Organic compounds (e.g., PCBs, pesticides, polycyclic aromatic hydrocarbons)	Grab/corer	250 g	Solvent-rinsed glass jar with Teflon® lid[e]	Dry ice[e] or freezer storage for extended storage; otherwise refrigerate	≤ 4°C[e]/dark[f]	14 days[g]
Particle size	Grab/corer	100 g	Whirl-pac bag[e]	Refrigerate	< 4°C	Undetermined
Total organic carbon	Grab/corer	50 g	Heat treated glass vial with Teflon®-lined lid[e]	Dry ice[e] or freezer storage for extended storages; otherwise refrigerate	≤ 4°C[e]	14 days
Total solids/specific gravity	Grab/corer	50 g	Whirl-pac bag	Refrigerate	< 4°C	Undetermined
Miscellaneous	Grab/corer	≥ 50 g	Whirl-pac bag	Refrigerate	< 4°C	Undetermined
Sediment from which elutriate is prepared	Grab/corer	Depends on tests being performed	Glass with Teflon®-lined lid	Completely fill and refrigerate	4°C/dark/airtight	14 days
Biological Tests						
Dredged material	Grab/corer	12–15 L per sample	Plastic bag or container[h]	Completely fill and refrigerate; sieve	4°C/dark/airtight	14 days[i]
Reference sediment	Grab/corer	45–50 L per test	Plastic bag or container[h]	Completely fill and refrigerate; sieve	4°C/dark/airtight	14 days[i]
Control sediment	Grab/corer	21–25 L per test	Plastic bag or container[h]	Completely fill and refrigerate; sieve	4°C/dark/airtight	14 days[i]

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TABLE 5. (cont.)

Analyses	Collection Method[a]	Sample Volume[b]	Container[c]	Preservation Technique	Storage Conditions	Holding Times[d]
Water and Elutriate						
Chemical/Physical Analyses						
Particulate analysis	Discrete sampler or pump	500–2,000 mL	Plastic or glass	Lugols solution and refrigerate	4°C	Undetermined
Metals	Discrete sampler or pump	1 L	Acid-rinsed polyethylene or glass jar[i]	pH < 2 with HNO_3; refrigerate[j]	4°C 2°C[j]	Hg - 14 days Others - 6 months[k]
Total Kjeldahl nitrogen	Discrete sampler or pump	100–200 mL	Plastic or glass[k]	H_2SO_4 to pH < 2; refrigerate	4°C[k]	24 h[k]
Chemical oxygen demand	Discrete sampler or pump	200 mL	Plastic or glass[k]	H_2SO_4 to pH < 2; refrigerate	4°C[k]	7 days[k]
Total organic carbon	Discrete sampler or pump	100 mL	Plastic or glass[k]	H_2SO_4 to pH < 2; refrigerate	4°C[k]	<48 hours[k]
Total inorganic carbon	Discrete sampler or pump	100 mL	Plastic or glass[k]	Airtight seal; refrigerate[k]	4°C[k]	6 months[k]
Phenolic compounds	Discrete sampler or pump	1 L	Glass[k]	0.1–1.0 g $CuSO_4$; H_2SO_4 to pH < 2; refrigerate	4°C[k]	24 hours[k]
Soluble reactive phosphates	Discrete sampler or pump	--	Plastic or glass[k]	Filter; refrigerate[k]	4°C[k]	24 hours[k]
Extractable organic compounds (e.g., semi-volatile compounds)	Discrete sampler or pump	4 L	Amber glass bottle[j]	pH < 2, 6N HCl; airtight seal; refrigerate	4°C[j]	7 days for extraction; 40 days for sample extract analyses[j]
Volatile organic compounds	Discrete sampler or pump	80 mL	Glass vial[j]	pH < 2 with 1:1 HCL; refrigerate in airtight, completely filled container[j]	4°C[j]	14 days for sample analysis, if preserved[j]
Total phosphorus	Discrete sampler or pump	--	Plastic or glass[h]	H_2SO_4 to pH < 2; refrigerate	4°C[k]	7 days[k]

TABLE 5. (cont.)

Analyses	Collection Method[a]	Sample Volume[b]	Container[c]	Preservation Technique	Storage Conditions	Holding Times[d]
Total solids	Discrete sampler or pump	200 mL	Plastic or glass[k]	Refrigerate	4°C[k]	7 days[k]
Volatile solids	Discrete sampler or pump	200 mL	Plastic or glass[k]	Refrigerate	4°C[k]	7 days[k]
Sulfides	Discrete sampler or pump	--	Plastic or glass[k]	pH > 9 NaOH (ZnAc); refrigerate[k]	4°C[k]	24 hours[k]
Biological Tests						
Site water	Grab	Depends on tests being performed	Plastic carboy	Refrigerate	< 4°C	14 days
Dilution water	Grab or makeup	Depends on tests being performed	Plastic carboy	Refrigerate	< 4°C	14 days
Tissue						
Metals	Trawl/Teflon®-coated grab	5–10 g	Double Ziploc®[e]	Handle with non-metallic forceps; plastic gloves; dry ice[e]	≤ −20°C[e] or freezer storage	Hg - 28 days Others - 6 months[m]
PCBs and chlorinated pesticides	Trawl/Teflon®-coated grab	10–25 g	Hexane-rinsed double aluminum foil and double Ziploc®[e]	Handle with hexane-rinsed stainless steel forceps; dry ice[e]	≤ −20°C[e] or freezer storage	14 days[g]
Volatile organic compounds	Trawl/Teflon®-coated grab	10–25 g	Heat-cleaned aluminum foil and water-tight plastic bag[l]	Covered ice chest[l]	≤ −20°C[m] or freezer storage	14 days[m]
Semivolatile organic compounds	Trawl/Teflon®-coated grab	10–25 g	Hexane-rinsed double aluminum foil and double Ziploc®[e]	Handle with hexane-rinsed stainless steel forceps; dry ice[e]	≤ −20°C[e] or freezer storage	14 days[g]
Lipids	Trawl/Teflon®-coated grab	Part of organic analyses	Hexane-rinsed aluminum foil	Handle with hexane-rinsed stainless steel forceps; quick freeze	≤ −20°C or freezer storage	14 days[g]

Note: This table contains only a summary of collection, preservation, and storage procedures for samples. The cited references should be consulted for a more detailed description of these procedures.

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TABLE 5. (cont.)

PCB - polychlorinated biphenyl

[a] Collection method should include appropriate liners.

[b] Amount of sample required by the laboratory to perform the analysis (wet weight or volume provided, as appropriate). Miscellaneous sample size for sediment should be increased if auxiliary analytes that cannot be included as part of the organic or metal analyses are added to the list. The amounts shown are not intended as firm values; more or less tissue may be required depending on the analytes, matrices, detection limits, and particular analytical laboratory.

[c] All containers should be certified as clean according to U.S. EPA (1990c).

[d] These holding times are for sediment, water, and tissue based on guidance that is sometimes administrative rather than technical in nature. There are no promulgated, scientifically based holding time criteria for sediments, tissues, or elutriates. References should be consulted if holding times for sample extracts are desired. Holding times are from the time of sample collection.

[e] NOAA (1989).

[f] Tetra Tech (1986a).

[g] Sample may be held for up to 1 year if ≤ -20°C.

[h] Polypropylene should be used if phthalate bioaccumulation is of concern.

[i] Two weeks is recommended; sediments must not be held for longer than 8 weeks prior to biological testing.

[j] U.S. EPA (1987a); 40 CFR Part 136, Table III.

[k] Plumb (1981).

[l] If samples are not preserved to pH < 2, then aromatic compounds must be analyzed within 7 days.

[m] Tetra Tech (1986b).

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2.5.8.1 Sample Handling

Sufficient sample volume should be collected to:

- Perform the necessary analyses
- Partition the samples, either in the field or as soon as possible after sampling, for respective storage and analytical requirements (e.g., freezing for trace metal analysis or refrigeration for bioassays)
- Archive portions of the sample for possible later analysis.
- Provide sample for replicate or QA analyses, if specified.

Sample handling is project- and analysis-specific, as well as being based on what is practical and possible. Generally, samples to be analyzed for trace metals should not come into contact with metals, and samples to be analyzed for organic compounds should not come into contact with plastics. All sample containers should be scrupulously cleaned (acid-rinsed for analysis of metals, solvent-rinsed for analysis of organic compounds).

For analysis of volatile compounds, samples should completely fill the storage container, leaving no airspace. These samples should be refrigerated but never frozen or the containers will crack. Samples for other kinds of chemical analysis are sometimes frozen. Only wide-mouth ("squat") jars should be used for frozen samples; narrow-mouth jars are less resistant to cracking. If the sample is to be frozen, sufficient air space should be left to allow expansion to take place (i.e., the wide-mouth sample container should be filled to no more than the shoulder of the bottle [just below the neck of the bottle] and the container should be frozen at an angle). Container labels have to withstand soaking, drying, and freezing without becoming detached or illegible. The labeling system should be tested prior to use in the field.

Sediment samples for biological testing should have larger (possible predatory) animals removed from the sediment by screening or press sieving prior to testing. Other matter retained on the screen with the organisms, such as shell fragments, gravel, and debris, should be recorded and discarded. Prior to use in bioassays, individual test sediments should be thoroughly homogenized with clean instruments (until color and textural homogeneity is achieved).

2.5.8.2 Sample Preservation

Preservation steps should be taken immediately upon sediment collection. There is no universal preservation or storage technique, although storage in the dark at 4°C is generally used for all samples held for any length of time prior to processing, and for some samples after processing. A technique for one group

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of analyses may interfere with other analyses. This problem can be overcome by collecting sufficient sample volume to use specific preservation or storage techniques for specific analytes or tests. Preservation, whether by refrigeration, freezing, or addition of chemicals, should be accomplished as soon as possible after collection, onboard the collecting vessel whenever possible. If final preservation techniques cannot be implemented in the field, the sample should be temporarily preserved in a manner that retains its integrity.

Onboard refrigeration is easily accomplished with coolers and ice; however, samples should be segregated from melting ice and cooling water. Sediment samples that are to be frozen on board may be stored in an onboard freezer or may simply be placed in a cooler with dry ice or blue ice. Sample containers to be frozen (wide-mouth jars; see Section 2.5.7.1) should not be filled completely because expansion of the sample could cause the container to break. Sediment samples for biological analysis should be preserved at 4°C, never frozen or dried. Additional guidance on sample preservation is given in Table 5.

2.5.8.3 Sample Storage

The elapsed time between sample collection and analysis should be as short as possible. Sample holding times for chemical evaluations are analysis-specific (Table 5). Sediments for bioassay (toxicity and/or bioaccumulation) testing should be tested as soon as possible, preferably within 2 weeks of collection. Sediment toxicity does change with time. Studies to date suggest that sediment storage time should never exceed 8 weeks (at 4°C, in the dark, excluding air) (Becker and Ginn 1990; Tatem et al. 1991) because toxicity may change with storage time. Sample storage conditions (e.g., temperature, location of samples) should be documented.

2.5.9 Logistical Considerations and Safety Precautions

A number of frustrations in sample collection and handling can be minimized by carefully thinking through the process and requirements before going to the field. Contingency plans are essential. Well-trained, qualified, and experienced field crews should be used. Backup equipment and sampling gear, and appropriate repair parts, are advisable. A surplus of sampling containers and field data sheets should be available. Sufficient ice and adequate ice chest capacity should be provided, and the necessity of replenishing ice before reaching the laboratory should be considered. A vessel with adequate deck space is safer and allows for more efficient work than an overcrowded vessel. Unforeseeable circumstances (e.g., weather delays) are to be expected during field sampling, and time to adequately accommodate the unforeseen has to be included in sampling schedules.

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Appropriate safety and health precautions must be observed during field sampling and sample processing activities. The EPA *Standard Operating Safety Guides* (U.S. EPA 1984b) should be used as a guidance document to prepare a site-specific health and safety plan. The health and safety plan should be prepared as a separate document from the QA project plan. Requirements implementing the Occupational Safety and Health Act at 29 CFR §1910.120 (Federal Register, Vol. 54, No. 43) should be met for medical surveillance, personal protection, respirator fit testing (if applicable), and hazardous waste operations training (if applicable) by all personnel working in contaminated areas or working with contaminated media.

The procedures and practices established in the site-specific health and safety plan should be observed by all individuals participating in the field activities. Safety requirements should also be met by all observers present during field audits and inspections. The plan should include the following information:

- Site location and history
- Scope of work
- Site control
- Hazard assessment (chemical and physical hazards)
- Levels of protection and required safety equipment
- Field monitoring requirements
- Decontamination
- Training and medical monitoring requirements
- Emergency planning and emergency contacts.

2.6 SAMPLE CUSTODY

Recordkeeping procedures are described in detail in this section of the QA project plan, including specific procedures to document the physical possession and condition of samples during their transport and storage. This section also describes how excess or used samples will be disposed of at the end of the project.

2.6.1 Sample Custody and Documentation

Sample custody and documentation are vital components of all dredged material evaluations, particularly if any of the data may be used in a court of law. It is important to record all events associated with a sample so that the validity of the resulting data may be properly interpreted. Thorough

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documentation provides a means to track samples from the field through the laboratory and prevent sample loss. The contents and location of all documents related to dredged sediment samples should be specified, and access to the samples should be controlled.

The possession of samples should be documented from sample collection through laboratory analysis. Recording basic information during sample handling is good scientific practice even if formal custody procedures are not required. Sample custody procedures, including examples of forms to be used, should be described in the QA project plan. Minimum requirements for documentation of sample handling and custody on simple projects should include the following information:

- Sample location, project name, and unique sample number
- Sample collection date (and time if more than one sample may be collected at a location in a day)
- Any special notations on sample characteristics or problems
- Initials of the person collecting the sample
- Date sample sent to the laboratory
- Conditions under which the samples were sent to the laboratory.

For large or sensitive projects that may result in enforcement actions or other litigation, a strict system for tracking sample custody should be used to assure that one individual has responsibility for a set of samples at all times. For these projects, only data that have clear documentation of custody can be accepted without qualification.

A strict system of sample custody implies the following conditions:

- The sample is possessed by an individual and secured so that no one can tamper with it
- The location and condition of the sample is known and documented at all times
- Access to the sample is restricted to authorized personnel only.

Where samples may be needed for potential litigation, chain-of-custody procedures should be followed. Chain-of-custody procedures are initiated during sample collection. Chain-of-custody forms are often used to document the transfer of a sample from collection to receipt by the laboratory (or between different facilities of one laboratory). Although not always required, these forms provide an easy means of recording information that may be useful weeks or months after sample collection. When these forms are used, they are provided

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to field technicians at the beginning of a project. The completed forms accompany the samples to the laboratory and are signed by the relinquisher and receiver every time the samples change hands. After sample analysis, the original chain-of-custody form is returned by the laboratory. The form is filed and becomes part of the permanent project documentation. An example of a chain-of-custody form is provided in Appendix A. Additional custody requirements for field and laboratory operations should be described in the QA project plan, when appropriate.

When in doubt about the level of documentation required for sampling and analysis, a strict system of documentation using standard forms should be used. Excess documentation can be discarded; lack of adequate documentation in even simple projects sometimes creates the unfortunate impression that otherwise reasonable data are unusable or limited. Formal chain-of-custody procedures are outlined briefly in the statements of work for laboratories conducting analyses of organic and inorganic contaminants under EPA's Contract Laboratory Program (CLP) (U.S. EPA 1990d,e).

2.6.1.1 Field Operations

The potential for sample deterioration and/or contamination exists during sample collection, handling, preservation, and storage. Approved protocols and standard operating procedures should be followed to ensure all field sampling equipment is acceptably calibrated and to prevent deterioration or contamination. Experienced personnel should be responsible for maintaining the sample integrity from collection through analysis, and field operations should be overseen by the project manager. A complete record of all field procedures, an inventory log, and a tracking log should be maintained. A field tracking report (see example in Appendix A) should identify sample custody and conditions in the field prior to shipment.

Dates and times of collection, station locations, sampling methods, and sample handling, preservation, and storage procedures should be documented immediately, legibly, and indelibly so that they are easily traceable. Any circumstances potentially affecting sampling procedures should be documented. The data recorded should be thorough enough to allow station relocation and sample tracking. An example of a station location log is provided in Appendix A. Any field preparation of samples should also be described. In addition, any required calibration performed for field instruments should be documented in the field logbook. Samples should be identified with a previously prepared label (see example in Appendix A) containing at least the following information:

- Project title
- Sample identification number

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- Location (station number) and depth
- Analysis or test to be performed
- Preservation and storage method
- Date and time of collection
- Special remarks if appropriate
- Initials of person collecting the sample
- Name of company performing the work.

2.6.1.2 Laboratory Operations

Documentation is necessary in the laboratory where chemical and biological analyses are performed. A strict system of sample custody for laboratory operations should include the following items:

- Appointment of a sample custodian, authorized to check the condition of and sign for incoming field samples, obtain documents of shipment, and verify sample custody records
- Separate custody procedures for sample handling, storage, and disbursement for analysis in the laboratory
- A sample custody log consisting of serially numbered, standard laboratory tracking report sheets.

A laboratory tracking report (Appendix A) should be prepared for each sample. The location of samples processed through chain-of-custody must be known at all times. Samples to be used in a court of law must be stored in a locked facility to prevent tampering or alteration.

A procedure should be established for the retention of all field and laboratory records and samples as various tasks or phases are completed. Replicates, subsamples of analyzed samples, or extra unanalyzed samples should be kept in a storage bank. These samples can be used to scrutinize anomalous results or for supplemental analyses, if additional information is needed. All samples should be properly stored and inventoried. The retention and archiving procedure should indicate the storage requirements, location, indexing codes, retention time, and security requirements for samples and data.

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2.6.2 Storage and Disposal of Samples

In the statement of work, the laboratory should be instructed to retain all remaining sample material (under appropriate temperature and light conditions) at least until after the QA review has been completed. In addition, sample extracts or digestates should be appropriately stored until disposal is approved by the project manager. With proper notice, most laboratories are willing to provide storage for a reasonable time period (usually on the order of weeks) following analysis. However, because of limited space at the laboratory, the project manager may need to make arrangements for long-term storage at another facility.

Samples must be properly disposed when no longer needed. Ordinary sample-disposal methods are usually acceptable, and special precautions are seldom appropriate. Under Federal law [40 CFR 261.5(a)], where highly contaminated wastes are involved, if the waste generated is less than 100 Kg per month, the generator is conditionally exempt as a small-quantity generator and may accumulate up to 1,000 Kg of waste on the property without being subject to the requirements of Federal hazardous waste regulations. However, State and local regulations may require special handling and disposal of contaminated samples. When samples have to be shipped, 49 CFR 100-177 should be consulted for current Department of Transportation regulations on packing and shipping.

Over the last few years, there has been a growing awareness of the ecological and economic damage caused by introduced species. Because both east and west coast species are often used in bioaccumulation tests, there is a real potential of introducing bioaccumulation test species or associated fauna and flora (e.g., pathogens, algae used in transporting the worms). It is the responsibility of the persons conducting the bioaccumulation or toxicity tests to assure that no non-indigenous species are released. The general procedures to contain non-indigenous species are to collect and then poison all water, sediment, organisms and associated packing materials (e.g., algae, sediment) before disposal. Chlorine bleach can be used as the poison. A double containment system is used to keep any spillage from going down the drain. Guidance on procedures used in toxicity tests can be found in Appendix B of DeWitt et al. (1992a). Flow-through tests can generate large quantities of water, and researchers should plan on having sufficient storage facilities.

2.7 CALIBRATION PROCEDURES AND FREQUENCY

Procedures for minimizing bias and properly maintaining the precision of each piece of equipment to be used in the field or laboratory are detailed in this section of the QA project plan. Procedures are also described for obtaining, using, and storing chemical standards of known purity used to quantify

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analytical results, and reference chemicals used as positive controls in toxicity tests. Instruments that require routine calibration include, for example, navigation devices, analytical balances, and water quality meters.

Calibration of analytical instruments is a high priority and is always required for any project requiring quantitative data (even if only estimated quantities are necessary). Calibration is essential because it is the means by which instrument responses are properly translated into chemical concentrations. Instrument calibration is performed before sample analysis begins and is continued during sample analysis at intervals specified in each analytical method to ensure that the data quality objectives established for a project are met.

Because there are several analytical techniques that can be used for the same target analyte, each of which may provide different guidance for performing instrument calibration, it is important to establish a minimum calibration procedure for any chemical analysis that will be performed. Uniform adherence to a minimum calibration procedure will also improve the comparability of data generated by multiple laboratories that may be used for a specific project or among projects. All requirements for performing instrument calibrations should be clearly stated in the QA project plan and the laboratory statement of work prepared for any project.

In addition to performing instrument calibrations, the acceptability of the calibrations performed should be evaluated. To provide control over the calibration process, specific guidelines should be specified. The basic elements of the calibration process include the calibration frequency, number of calibration standards and their concentrations, and the calibration acceptance criteria. A summary of these elements is provided below.
Examples of the differences in calibration procedures (specifically for the analysis of organic compounds) for different analytical methods are provided in Table 6.

2.7.1 Calibration Frequency

The general process of verifying that an instrument is functioning acceptably is to perform initial and continuing calibrations. Initial calibration should be performed prior to sample analysis to determine whether the response of the instrument is linear across a range of target analyte concentrations (i.e., the working linear range). In addition to establishing the initial calibration for an instrument, it is critical that the stability of the instrument response be verified during the course of ongoing sample analyses. The verification of instrument stability is assessed by analyzing continuing calibration standards at regular intervals during the period that sample analyses are performed. Although each analytical method provides guidance for the frequency at which continuing

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TABLE 6. EXAMPLE CALIBRATION PROCEDURES

Calibration Criteria	SW-846 Methods for Organic Compounds[a]	EPA CLP Methods for Organic Compounds[b]
Number of standards for initial calibration	Minimum of five for all methods	Five for all GC/MS analyses Three for pesticides One for PCBs and multicomponent pesticides
Concentration of lowest initial calibration standard	All target analytes near, but above, the TDL	Contractually set (e.g., 10 µg/L for volatile organic compounds)
Concentrations for initial calibration to establish the instrument's working linear range	1. Bracket the expected concentration range of analytes expected in samples 2. Bracket the full instrument/detector linear range	Contractually set (e.g., 10, 50, 100, 150, and 200 µg/L for volatile organic compounds)
Concentration of continuing calibration standards	Not specified, except for GC/MS methods	Contractually set (e.g., 50 µg/L for all GC/MS analyses)
Frequency of calibrations	Repeat when acceptance criteria not met	Repeat when acceptance criteria not met
Acceptance criteria for initial calibration[c]	Calculate analyte RRFs or RFs, then RSD should be ≤ 30 percent for GC/MS methods and ≤ 20 percent for all other methods Alternative: generate a least squares linear regression (peak height/area vs. concentration) and use equation to calculate sample results	Calculate analyte RRFs or RFs, then RSD should be ≤ 30 percent for GC/MS methods and ≤ 20 percent for pesticides Alternative: none
Acceptance criteria for continuing calibration[c]	Calculate analyte RRFs or RFs, then difference to mean RRF or RF of initial calibration should be ≤ 25 percent for GC/MS methods and ≤ 15 percent for all other methods Alternative: none	Calculate analyte RRFs or RFs, then difference to mean RRF or RF of initial calibration should be ≤ 25 percent for GC/MS methods and ≤ 15 percent for pesticides Alternative: none

Note:
CLP - Contract Laboratory Program
GC/MS - gas chromatography/mass spectrometry
PCB - polychlorinated biphenyl
RF - response factor (i.e., calibration factor)
RRF - relative response factor
RSD - relative standard deviation
TDL - target detection limit

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TABLE 6. (cont.)

[a] U.S. EPA (1986a).

[b] U.S. EPA (1990b).

[c] The acceptance criteria for instrument calibration (i.e., initial and continuing calibration) may not be available for all organic compounds listed in Table 3 (e.g., resin acids and guaiacols). The determination of acceptable instrument calibration criteria for organic compounds not specifically stipulated in SW-846 or EPA CLP methods should be assessed using best professional judgment (e.g., ≤ 50 percent RSD).

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calibration standards should be performed, it is recommended that at a minimum these standards be analyzed at the beginning of each analytical for table 6 sequence, after every tenth sample, and at the end of the analytical sequence for all organic and inorganic compound analyses performed. The concentration of the continuing calibration standard should be equivalent to the concentration of the midpoint established during initial calibration of the working linear range of the instrument.

2.7.2 Number of Calibration Standards

Specific instrument calibration procedures are provided in most analytical methods; however, a wide variation exists in the number of calibration standards specified for different analyses. To ensure that consistent and reliable data are generated, a minimum number of calibration standards should be required for all laboratories performing chemical analyses.

Typically, as the number of calibration standards increases, the reliability of the results increases for concentrations detected above the TDL. The specific standards that are selected for calibration can have a significant impact on the validity of the data generated. Calibration standards should be established with respect to the range of standards required, the TDLs selected, and the linear range of the target analytes desired. Specific requirements for establishing the number of calibration standards, including recommendations on the concentrations to use, will be different for organic and inorganic analyses; however, some general recommended guidelines are provided below.

The working linear range of an instrument should be established prior to performing sample analyses. A minimum of five calibration standards for the analysis of organic compounds and three calibration standards for the analysis of inorganic compounds should be used when establishing the working linear range for all target analytes of concern. Generally, the working linear range of an instrument for a specific analysis should bracket the expected concentrations of the target analyte in the samples to be analyzed. In some instances, however, it may not be known what analyte concentrations to expect. A 5-point initial calibration sequence is recommended to establish the working linear range for organic chemical analyses.

In addition to the number of standards analyzed, the difference between the concentration of the lowest standard and the TDL and the difference between each standard used to establish the initial calibration are critical. The selection of the lowest initial calibration standard concentration will provide more confidence in the documented bias of results reported as undetected at the TDL or any results reported at very low concentrations. The selection of this standard will also ensure that target analytes can be reliably detected above instrument background noise and potential matrix interferences. For the

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dredged material program, this standard should be no lower than the TDL provided in Table 3.

The decision as to which specific concentrations (i.e., calibration range) should be used for a multipoint calibration requires careful consideration. While methods established by EPA CLP protocols provide stringent requirements for calibration analyses, these requirements are not clearly specified for other analytical methods (e.g., SW-846 methods) (see Table 6). A 5-point initial calibration sequence is recommended for all non-CLP methods. The concentrations of all standards should range from the lowest concentration meeting the requirements suggested above to the highest standard concentration equivalent to the upper linear range of the instrument/detector configuration. The concentrations of the remaining three standards should be evenly distributed between these concentrations. The calibration standards used to establish the working linear range should encompass a factor of 20 (i.e., 1 to 20, with the lowest concentration equal to 1 and the highest concentration equal to 20 times the concentration of the lowest concentration used).

2.7.3 Calibration Acceptance Criteria

Once the initial calibration has been performed, the acceptability of the calibration should be assessed to ensure that the bias of the data generated will be acceptable; this assessment should be performed by all laboratories prior to the analysis of any sample. In addition, the acceptability of all continuing calibrations should be assessed.

Although each analytical method provides guidance for determining the acceptability of instrument calibrations, there are multiple options available (e.g., least squares linear regression, percent relative standard deviations, and percent differences). A specific set of acceptance criteria should be determined prior to sample analysis, and these criteria should be contractually binding to avoid unnecessary qualification or rejection of the data generated. A summary of the most widely used calibration acceptance criteria currently in use for organic analyses is provided in Table 6. Calibration acceptance criteria should be used to assess the acceptability of the initial calibration sequence in terms of the relationship between the intercept of the calibration curve (i.e., the x-y intercept) and the predetermined TDLs and the overall reliability of the working linear range established.

The general criteria specified by SW-846 methods are typically more stringent for organic analyses than the EPA CLP requirements. Acceptance criteria, as summarized in Table 6, should be clearly defined before sample analyses are performed. All specific acceptance criteria for calibrations should be stated in the QA project plan and the laboratory statement of work.

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2.8 ANALYTICAL PROCEDURES

The methods cited in this section may be used to meet general data quality objectives for dredged material evaluations. However, other methods may provide similar results, and the final choice of analytical procedures should be based on the needs of each evaluation. In all cases, proven, current methods should be used; EPA-approved methods, if available, are preferred. Sample analysis procedures are identified in this section by reference to established, standard methods. Any modifications to these procedures and any specialized, nonstandard procedures are also described in detail. When preparing a QA project plan, only modifications to standard operating procedures or details of non-standard procedures need to be described in this section of the plan.

Any dredged material from estuarine or marine areas contains salt, which can interfere with the results obtained from some analytical methods. Any methods proposed for the analysis of sediment and water from estuarine or marine environments should explicitly address steps taken to control salt interference.

The following sections provide guidance on the selection of physical and chemical analyses to aid in evaluating dredged material proposed for disposal, and on the methods used to analyze these parameters. Information on the chemicals on the EPA priority pollutant and hazardous substance lists is provided in Appendix E.

2.8.1 Physical Analysis of Sediment

Physical characteristics of the dredged material must be determined to help assess the impact of disposal on the benthic environment and the water column and to help determine the appropriate dredging methods. This is the first step in the overall process of sediment characterization, and also helps to identify appropriate control and reference sediments for biological tests. In addition, physical analyses can be helpful in evaluating the results of analyses and tests conducted later in the characterization process.

The general analyses may include grain size distribution, total solids content, and specific gravity. Grain size analysis defines the frequency distribution of the size ranges of the particles that make up the sediment (e.g., Plumb 1981; Folk 1980). The general size classes of gravel, sand, silt, and clay are the most useful in describing the size distribution of particles in dredged material samples. Use of the Unified Soil Classification System (USCS) for physical characterization is recommended for the purpose of consistency with USACE engineering evaluations (ASTM 1992).

Measurement of total solids is a gravimetric determination of the organic and inorganic material remaining in a sample after it has been dried at a specified

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temperature. The total solids values generally are used to convert concentrations of contaminants from a wet-weight to a dry-weight basis.

The specific gravity of a sample is the ratio of the mass of a given volume of material to an equal volume of distilled water at the same temperature (Plumb 1981). The specific gravity of a dredged material sample helps to predict the behavior (i.e., dispersal and settling characteristics) of dredged material after disposal.

Other physical/engineering properties (e.g., Atterburg limits, settling properties) may be needed to evaluate the quality of any effluent discharged from confined disposal facilities. QA considerations for physical analysis of sediments are summarized in Section 2.10.3.

2.8.2 Chemical Analysis of Sediment

Chemical analysis provides information about the chemicals present in the dredged material that, if biologically available, could cause toxicity and/or be bioaccumulated. This information is valuable for exposure assessment and for deciding which of the contaminants present in the dredged material to measure in tissue samples. This section discusses the selection of target analytes and techniques for sediment analyses. QA considerations are summarized in Section 2.10.4.

2.8.2.1 Selection of Target Analytes

If the review of data from previous studies suggests that sediment contaminants may be present (see Section 2.5.2), but fails to produce sufficient information to develop a definitive list of potential contaminants, a list of target analytes should be compiled. Target analytes should be selected from, but not necessarily limited to, those listed in Table 3. The target analyte list should also include other contaminants that historical information or commercial and/or agricultural applications suggest could be present at a specific dredging site (e.g., tributyltin near shipyards, berthing areas, and marinas where these compounds have been applied). Analysis of polycyclic aromatic hydrocarbons (PAHs) in dredged material should focus on those PAH compounds listed in Table 3.

All PCB analyses should be made using congener-specific methods. The sum of the concentrations of specific congeners is an appropriate measure of total PCBs (NOAA, 1989). Congener-specific analyses also provide data that can be used for specialized risk assessments that reflect the widely varying toxicity of different PCB congeners.

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Sediments should be analyzed for TOC. This is particularly important if there are hydrophobic organic compounds on the target analyte list. The TOC content of sediment is a measure of the total amount of oxidizable organic material in a sample and also affects contaminant bioaccumulation by, and effects to, organisms (e.g., DeWitt et al. 1992b; Di Toro et al. 1991).

Sediments in which metals are suspected to be contaminants of concern may also be analyzed for acid volatile sulfide (AVS) (Di Toro et al. 1990; U.S. EPA 1991a). Although acceptable guidance on the interpretation of AVS measurements is not yet available, and AVS measurements are not generally required at this time, such measurements can provide information on the bioavailability of metals in anoxic sediments.

2.8.2.2 Selection of Analytical Techniques

Once the list of project-specific target analytes for sediments has been established, appropriate analytical methods should be determined (see Section 2.3). The analytical methods selected must be able to meet the TDLs established to meet the requirements of the intended uses of the data. Also, the methods selected will, to some degree, dictate the amount of sediment sample required for each analysis. Examples of methods that can be used to meet TDLs for dredged material evaluations are provided in Table 3. General sample sizes are provided in Table 5, and include possible requirements for more than one analysis for each group of analytes. The amount of sample used in an analysis affects the detection limits attainable by a particular method. The following overview summarizes various factors to be considered when selecting analytical methods for physical, inorganic, and organic analyses.

TOC analyses should be based on high-temperature combustion rather than on chemical oxidation, because some classes of organic compounds are not fully degraded by chemical/ultraviolet techniques. The volatile and nonvolatile organic components make up the TOC of a sample. Because inorganic carbon (e.g., carbonates and bicarbonates) can be a significant proportion of the total carbon in some sediment, the sample has to be treated with acid to remove the inorganic carbon prior to TOC analysis. The method of Plumb (1981) recommends the use of hydrochloric acid. An alternative choice might be sulfuric acid because it is nonvolatile, is used as the preservative, and does not add to the chloride burden of the sample. However, some functional groups (e.g., carboxylic acids) can be oxidized when inorganic carbonates are removed using both a non-oxidizing and an oxidizing acid. Whatever acid is used, it has to be demonstrated on sodium chloride blanks (for all marine samples) that there is no interference generated from the combined action of acid and salt in the sample. Acceptable methods for TOC analysis are provided in PSEP (1986) and U.S. EPA (1992b).

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For many metals analyses in marine/estuarine areas, the concentration of salt may be much greater than the concentration of the analyte of interest, and can cause unacceptable interferences in certain analytical techniques. In such cases, the freshwater approach of acid digestion followed by inductively coupled plasma-atomic emission spectrometry (ICP) or graphite furnace atomic absorption spectrometry (GFAA) should be coupled with appropriate techniques for controlling this interference. For example, the mercury method in U.S. EPA (1986a; Method 7471) may be used for the analysis of mercury in sediment. Tributyltin may be analyzed by the methods of Rice et al. (1987) and NCASI (1986), and selenium and arsenic by the method of EPRI (1986). Total digestion of metals is not necessary for dredged material evaluations, although this technique is used for complete chemical characterizations in some national programs (e.g., NOAA Status and Trends). The standard aqua regia extraction yields consistent and reproducible results. The recommended method for analysis of semivolatile and volatile priority pollutants in sediments is described in Tetra Tech (1986a), and is a modified version of established EPA analytical methods designed to achieve lower and more reliable detection limits. Analysis for organic compounds should always use capillary-column gas chromatography (GC): gas chromatography/mass spectrometry (GC/MS) techniques for semivolatile and volatile priority pollutants, and dual column gas chromatography/electron-capture detection (GC/ECD) for pesticides and PCBs (NOAA 1989). Alternatively, GC/MS using selected ion monitoring can be used for PCB and pesticide analysis. These analytically sound techniques yield accurate data on the concentrations of chemicals in the sediment matrix. The analytical techniques for semivolatile organic compounds generally involve solvent extraction from the sediment matrix and subsequent analysis, after cleanup, using GC or GC/MS. Extensive cleanup is necessitated by the likelihood of 1) biological macromolecules, 2) sulfur from sediments with low or no oxygen, and 3) oil and/or grease in the sediment. The analysis of volatile organic compounds incorporates purge-and-trap techniques with analysis by either GC or GC/MS. If dioxin (i.e., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [TCDD]) analysis is being performed, the methods of Kuehl et al. (1987), Smith et al. (1984), U.S. EPA (1989b; Method 8290), or U.S. EPA (1990f; Method 1613) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa- polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This method has been developed for analysis of water, soil, sediment, sludge, and tissue. Table 7 shows the 17 compounds determined by Method 1613.

Techniques for analysis of chemical contaminants have some inherent limitations for sediment samples. Interferences encountered as part of the sediment matrix, particularly in samples from heavily contaminated areas, may limit the ability of a method to detect or quantify some analytes. The most selective methods using GC/MS techniques are recommended for all nonchlorinated organic compounds because such analysis can often avoid

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TABLE 7. PCDD and PCDF Compounds Determined by Method 1613

Native Compound[1]
2,3,7,8-TCDF
2,3,7,8-TCDD
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,6,7,8-HpCDD
1,2,3,4,7,8,9-HpCDF
OCDD
OCDF

[1] Polychlorinated Dioxins and Furans

TCDD = Tetrachlorodibenzp-p-dioxin
TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-p-dioxin
PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-p-dioxin
HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-p-dioxin
HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-p-dioxin
OCDF = Octachlorodibenzofuran

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problems due to matrix interferences. GC/ECD methods are recommended by the EPA as the primary analytical tool for all PCB and pesticide analyses because GC/ECD analysis (e.g., NOAA 1989) will result in lower detection limits. The analysis and identification of PCBs by GC/ECD methods are based upon relative retention times and peak shapes. Matrix interferences may result in the reporting of false negatives, although the congener-specific PCB analysis reduces this concern relative to use of the historical Aroclor®-matching procedure.

For dredged material evaluations, the concentration of total PCBs should be determined by summing the concentrations of specific individual PCB congeners identified in the sample (see Table 8). The minimum number of PCB congeners that should be analyzed are listed in the first column of Table 7 (i.e., "summation" column) (NOAA 1989). This summation is considered the most accurate representation of the PCB concentration in samples. Additional PCB congeners are also listed in Table 8. McFarland and Clarke (1989) recommend these PCB congeners for analysis based on environmental abundance, persistence, and biological importance. Sample preparation for PCB congener analysis should follow the techniques described in Tetra Tech (1986a) or U.S. EPA (1986a), but with instrumental analysis and quantification using standard capillary GC columns on individual PCB isomers according to the methods reported by NOAA (1989) (see also Dunn et al. 1984; Schwartz et al. 1984; Mullin et al. 1984; Stalling et al. 1987).

Although the methods mentioned above are adequate for detecting and quantifying concentrations of those PCB congeners comprising the majority of total PCBs in environmental samples, they are not appropriate for separating and quantifying PCB congeners which may coelute with other congeners and/or may be present at relatively small concentrations in the total PCB mixture. Included in this latter group of compounds, for example, are PCBs 126 and 169, two of the more toxic nonortho-substituted PCB congeners (Table 8). In order to separate these (and other toxic nonortho-substituted congeners), it is necessary to initially utilize an enrichment step with an activated carbon column (Smith 1981). Various types of carbon columns have been used, ranging from simple gravity columns (e.g., in a Pasteur pipette) to more elaborate (and efficient) columns using high-pressure liquid chromatography (HPLC) systems (see Schwartz et al. 1993). The preferred method of separation and quantitation of the enriched PCB mixture has been via high resolution GC/MS with isotope dilution (Kuehl et al. 1991; Ankley et al. 1993; Schwartz et al. 1993). However, recent studies have shown that if the carbon enrichment is done via HPLC, the nonortho-substituted PCB congeners of concern also may be quantifiable via more widely available GC/ECD systems (Schwartz et al. 1993).

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TABLE 8. POLYCHLORINATED BIPHENYL CONGENERS RECOMMENDED FOR QUANTITATION AS POTENTIAL CONTAMINANTS OF CONCERN

PCB Congener[a]	Congener Number[b]		
	Summation[c]	Highest Priority[d]	Second Priority[e]
2,4'-Dichlorobiphenyl	8		
2,2',5-Trichlorobiphenyl	18		18
2,4,4'-Trichlorobiphenyl	28		
3,4,4'-Trichlorobiphenyl			37
2,2',3,5'-Tetrachlorobiphenyl	44		44
2,2',4,5'-Tetrachlorobiphenyl			99
2,2',5,5'-Tetrachlorobiphenyl	52		52
2,3',4,4'-Tetrachlorobiphenyl	66		
2,3',4',5-Tetrachlorobiphenyl			70
2,4,4',5-Tetrachlorobiphenyl			74
3,3',4,4'-Tetrachlorobiphenyl	77	77	
3,4,4',5-Tetrachlorobiphenyl			81
2,2',3,4,5'-Pentachlorobiphenyl		87	
2,2',3,4',5-Pentachlorobiphenyl		49	
2,2',4,5,5'-Pentachlorobiphenyl	101	101	
2,3,3',4,4'-Pentachlorobiphenyl	105	105	
2,3,4,4',5-Pentachlorobiphenyl			114
2,3',4,4',5-Pentachlorobiphenyl	118	118	
2,3',4,4',6-Pentachlorobiphenyl			119
2',3,4,4',5-Pentachlorobiphenyl			123
3,3',4,4',5-Pentachlorobiphenyl	126[f]	126[f]	
2',3,3',4,4'-Hexachlorobiphenyl	128	128	
2,2',3,4,4',5'-Hexachlorobiphenyl	138	138	
2,2',3,5,5',6-Hexachlorobiphenyl			151
2,2',4,4',5,5'-Hexachlorobiphenyl	153	153	
2,3,3',4,4',5-Hexachlorobiphenyl		156	
2,3,3',4,4',5-Hexachlorobiphenyl			157
2,3,3',4,4',6-Hexachlorobiphenyl			158
2,3',4,4',5,5'-Hexachlorobiphenyl			167
2,3',4,4',5',6-Hexachlorobiphenyl			168

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TABLE 8. (cont.)

PCB Congener[a]	Congener Number[b]		
	Summation[c]	Highest Priority[d]	Second Priority[e]
3,3',4,4',5,5'-Hexachlorobiphenyl	169[f]	169[f]	
2,2',3,3',4,4',5-Heptachlorobiphenyl	170	170	
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180	180	
2,2',3,4,4',5',6-Heptachlorobiphenyl		183	
2,2',3,4,4',6,6'-Heptachlorobiphenyl		184	
2,2',3,4',5,5',6-Heptachlorobiphenyl	187		187
2,3,3',4,4',5,5' Heptachlorobiphenyl			189
2,2',3,3',4,4',5,6-Octachlorobiphenyl		195	
2,2',3,3',4,5,5',6'-Octachlorobiphenyl			201
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl		206	
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl		209	

Note: PCB - polychlorinated biphenyl

[a] PCB congeners recommended for quantitation, from dichlorobiphenyl through decachlorobiphenyl.

[b] Congeners are identified by their International Union of Pure and Applied Chemistry (IUPAC) number, as referenced in Ballschmiter and Zell (1980) and Mullin et al. (1984).

[c] These congeners are summed to determine total PCB concentration using the approach in NOAA (1989).

[d] PCB congeners having highest priority for potential environmental importance based on potential for toxicity, frequency of occurrence in environmental samples, and relative abundance in animal tissues (McFarland and Clarke 1989).

[e] PCB congeners having second priority for potential environmental importance based on potential for toxicity, frequency of occurrence in environmental samples, and relative abundance in animal tissues (McFarland and Clarke 1989).

[f] To separate PCBs 126 and 169, it is necessary to initially utilize an enrichment step with an activated carbon column (Smith 1981).

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The overall toxicity of nonortho-substituted PCBs at a site can be assessed based on a comparison with the toxicity of 2,3,7,8-TCDD. A similar procedure can be used for assessing the toxicity of a mixture of dioxins and furans. In this "toxicity equivalency factor" (TEF) approach, potency values of individual congeners (relative to TCDD) and their respective sediment concentrations are used to derive a summed 2,3,7,8-TCDD equivalent (U.S. EPA 1989d; Table 9). EPA and the USACE are developing guidance on the use of this approach.

To ensure that contaminants not included in the list of target analytes are not overlooked in the chemical characterization of the dredged material, the analytical results should also be scrutinized by trained personnel. The presence of persistent unknown analytes should be noted. Methods involving GC/MS techniques for organic compounds are recommended for the identification of any unknown analytes.

2.8.3 Chemical Analysis of Water

Analysis to determine the potential release of dissolved contaminants from the dredged material (standard elutriate) may be necessary to make determinations of water column toxicity (see U.S. EPA and USACE 1994). Elutriate tests involve mixing dredged material with dredging site water and allowing the mixture to settle. The portion of the dredged material that is considered to have the potential to impact the water column is the supernatant remaining after undisturbed settling and centrifugation. Chemical analysis of the elutriate allows a direct comparison, after allowance for mixing, to applicable water quality standards. When collecting samples for elutriate testing, consideration should be given to the large volumes of water and sediment required to prepare replicate samples for analysis. In some instances, when there is poor settling, the elutriate preparation has to be performed successively several times to accumulate enough water for testing. The following sections discuss the selection of target analytes and techniques for water analyses. QA considerations are summarized in Section 2.10.5.

2.8.3.1 Selection of Target Analytes

Historical water quality information from the dredging site should be evaluated along with data obtained from the chemical analysis of sediment samples to select target analytes. Chemical evaluation of the dredged material provides a known list of contaminants that might affect the water column. All target analytes identified in the sediment should initially be considered potential targets for water analysis. Nonpriority pollutant chemical components which are found in measurable concentrations in the sediments should be included as target analytes if review of the literature indicates that these analytes have the

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TABLE 9. Methodology for Toxicity Equivalency Factors

Because toxicity information on some dioxin and furan species is scarce, a structure-activity relationship has been assumed. The toxicity of each cogener is expressed as a fraction of the toxicity of 2,3,7,8 TCDD.

Compound	TEF
2,3,7,8 TCDD	1
other TCDD	0
2,3,7,8-PeCDDs	0.5
other PeCDDs	0
2,3,7,8-HxCDDs	0.1
other HxCDDs	0
2,3,7,8-HpCDDs	0.01
other HpCDDs	0
OCDD	0.001
2,3,7,8-TCDF	0.1
other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
other PeCDFs	0
2,3,7,8-HxCDFs	0.1
other HxCDFs	0
2,3,7,8-HpCDFs	0.01
other HpCDFs	0
OCDF	0.001

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potential to bioaccumulate in animals (i.e., have a high K_{ow} or bioconcentration factor [BCF]) and/or are of toxicological concern) (Table 10).

2.8.3.2 Selection of Analytical Techniques

In contrast to freshwater, there generally are no EPA-approved methods for analysis of saline water although widely accepted methods have existed for some time (e.g., Strickland and Parsons 1972; Grasshof et al. 1983; Parsons et al. 1984). Application of the freshwater methods to saltwater will frequently result in higher detection limits than are common for freshwater unless care is taken to control the effects of salt on the analytical signal. Modifications or substitute methods (e.g., additional extract concentration steps, larger sample sizes, or concentration of extracts to smaller volumes) might be necessary to properly determine analyte concentrations in saltwater or to meet the desired TDLs. It is extremely important to ascertain a laboratory's ability to execute methods and attain acceptable TDLs in matrices containing up to 3 percent sodium chloride.

Once the list of target analytes for water has been established, analytical methods should be determined. The water volume required for specific analytical methods may vary. A minimum of 1 L of elutriate should be prepared for metals analysis (as little as 100 mL may be analyzed). One liter of elutriate should be analyzed for organic compounds. Sample size should also include the additional volume required for the matrix spike and matrix spike duplicate analyses, required for analysis of both metals and organic compounds. Sample size is one of the limiting factors in determining detection limits for water analyses, but TDLs below the water quality standard should be the goal in all cases. Participating laboratories should routinely report detection limits achieved for a given analyte.

Detailed methods for the analysis of organic and inorganic priority pollutants in water are referenced in 40 CFR 136 and in U.S. EPA (1983). Additional approved methods include U.S. EPA (1986a,b; 1988a,b,c; 1990d,e), APHA (1989), ASTM (1991a), and Tetra Tech (1985). Analysis of the semivolatile organic priority pollutants involves a solvent extraction of water with an optional sample cleanup procedure and analysis using GC or GC/MS. The volatile priority pollutants are determined by using purge-and-trap techniques and are analyzed by either GC or GC/MS. If dioxin (i.e., 2,3,7,8,-TCDD) analysis is necessary, Kuehl et al. (1987), Smith et al. (1984), U.S. EPA (1989b; Method 8290), or U.S. EPA (1990f; Method 1613) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa-PCDDs and PCDFs.

A primary requirement for analysis of inorganic and organic priority pollutants is to obtain detection limits that will result in usable, quantitative data that can

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TABLE 10. OCTANOL/WATER PARTITION COEFFICIENTS FOR ORGANIC COMPOUND PRIORITY POLLUTANTS AND 301(h) PESTICIDES

Pollutant	Octanol/Water Partition Coefficient (log K_{ow})	Pollutant	Octanol/Water Partition Coefficient (log K_{ow})
Di-*n*-octyl phthalate	9.2	Parathion[a]	3.8
Indeno[1,2,3-cd]pyrene	7.7	Chlorobenzene	3.8
Benzo[ghi]perylene	7.0	2,4,6-Trichlorophenol	3.7
PCB-1260	6.9	ß-Endosulfan	3.6
Mirex[a]	6.9	Endosulfan sulfate	3.6
Benzo[k]fluoranthene	6.8	α-Endosulfan	3.6
Benzo[b]fluoranthene	6.6	Naphthalene	3.6
PCB-1248	6.1	Fluorotrichloromethane[b]	3.5
2,3,7,8-TCDD (dioxin)	6.1	1,4-Dichlorobenzene	3.5
Benzo[a]pyrene	6.0	1,3-Dichlorobenzene	3.4
Chlordane	6.0	1,2-Dichlorobenzene	3.4
PCB-1242	6.0	Toxaphene	3.3
4,4'-DDD	6.0	Ethylbenzene	3.1
Dibenz[a,h]anthracene	6.0	*N*-Nitrosodiphenylamine	3.1
PCB-1016	5.9	*P*-Chloro-*m* cresol	3.1
4,4'-DDT	5.7	2,4-Dichlorophenol	3.1
4,4'-DDE	5.7	3,3'-Dichlorobenzene	3.0
Benz[a]anthracene	5.6	Aldrin	3.0
Chrysene	5.6	1,2-Diphenylhydrazine	2.9
Endrin aldehyde	5.6	4-Nitrophenol	2.9
Fluoranthene	5.5	Malathion[a]	2.9
Hexachlorocyclopentadiene	5.5	Tetrachloroethene	2.9
Dieldrin	5.5	4,6-Dinitro-*o*-cresol	2.8
Heptachlor	5.4	Tetrachloroethene	2.6
Heptachlor epoxide	5.4	Bis[2-chloroisopropyl]ether	2.6
Hexachlorobenzene	5.2	1,1,1-Trichloroethane	2.5
Di-*n*-butyl phthalate	5.1	Trichloroethene	2.4
4-Bromophenyl phenyl ether	5.1	2,4-Dimethylphenol	2.4
Pentachlorophenol	5.0	1,1,2,2-Tetrachloroethane	2.4
4-Chlorophenyl phenyl ether	4.9	Bromoform	2.3
Pyrene	4.9	1,2-Dichloropropane	2.3
2-Chloronaphthalene	4.7	Toluene	2.2
Endrin	4.6	1,1,2-Trichloroethane	2.2
PCB-1232	4.5	Guthion[a]	2.2
Phenanthrene	4.5	Dichlorodiflouromethane[b]	2.2
Fluorene	4.4	2-Chlorophenol	2.2
Anthracene	4.3	Benzene	2.1
Methoxychlor[a]	4.3	Chlorodibromomethane	2.1
Hexachlorobutadiene	4.3	2,4-Dinitrotoluene	2.1
1,2,4-Trichlorobenzene	4.2	2,6-Dinitrotoluene	2.0
Bis[2-ethylhexyl]phthalate	4.2	*trans*-1,2-Dichloropropene	2.0
Acenaphthylene	4.1	*cis*-1,3-Dichloropropene	2.0
Butyl benzyl phthalate	4.0	Demeton[a]	1.9
PCB-1221	4.0	Chloroform	1.9
Hexachloroethane	3.9	Dichlorobromomethane	1.9
Acenaphthene	3.9	Nitrobenzene	1.9
α-Hexachlorocyclohexane	3.8	Benzidine	1.8
δ-Hexachlorocyclohexane	3.8	1,1-Dichloroethane	1.8
ß-Hexachlorocyclohexane	3.8	2-Nitrophenol	1.8
γ-Hexachlorocyclohexane	3.8	Isophorone	1.7

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TABLE 10. (cont.)

Pollutant	Octanol/Water Partition Coefficient (log K_{ow})	Pollutant	Octanol/Water Partition Coefficient (log K_{ow})
Dimethyl phthalate	1.6	2-Chloroethylvinylether	1.3
Chloroethane	1.5	Bis[2-chloroethoxy]methane	1.3
2,4-Dinitrophenol	1.5	Acrylonitrile	1.2
1,1-Dichloroethylene	1.5	Bis[2-chloroethyl]ether	1.1
Phenol	1.5	Bromomethane	1.0
1,2-Dichloroethane	1.4	Acrolein	0.9
Diethyl phthalate	1.4	Chloromethane	0.9
N-nitrosodipropylamine	1.3	Vinyl chloride	0.6
Dichloromethane	1.3	*N*-nitrosodimethylamine	0.6

Source: Tetra Tech (1985)

Note: Mixtures, such as PCB Aroclors ®, cannot have discrete K_{ow} values; however, the value given is a rough estimate for the mean. [It is recommended that all PCB analyses use congener-specific methods. All PCB congeners have a log K_{ow} > 4 (L. Burkhardt, EPA Duluth, pers. comm.).]

[a] 301(h) pesticides not on the priority pollutant list.

[b] No longer on priority pollutant or 301(h) list.

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subsequently be compared against applicable water quality standards or criteria, as appropriate. Analysis of saline water for metals is subject to matrix interferences from salts, particularly sodium and chloride ions, when the samples are concentrated prior to instrumental analysis. The gold amalgamation method using cold-vapor atomic absorption spectrometry (CVAA) analysis is recommended to eliminate saline water matrix interferences for mercury analysis. Methods using solvent extraction and atomic absorption spectrometry analysis may be required to reduce saline water matrix interferences for other target metals. Other methods appropriate for metals include: cadmium, copper, lead, iron, zinc, silver (Danielson et al. 1978); arsenic (EPRI 1986); selenium and antimony (Sturgeon et al. 1985); low levels of mercury (Bloom et al. 1983); and tributyltin (Rice et al. 1987). GFAA techniques after extraction are recommended for the analysis of metals, with the exception of mercury. All PCB and pesticide analyses should be performed using GC/ECD methods because such analysis (e.g., NOAA 1989) will result in lower detection limits. PCBs should be quantified as specific congeners (Mullin et al. 1984; Stalling et al. 1987) and as total PCBs based on the summation of particular congeners (NOAA 1989).

2.8.4 Chemical Analysis of Tissue

This section discusses the selection of target analytes and techniques for tissue analyses. QA considerations are summarized in Section 2.10.6.

2.8.4.1 Selection of Target Analytes

Bioaccumulation is evaluated by analyzing tissues of test organisms for contaminants determined to be of concern for a specific dredged material. Sediment contaminant data and available information on the bioaccumulation potential of those analytes have to be interpreted to establish target analytes.

The *n*-octanol/water partition coefficient (K_{ow}) is used to estimate the BCFs of chemicals in organism/water systems (Chiou et al. 1977; Kenaga and Goring 1980; Veith et al. 1980; Mackay 1982). The potential for bioaccumulation generally increases as K_{ow} increases, particularly for compounds with log K_{ow} less than approximately 6. Above this value, there is less of a tendency for bioaccumulation potential to increase with increasing K_{ow}. Consequently, the relative potential for bioaccumulation of organic compounds can be estimated from the K_{ow} of the compounds. U.S. EPA (1985) recommends that compounds for which the log K_{ow} is greater than 3.5 be considered for further evaluation of bioaccumulation potential. The organic compound classes of priority pollutants with the greatest potential to bioaccumulate are PAHs, PCBs, pesticides, and some phthalate esters. Generally, the volatile organic, phenol, and organonitrogen priority pollutants are not readily bioaccumulated, but exceptions

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include the chlorinated benzenes and the chlorinated phenols. Table 10 provides data for organic priority pollutants based on K_{ow}. Specific target analytes for PCBs and PAHs are discussed in Section 2.8.2. The water content and percent lipids in tissue should be routinely determined as a part of tissue analyses for organic contaminants.

Table 11 ranks the bioaccumulation potential of the inorganic priority pollutants based on calculated BCFs. Dredged material contaminants with BCFs greater than 1,000 (log BCF > 3) should be further evaluated for bioaccumulation potential.

Tables 10 and 11 should be used with caution because they are based on calculated bioconcentration from water. Sediment bioaccumulation tests, in contrast, are concerned with accumulation from a complex medium via all possible routes of uptake. The appropriate use of the tables is to help in selecting contaminants of concern for bioaccumulation analysis by providing a general indication of the relative potential for various chemicals to accumulate in tissues.

The strategy for selecting contaminants for tissue analysis should include three considerations:

- The target analyte is a contaminant of concern and is present in the sediment as determined by sediment chemical analyses
- The target analyte has a high potential to accumulate and persist in tissues
- The target analyte is of toxicological concern.

Contaminants with a lower potential to bioaccumulate, but which are present at high concentrations in the sediments, should also be included in the target list because bioavailability can increase with concentration. Conversely, contaminants with a high accumulation potential and of high toxicological concern should be considered as target analytes, even if they are only present at low concentrations in the sediments. Nonpriority-pollutant contaminants that are found in measurable concentrations in the sediments should be included as targets for tissue analysis if they have the potential to bioaccumulate and persist in tissues, and are of toxicological concern.

2.8.4.2 Selection of Analytical Techniques

At present, formally approved standard methods for the analysis of priority pollutants and other contaminants in tissues are not available. However, studies conducted for EPA and other agencies have developed analytical

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TABLE 11. BIOCONCENTRATION FACTORS (BCF) OF INORGANIC PRIORITY POLLUTANTS

Inorganic Pollutant	Log BCF
Metals	
Methylmercury	4.6
Phenylmercury	4.6
Mercuric acetate	3.5
Copper	3.1
Zinc	2.8
Arsenic	2.5
Cadmium	2.5
Lead	2.2
Chromium IV	2.1
Chromium III	2.1
Mercury	2.0
Nickel	1.7
Thallium	1.2
Antimony	ND
Silver	ND
Selenium	ND
Beryllium	ND
Nonmetals	
Cyanide	ND
Asbestos	ND

Source: Tetra Tech (1986b)

Note: ND - no data

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methods capable of identifying and quantifying most organic and inorganic priority pollutants in tissues. The amount of tissue required for analysis is dependent on the analytical procedure and the tissue moisture content. General guidance, but *not* firm recommendations, for the amount of tissue required is provided in Table 5. The required amounts may vary depending on the analytes, matrices, detection limits, and particular analytical laboratory. Tissue moisture content should be determined for each sample to enable data to be converted from a wet-weight to a dry-weight basis for some data users.

Detection limits depend on the sample size as well as the specific analytical procedure. Recommended TDLs for dredged material evaluations are provided in Section 2.3.2 (see Table 3). TDLs should be specified based on the intended use of the data and specific needs of each evaluation.

The recommended methods for the analysis of semivolatile organic pollutants are described in NOAA (1989). The procedure involves serial extraction of homogenized tissue samples with methylene chloride, followed by alumina and gel-permeation column cleanup procedures that remove co-extracted lipids. An automated gel-permeation procedure described by Sloan et al. (1993) is recommended for rapid, efficient, reproducible sample cleanup. The extract is concentrated and analyzed for semivolatile organic pollutants using GC with capillary fused-silica columns to achieve sufficient analyte resolution. If dioxin (i.e., 2,3,7,8-TCDD) analysis is being performed, the methods of Mehrle et al. (1988), Smith et al. (1984), Kuehl et al. (1987), U.S. EPA (1989b; Method 8290), or U.S. EPA (1990f; Method 1613) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa-PCDDs and PCDFs.

Chlorinated hydrocarbons (e.g., PCBs and chlorinated pesticides) should be analyzed by GC/ECD. PCBs should be quantified as specific congeners (Mullin et al. 1984; Stalling et al. 1987) and not by industrial formulations (e.g., Aroclors®) because the levels of PCBs in tissues result from complex processes, including selective accumulation and metabolism (see the discussion of PCBs in Section 2.8.2.2). Lower detection limits and positive identification of PCBs and pesticides can be obtained by using chemical ionization mass spectrometry.

The same tissue extract is analyzed for other semivolatile pollutants (e.g., PAHs, phthalate esters, nitrosamines, phenols) using GC/MS as described by NOAA (1989), Battelle (1985), and Tetra Tech (1986b). These GC/MS methods are similar to EPA Method 8270 for solid wastes and soils (U.S. EPA 1986a). Lowest detection limits are achieved by operating the mass spectrometer in the selective ion monitoring mode. Decisions to perform analysis of nonchlorinated hydrocarbons and resulting data interpretation should consider that many of these analytes are readily metabolized by most fish and many

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invertebrates. Analytical methods for analysis of tissue samples for volatile priority pollutants are found in Tetra Tech (1986b).

Tissue lipid content is of importance in the interpretation of bioaccumulation information. A lipid determination should be performed on all biota submitted for organic analysis if 1) food chain models will be used, 2) test organisms could spawn during the test, or 3) special circumstances occur, such as those requiring risk assessment. Bligh and Dyer (1959) provide an acceptable method, and the various available methods are evaluated by Randall et al. (1991).

Analysis for priority pollutant metals involves a nitric acid or nitric acid/perchloric acid digestion of the tissue sample and subsequent analysis of the acid extract using atomic absorption spectrometry or ICP techniques. Procedures in Tetra Tech (1986b) are generally recommended. NOAA (1989) methods may also be used and are recommended when low detection levels are required. Microwave technology may be used for tissue digestion to reduce contamination and to improve recovery of metals (Nakashima et al. 1988). This methodology is consistent with tissue analyses performed by NOAA (1989), except for the microwave heating steps. Mercury analysis requires the use of CVAA methods (U.S. EPA 1991c). The matrix interferences encountered in analysis of metals in tissue may require case-specific techniques for overcoming interference problems. If tributyltin analysis is being performed, the methods of Rice et al. (1987), NCASI (1986), or Uhler et al. (1989) should be consulted.

2.9 DATA VALIDATION, REDUCTION, AND REPORTING

This section describes procedures for data compilation and verification prior to being accepted for making technical conclusions. In addition, special equations may be required and used to make calculations, models may be used in data analysis, criteria may be used to validate the integrity of data that support final conclusions, and methods may be used to identify and treat data that may not be representative of environmental conditions.

The following specific information should be included in the QA project plan:

- The principal criteria that will be used to validate data integrity during collection and reporting of data (the criteria selected will depend on the level of validation required to meet the data quality objectives)
- The data reduction scheme planned for collected data, including all equations used to calculate the concentration or value of the measured parameter and reporting units

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- The methods used to identify and treat outliers (i.e., data that fall outside the upper and lower limits such as ±3 standard deviations of the mean value) and nondetectable data
- The data flow or reporting scheme from collection of original data through storage of validated concentrations (a flowchart is usually necessary)
- Statistical formulas and sample calculations planned for collected data
- Key individuals who will handle the data in this reporting scheme.

QC procedures designed to eliminate errors during the mathematical and/or statistical reduction of data should also be included in the QA project plan. QC in data processing may include both manual and automated review. Input data should be checked and verified to confirm compatibility and to flag outliers for confirmation (i.e., verify that data are outliers and not data for highly contaminated sediment, water, or tissue). Computerized data plots can be routinely used as a tool for rapid identification of outliers that can then be verified using standard statistical procedures.

2.9.1 Data Validation

Once the laboratory has completed the requested sample analyses, the analytical results are compiled, printed out, and submitted as a data package, which has been signed by the laboratory's project manager. This package may include computer disks, magnetic tape, or other forms of electronically stored information. Data packages may range in size from a few pages to several cartons of documents, depending on the nature and extent of the analyses performed. The cost of this documentation can vary from no charge (in cases where only the final results of an analysis are reported) to hundreds of dollars over the cost of reporting only the final results of an analysis.

The data and information collected during the dredged material evaluation should be carefully reviewed as to their relevancy, completeness, and quality. The data must be relevant to the overall objective of the project. Data quality should be verified by comparing reported detection limits and QC results to TDLs and QC limits, respectively, specified for the current dredged material evaluation.

As soon as new data packages are received from the laboratory, they should be checked for completeness and data usability and, ideally, dated and duplicated. Dating is important for establishing the laboratory's adherence to schedules identified in the statement of work. Duplication assures that a clean reference copy is always kept on file. Checking each element of the data

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package for completeness of information, precision of analytical methods, and bias of all measurements helps to determine whether acceptable data from each type of analysis have been supplied by the laboratory.

Screening for data quality requires knowledge of the sample holding times and conditions, the types of analyses requested, and the form in which data were to be delivered by the laboratory. Review of the statement of work is essential to determine any special conditions or requests that may have been stated at the onset of the analyses. Recommended lists of laboratory deliverables for different types of chemical analyses are provided in Tables 1 and 2. This initial screening of data can be performed by appropriate staff or the project manager.

Data validation, or the process of assessing data quality, can begin after determining that the data package is complete. Analytical laboratories strive to produce data that conform to the requested statement of work, and they typically perform internal checks to assure that the data meet a standard level of quality. However, data validation is an independent check on laboratory performance and is intended to assure that quality of reported data meets the needs identified in the QA project plan.

Data validation involves all procedures used to accept or reject data after collection and prior to use. These include screening, editing, verifying, and reviewing through external performance evaluation audits. Data validation procedures ensure that objectives for data precision and bias were met, that data were generated in accordance with the QA project plan and standard operating procedures, and that data are traceable and defensible. All chemical data should be reported with their associated analytical sensitivity, precision, and bias. In addition, the quantification level achieved by the laboratory should be compared to specific TDLs.

The QA project plan should also specify an appropriate level of data validation for the intended data use. Examples of four alternative levels of validation effort for chemical data are summarized in Table 12. These four data validation levels range from complete, 100-percent review of the data package (Level 1) to acceptance of the data package without any evaluation (Level 4).

The QA project plan should also specify who will perform the evaluations called for in Levels 1, 2, or 3. The following options should be considered for chemical data:

- Perform a brief assessment and rely on specialists to resolve outstanding concerns. This assessment is equivalent to Level 3 (Table 12).
- Perform a complete review for Level 1 or 2 using qualified staff and technical guidelines for QA specialists (see Footnote a in Table 12).

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TABLE 12. LEVELS OF DATA VALIDATION

Level 1	100 percent of the data (including data for laboratory quality control samples) are independently validated using the data quality objectives established for the project. Calculations and the possibility of transcription errors are checked. Instrument performance and original data for the analytical standards used to calibrate the method are evaluated to ensure that the values reported for detection limits and data values are appropriate. The bias and precision of the data are calculated and a summary of corrections and data quality is prepared.[a]
Level 2	20 percent of the sample data and 100 percent of the laboratory quality control samples are validated. Except for the lower level of effort in checking data for samples, the same checks conducted in Level 1 are performed. If transcription errors or other concerns (e.g., correct identification of chemicals in the samples) are found in the initial check on field samples, then data for an additional 10–20 percent of the samples should be reviewed. If numerous errors are found, then the entire data package should be reviewed.
Level 3	Only the summary results of the laboratory analyses are evaluated. The data values are assumed to be correctly reported by the laboratory. Data quality is assessed by comparing summary data reported by the laboratory for blanks, bias, precision, and detection limits with data quality objectives in the QA project plan. No checks on the calibration of the method are performed, other than comparing the laboratory's summary of calibrations with limits specified in the QA project plan.
Level 4	No additional validation of the data is performed. The internal reviews performed by the laboratory are judged adequate for the project.

[a] Screening checks that can be easily performed by the project manager are provided in (U.S. EPA 1991d). Step-by-step procedures used by quality assurance specialists to validate data for analyses of organic compounds and metals can be found in EPA's functional guidelines for data review (U.S. EPA 1988a,b). These guidelines were developed for analyses conducted according to the statements of work for EPA's Contract Laboratory Program and are updated periodically. Regional interpretation of these detailed procedures is also contained in *Data Validation Guidance Manual for Selected Sediment Variables* (PTI 1989b), a draft report released by the Washington Department of Ecology's Sediment Management Unit in June 1989. A simplified version of this guidance is provided in *Data Quality Evaluation for Proposed Dredged Material Disposal Projects* (PTI 1989a), another report released by the Sediment Management Unit in June 1989.

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- Send the data package to an outside technical specialist for review, specifying either Level 1, 2, or 3.

Providing instructions for conducting a thorough technical validation of chemical data is beyond the scope of this document. Examples of detailed technical guidance of this nature can be found in a pair of publications, *Laboratory Data Validation: Functional Guidelines for Evaluating Inorganics Analyses* (U.S. EPA 1988a) and *Laboratory Data Validation: Functional Guidelines for Evaluating Organics Analyses* (U.S. EPA 1988b). Examples of simple evaluations that can be conducted by a project manager are also provided in U.S. EPA (1991d). The evaluation criteria in Figure 1 (abstracted from U.S. EPA [1991d]) provide several signs that should alert a project manager to potential problems with data acceptability.

2.9.2 Data Reduction and Reporting

The QA project plan should summarize how validated data will be analyzed to reach conclusions, including major tools that will be used for statistical evaluations. In this section, a flow chart is useful to show the reduction of original laboratory data to final tabulated data in the project report. A summary should also be provided of the major kinds of data analyses that will be conducted (e.g., health risk assessments, mapping of chemical distributions). In addition, the format, content, and distribution of any data reports for the project should be summarized.

2.10 INTERNAL QUALITY CONTROL CHECKS

The various control samples that will be used internally by the laboratory or sample collection team to assess quality are described in this section of the QA project plan. For most environmental investigations, 10–30 percent of all samples may be analyzed specifically for purposes of quality control. In some special cases (e.g., when the number of samples is small and the need to establish the validity of analytical data is large), as many as 50 percent of all samples are used for this purpose. These QC samples may be used to check the bias and precision of the overall analytical system and to evaluate the performances of individual analytical instruments or the technicians that operate them.

In addition to calibration procedures described in Section 2.7, this section of the guidance document (and Appendix C) summarizes the most widely used QC samples as follows:

- Blanks

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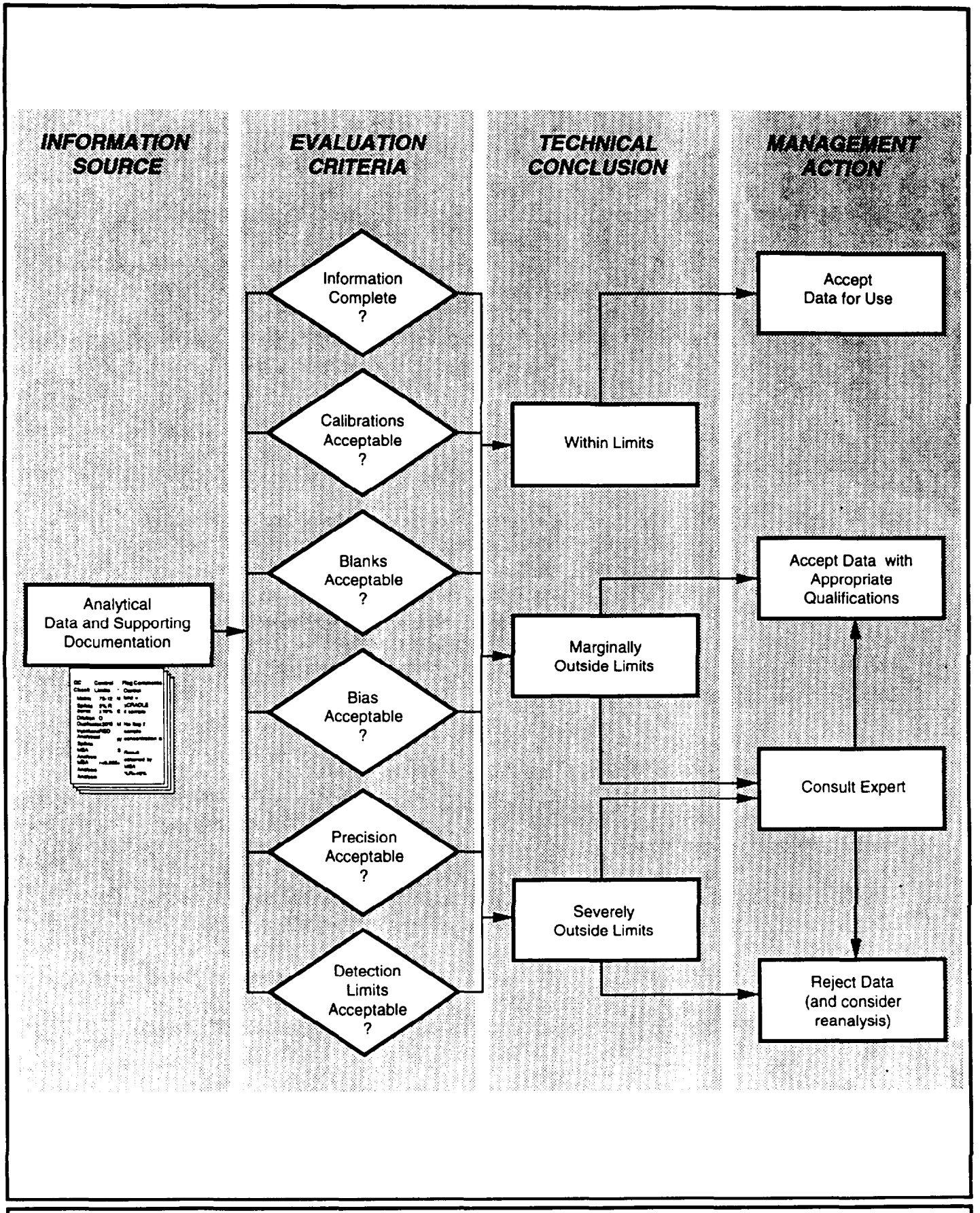

Figure 1. Guidance for data assessment and screening for data quality.

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- Matrix spike samples
- Surrogate spike compounds
- Check standards, including:
  - Spiked method blanks
  - Laboratory control samples
  - Reference materials
- Matrix replicates (split in the laboratory from one field sample)
- Field replicates (collected as separate field samples from one location).

QC procedures for sediment, water, and tissue analyses are discussed in more detail in the following sections. Field QC results are not used to qualify data, but only to help support conclusions arrived at by the review of the entire data set.

The government authorities for the program may require that certain samples be submitted on a routine basis to government laboratories for analysis, and EPA or USACE may participate in some studies. These activities provide an independent QA check on activities being performed and on data being generated and are discussed in Section 2.11 (*Performance and System Audits*).

2.10.1 Priority and Frequency of Quality Control Checks

Which QC samples will be used in analyses should be determined during project planning. The frequency of QC procedures is dependent upon the type of analysis and the objectives of the project (as established in Section 2.3). The statements of work for EPA's CLP (U.S. EPA 1990d,e) specify the types of checks to be used during sample analysis. Determining the actual numbers of samples and how often they must be used is also a part of this process. These specifications, called QC sample frequencies, represent the minimum levels of effort for a project. Increasing the frequency of QC samples may be an appropriate measure when the expected concentrations of chemicals are close to the detection limit, when data on low chemical concentrations are needed, when there is a suspected problem with the laboratory, or when existing data indicate elevated chemical concentrations such that removal or other actions may be required. In such cases, the need for increased precision may justify the cost of extra QC samples.

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The relative importance, rationale, and relative frequency of calibration and each kind of QC sample are discussed in Appendix C. The following priority, rationale, and frequency of use is recommended for each procedure:

1. **Method blank samples** are one of the highest priority checks on QC, because they provide an assessment of possible laboratory contamination (and the means to correct results for such contamination), and are used to determine the detection limit. As a result, method blank analyses are always required; at least one analysis is usually performed for each group of samples that are processed by a laboratory. In contrast, the need for other kinds of blank samples (bottle, transport, or field equipment) is usually project-specific and depends on the likelihood of contamination from solvents, reagents, and instruments used in the project; the matrix being analyzed; or the contaminants of concern. A bottle blank consists of an unopened empty sampling bottle that is prepared and retained in the field laboratory. A trip travel blank consists of deionized water and preservative (as added to the samples) that is prepared in the laboratory and transported to the sampling site. A field or decontamination blank consists of deionized water from the sample collection device and preservative (as added to the samples) that is prepared at the sampling site.

2. **Matrix spike samples** are high-priority checks on QC and should always be analyzed to indicate the bias of analytical measurements due to interfering substances or matrix effects. The suggested frequency is 1 matrix spike for every 20 samples analyzed. If more than 1 matrix type is present (e.g., samples containing primarily sand and samples containing primarily of silt within the same group), then each matrix type should be spiked at the suggested frequency. Duplicate matrix spike samples analyzed at a frequency of 1 duplicate for every 20 samples can serve as an acceptable means of indicating both the bias and precision of measurement for a particular sample. Duplicate matrix spike samples may provide the only information on precision for contaminants that are rarely detected in samples.

3. **Surrogate spike compounds** are high-priority checks on QC that are used to evaluate analytical recovery (e.g., sample extraction efficiency) of organic compounds of interest from individual samples. Surrogate spike compounds should be added to every sample, including blanks and matrix spike samples, prior to performing sample processing, to monitor extraction efficiency on a sample-by-sample basis. This kind of check is only used when the identity of the surrogate compound can be reasonably confirmed (e.g., by mass spectroscopy). Because a surrogate compound is

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chemically similar to the associated compound of interest and is added to the sample in a known amount, its known recovery is indicative of that of the compound of interest.

Variations in recovery that can be seen using surrogate spike compounds with each sample will not necessarily be reflected in duplicate matrix spike analyses conducted on only a few of the samples. The reasons for possible differences between surrogate spike analyses and matrix spike analyses relate to sample heterogeneity and how these QC samples are prepared. For example, matrix spike analyses provide an indication of chemical recovery for the general sample matrix tested. However, this matrix may differ among individual samples leading to a range of recoveries for surrogate spike compounds among samples. In addition, surrogate spike compounds are often added at a lower concentration than matrix spike compounds. This difference in spiking concentration sometimes results in reasonable recovery of the higher-concentration matrix spike compounds but poorer recovery of the lower-concentration surrogate spike compounds. Finally, matrix spike compounds are typically identical to compounds of interest in the samples, while surrogate spike compounds are usually selected because they are not present in environmental samples, but still mimic the behavior of compounds of interest. Therefore, there can be more uncertainty in quantifying the recovery of matrix spike compounds (after subtracting the estimated concentration of the compounds of interest in the sample) than the recovery of surrogate spike compounds.

4. **Check standards** should be used whenever available as a high-priority check on laboratory performance. Check standards include laboratory control samples, reference materials prepared by an independent testing facility, and spiked method blanks prepared by the laboratory. By comparing the results of check standards with those of sample-specific measurements (e.g., matrix spike samples and surrogate compound recovery), an overall assessment of bias and precision can be obtained. The laboratory should be contacted prior to analysis to determine what laboratory control samples can be used. Catalogues from organizations such as National Institute for Standards and Technology and the National Research Council of Canada are available that list reference materials for different sediment, water, and tissue samples (see Section 2.11.2).

   Reference materials provide a standardized basis for comparison among laboratories or between different rounds of analysis at one laboratory. Therefore, reference materials should always be used

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when comparison of results with other projects is an intended data use. At least 1 analysis of a reference material for every 20 samples is recommended for this purpose. Similarly, spiked method blanks should be used as acceptable checks on laboratory performance whenever a new procedure is used or when laboratories with no established track record for a standard or nonstandard procedure will be performing the analysis.

5. **Analytical replicate samples** should be included as a medium-priority check on laboratory precision. Analytical replicate samples better indicate the precision of measurements on actual samples than do matrix spike duplicates because the contaminants have been incorporated into the sample by environmental processes rather than having been spiked in a laboratory setting. The suggested frequency is 1 replicate sample for every 20 samples for each matrix type analyzed. For organic analyses, analysis of analytical spike duplicate samples are sometimes a higher priority than matrix replicate samples if budgets are limited. The reason for this preference is because many organic compounds of interest may not be present in samples unless they are added as spiked compounds.

6. **Field replicate samples** should be included if measuring sampling variability is a critical component of the study design. Otherwise, collection of field replicate samples is discretionary and a lower priority than the other QC samples. Field replicate samples should be submitted to the laboratory as blind samples. When included, the suggested frequency is at least 1 field replicate for every 20 samples analyzed. One of the field replicate samples should also be split by the laboratory into analytical duplicates so that both laboratory and laboratory-plus-sampling variability can be determined on the same sample. By obtaining both measures on the same sample, the influence of sampling variability can be better discerned. It is possible that analytical variability can mask sampling variability at a location.

2.10.2 Specifying Quality Control Limits

Prior to performing a chemical analysis, recognized limits on analytical performance should be established. These limits are established largely through the analysis of QC samples. QC limits apply to all internal QC checks for field measurements, physical characterizations, bioaccumulation studies, and toxicity tests. Many laboratories have established limits that are applicable to their own measurement systems. These limits should be evaluated to ensure that they are at least as stringent as general guidelines or that the reasons for a less

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stringent limit are acceptable. Also, if a laboratory has consistently demonstrated better performance than indicated by general guidelines, limits tied to this better performance should be used to indicate when there may be a problem at that laboratory. For example, if surrogate recoveries for benzene in sediment samples have consistently been between 85 and 105 percent, a recovery of 70 percent indicates an analytical problem that should be investigated even if the general guideline for acceptable recovery is 50 percent. It may be useful to establish different kinds of limits when working with laboratories. For example, the following two kinds of limits are used by PSEP (1990c) and are similar to limits used in EPA's CLP.

Warning limits are values indicating that data from the analysis of QC samples should be qualified (e.g., that they represent estimated or questionable values) before they can be relied upon in a project. These limits serve to warn the project staff that the analytical system, instrument, or method may not be performing normally and that data should be qualified as "estimated" before using the results for technical analysis. The standard value for warning limits are ±2 times the standard deviation (U.S. EPA 1979). Examples of warning limits used by the Puget Sound Estuary Program are provided in Table 13. Such limits provide a means of ensuring that reported data are consistently qualified, an important consideration when combining data in a regional database.

If necessary to meet project goals, project managers may specify warning limits as more stringent contractual requirements in laboratory statements of work. For example, Puget Sound Estuary Program guidelines for organic compound analyses state that the warning limits for the minimum recovery of surrogate spike and matrix spike compounds are 50 percent of the amount added prior to sample extraction. Data that do not meet this minimum requirement would normally be qualified as estimates. However, the project manager could apply more stringent criteria and decide to reject data that do not meet warning limits, which would require reanalysis of the samples associated with those QC samples that do not meet these limits. These more stringent criteria are termed control limits.

Control limits are limits placed on the acceptability of data from the analysis of QC samples. Exceedance of control limits informs the analyst and the project manager that the analytical system or instrument is performing abnormally and needs to be corrected. Control limits should be contractually binding on laboratories, and statements of work should provide the project manager or designee with sole discretion in enforcing the limits. Data obtained under these circumstances should be corrected before they are resubmitted by the laboratory. Data that exceed control limits are often rejected and excluded from a project database, although there may be special circumstances that warrant acceptance of the data as estimated values. The reasons for making such an

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TABLE 13. EXAMPLE WARNING AND CONTROL LIMITS FOR CALIBRATION AND QUALITY CONTROL SAMPLES[a]

Analysis Type	Recommended Warning Limit	Recommended Control Limit
Ongoing calibration	Project manager decision[b]	> ±25 percent of the average response measured in the initial calibration
Surrogate spikes	< 50 percent recovery[c]	Follow EPA Contract Laboratory Program guidelines
Method blanks	Exceeds the TDL	Exceeds 5 times the TDL
Reference materials	95 percent confidence interval, if certified	To be determined
Matrix spikes	50–150 percent recovery	To be determined[d]
Spiked method blanks (check standards)	50–150 percent recovery	To be determined
Matrix replicates	35 percent coefficient of variation	> ±50 percent coefficient of variation (or a factor of 2 for duplicates)
Field replicates	Project manager decision	Project manager decision

Note: TDL - target detection limit

[a] Warning and control limits used in the Puget Sound Estuary Program for the analysis of organic compounds (PSEP 1990c).

[b] See U.S. EPA (1991d) for specific examples of project manager decisions for warning or control limits.

[c] Except when using the isotope dilution technique.

[d] Zero percent spike recovery requires rejection of data.

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exception should always be documented in a QA report for the data (see Appendix F).

Unlike warning limits, control limits and appropriate corrective actions (such as instrument recalibration, elimination of sources of laboratory contamination, or sample reanalysis) should be clearly identified in the statement of work. The standard value for control limits are ±3 times the standard deviation (U.S. EPA 1979). Examples of regional control limits used by the Puget Sound Estuary Program are also provided in Table 13. In those cases that require a project manager's decision to determine the appropriate control limit, it is recommended that the associated warning limit be used as an control limit to produce data that will have broad applicability (including use in enforcement proceedings). Control limits should be enforced with discretion because some environmental samples are inherently difficult to analyze. Recommended actions under different circumstances are provided below.

2.10.3 Quality Control Considerations for Physical Analysis of Sediments

The procedures used for the physical analysis of sediments should include a QC component. QC procedures for grain size analysis and total solids/specific gravity determinations are necessary to ensure that the data meet acceptable criteria for precision and bias. To measure precision, triplicate analyses should be performed for every 20 samples analyzed. TOC is a special case, where all samples should be analyzed in triplicate, as recommended by the analytical method. In addition, 1 procedural blank per 20 samples should be run, and the results reported for TOC analysis. Standards used for TOC determinations should be verified by independent check standards to confirm the bias of the results. Quality control limits should be agreed upon for each analytical procedure, and should be consistent with the overall QA project plan.

2.10.4 Quality Control Considerations for Chemical Analysis of Sediments

Methods for the chemical analysis of priority pollutants in sediments should include detailed QC procedures and requirements that should be followed rigorously throughout the evaluation. General procedures include the analysis of a procedural blank, a matrix duplicate, a matrix spike along with every 10–20 samples processed, and surrogate spike compounds. All analytical instruments should be calibrated at least daily (see Section 2.7.1). All calibration data should be submitted to the laboratory project QA coordinator for review. The QA/QC program should document the ability of the selected methods to address the high salt content of sediments from marine and estuarine areas.

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Analytical precision can be measured by analyzing 1 sample in duplicate or triplicate for every 10–20 samples analyzed. If duplicates are analyzed, the relative percent difference should be reported; however, if triplicates are analyzed, the percent relative standard deviation should be reported.

2.10.5 Quality Control Considerations for Chemical Analysis of Water

Methods recommended for the chemical analysis of priority pollutants in water include detailed QC procedures and requirements that should be followed closely throughout the evaluations. General procedures should include the analysis of a procedural blank, a matrix duplicate, a matrix spike for every 10–20 samples processed, and surrogate spike compounds (for organic analyses only). Analytical precision can be measured by analyzing 1 sample in triplicate or duplicate for every 10–20 samples analyzed. If duplicates are analyzed, the relative percent difference should be reported; however, if triplicates are analyzed, the percent relative standard deviation should be reported. Analytical bias can be measured by analyzing SRM, a matrix containing a known amount of a pure reagent. Recoveries of surrogate spikes and matrix spikes should be used to measure for precision and bias; results from these analyses should be well documented. Special quality control is required for ICP and GC/MS analyses. Initial calibrations using three or five standards (varying in concentration) are required for analyses of inorganic and organic compounds, respectively, before analyzing samples (see Section 2.7.2). Subsequent calibration checks should be performed for every 10–20 samples analyzed.

2.10.6 Quality Control Considerations for Chemical Analysis of Tissue

Methods recommended for the chemical analysis of priority pollutants in tissue include detailed QC procedures and requirements that should be followed closely throughout the evaluations. General procedures should include the analysis of a procedural blank, a matrix duplicate, a matrix spike for every 10–20 samples processed, and surrogate spike compounds (for organic analyses only). Analytical precision can be measured by analyzing 1 sample in triplicate or duplicate for every 10–20 samples analyzed. If duplicates are analyzed, the relative percent difference should be reported; however, if triplicates are analyzed, the percent relative standard deviation should be reported. Analytical bias can be measured with the appropriate SRMs. Precision and bias determinations should be performed with the same frequency as the blanks and matrix spikes.

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2.11 PERFORMANCE AND SYSTEM AUDITS

Procedures to determine the effectiveness of the QC program and its implementation are summarized in this section of the QA project plan. Each QA project plan should describe the various audits required to monitor the capability and performance of all measurement systems. Audits include a careful evaluation of both field and laboratory QC procedures. They are an essential part of the field and laboratory QA program and consist of two basic types: performance audits and system audits. For example, analyses of performance evaluation samples may simply be used for comparison with the results of independent laboratories (a form of performance audit), or comprehensive audits may be conducted by the government of the entire field or laboratory operations (a system audit).

Performance and system audits should be conducted by individuals not directly involved in the measurement process. A performance auditor independently collects data using performance evaluation samples, field blanks, trip blanks, duplicate samples, and spiked samples. Performance audits may be conducted soon after the measurement systems begin generating data. They may be repeated periodically as required by task needs, duration, and cost. U.S. EPA (1991e) should be reviewed for auditing the performance of laboratories performing aquatic toxicity tests.

A systems audit consists of a review of the total data production process. It includes onsite reviews of field and laboratory operational systems. EPA and/or USACE will develop and conduct external system audits based on the approved project plan. An example of a systems audit checklist is provided in Appendices A and G.

2.11.1 Procedures for Pre-Award Inspections of Laboratories

The pre-award inspection is a kind of system audit for assessing the laboratory's overall capabilities. This assessment includes a determination that the laboratory personnel are appropriately qualified and that the required equipment is available and is adequately maintained. It establishes the groundwork necessary to ensure that tests will be conducted properly, provides the initial contact between government and laboratory staff, and emphasizes the importance that government places on quality work and products.

The purpose of the pre-award inspection is to verify the following:

- The laboratory has an independent QA/QC program
- Written work plans are available for each test that describe the approach to be used in storing, handling, and analyzing samples

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- Technically sound, written standard operating procedures are available for all study activities
- Qualifications and training of staff are appropriate and documented
- All equipment is properly calibrated and maintained
- Approved analytical procedures are being followed.

2.11.2 Interlaboratory Comparisons

It is important that data collected and processed at various laboratories be comparable. As part of the performance audit process, laboratories may be required to participate in analysis of performance evaluation samples related to specific projects. In particular, laboratory proficiency should be demonstrated before a laboratory negotiates a contract and yearly thereafter. Each laboratory participating in a proficiency test is required to analyze samples prepared to a known concentration. Analytes used in preparation of the samples should originate from a recognized source of SRMs such as the National Institute for Standards and Technology. Proficiency testing programs already established by the government may be used (e.g., EPA Environmental Monitoring and Systems Laboratory scoring system), or a program may be designed specifically for dredged material evaluations.

In addition, the performance evaluation samples prepared by EPA Environmental Monitoring and Systems Laboratory (Las Vegas, Nevada) for the CLP may be used to assess interlaboratory comparability. Analytical results are compared with predetermined criteria of acceptability (e.g., values that fall within the 95 percent confidence interval are considered acceptable). The QA project plan should indicate, where applicable, scheduled participation in all interlaboratory calibration exercises.

Reference materials are substances with well-characterized properties that are useful for assessing the bias of an analysis and auditing analytical performances among laboratories. SRMs are certified reference materials containing precise concentrations of chemicals, accurately determined by a variety of technically valid procedures, and are issued by the National Institute of Standards and Technology. Currently, SRMs are not available for the physical measurements or all pollutants in sediments; however, where possible, available SRMs or other regional reference materials that have been repeatedly tested should be analyzed with every 20 samples processed.

SRMs for most organic compounds are not currently available for seawater, but reference materials for many inorganic chemicals may be obtained from the organizations listed in Table 14. Seawater matrix spikes of target analytes (e.g., seawater spiked with National Institute for Standards and Technology

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TABLE 14. SOURCES OF STANDARD REFERENCE MATERIALS

PCBs		
National Research Council of Canada	Marine sediment	HS–1 and HS–2
PAHs		
National Research Council of Canada	Marine sediment	HS–3, HS–4, HS–5, HS–6
National Institute for Standards and Technology	Sediment	SRM #1647 and SRM #1597
Metals		
National Bureau of Standards	Estuarine sediment	SRM #1646
National Research Council of Canada	Marine sediment	MESS–1, BCSS–1, PACS–1
	Dogfish liver	DOLT-1
	Dogfish muscle	DORM-1
	Lobster hepatopancreas	TORT-1
International Atomic Energy Agency	Marine sediment	SD–N–1/2(TM)
	Fish flesh	MA-A-2(TM)
	Mussel tissue	MAL-1(TM)

Standard reference materials (SRMs) may be obtained from the following organizations:

Organic Constituents

U.S. Department of Commerce
National Institute for Standards and Technology
Office of Standard Reference Materials
Room B3111 Chemistry Building
Gaithersburg, Maryland 20899
Telephone: (301) 975–6776

Marine Analytical Chemistry Standards Program
National Research Council of Canada
Atlantic Research Laboratory
1411 Oxford Street
Halifax, Nova Scotia, Canada B3H 3Z1
Telephone: (902) 426–8280

Inorganic Constituents

U.S. Department of Commerce
National Institute for Standards and Technology
Office of Standard Reference Materials
Room B3111 Chemistry Building
Gaithersburg, Maryland 20899
Telephone: (301) 975–6776

Marine Analytical Chemistry Standards Program
National Research Council of Canada
Division of Chemistry
Montreal Road
Ottawa, Ontario, Canada K1A 0R9
Telephone: (613) 993–2359

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SRM 1647 for PAH) should be used to check analytical bias. Some available SRMs for priority pollutant metals in seawater are National Research Council of Canada seawater CASS–1 and seawater NASS–2.

SRMs for organic priority pollutants in tissues are currently not available. The National Institute of Standards and Technology is presently developing SRMs for organic analytes. Tissue matrix spikes of target analytes should be used to fulfill analytical accuracy requirements for organic analyses.

Because new SRMs appear constantly, current listings of appropriate agencies should be consulted frequently. SRMs that are readily available and commonly used are included in Table 14.

2.11.3 Routine System Audits

Routine system audits during the technical evaluation ensure that laboratories are complying with the QA project plan. It is suggested that checklists be developed for reviewing training records, equipment specifications, QC procedures for analytical tasks, management organization, etc. The government should also establish laboratory review files for quick assessment of the laboratory's activity on a study, and to aid in monitoring the overall quality of the work. Procedures for external system audits by the government are similar to the internal systems audits conducted by the laboratories themselves.

2.12 FACILITIES

The QA Project Plan should provide a complete, detailed description of the physical layout of the laboratory, define space for each test area, describe traffic-flow patterns, and document special laboratory needs. The design and layout of laboratory facilities are important to maintain sample integrity and prevent cross-contamination. The specific areas to be used for the various evaluations should be identified. Aspects of the dredging study that warrant separate facilities include the following:

- Receiving
- Sample storage
- Sample preparation
- Sample testing
- Reagent storage
- Data reduction and analysis.

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2.13 PREVENTIVE MAINTENANCE

Procedures for maintaining field and laboratory equipment in a ready state are described in this section, including identification of critical spare parts that must be available to ensure that data completeness will not be jeopardized by equipment failure. Regular servicing must be implemented and documented.

The QA project plan should describe how field and laboratory equipment essential to sample collection and analysis will be maintained in proper working order. Preventive maintenance may be in the form of: 1) scheduled maintenance activities to minimize costly downtime and ensure accuracy of measurement systems, and 2) available spare parts, backup systems, and equipment. Equipment should be subject to regular inspection and preventive maintenance procedures to ensure proper working order. Instruments should have periodic calibration and preventive maintenance performed by qualified technical personnel, and a permanent record should be kept of calibrations, problems diagnosed, and corrective actions applied. An acceptance testing program for key materials used in the performance of environmental measurements (chemical and biological materials) should be applied prior to their use.

2.14 CALCULATION OF DATA QUALITY INDICATORS

Specific equations or procedures used to assess the precision, bias, and completeness of the data are identified in this section.

The calculations and equations used routinely in QA review (e.g., relative percent difference of duplicates) as well as the type of samples (e.g., blanks, replicates) analyzed to assess precision, bias, and completeness of the data must be presented in the QA project plan. Routine procedures for measuring precision and bias include the use of replicate analyses, SRMs, and matrix spikes. The following routine procedures can be used to measure precision and bias:

1. **Replicate analysis**

   Precision for duplicate chemical analyses will be calculated as the relative percent difference:

$$\text{Relative percent difference} = \frac{\text{abs}[D_1 - D_2]}{(D_1 + D_2)/2} \times 100$$

   where:

   D_1 = sample value

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D_2 = duplicate sample value
abs = absolute value.

Precision for the replicate will be calculated as the relative standard deviation:

$$\text{Percent relative standard deviation} = \frac{\sigma}{x} \times 100$$

where:

x = mean of three or more results
σ = standard deviation of three or more results.

$$\sigma = \left[\frac{\sum (x-x)^2}{n-1}\right]^{1/2}$$

2. Matrix and surrogate spikes

Bias of these measurements will be calculated as the ratio of the measured value to the known spiked quantity:

$$\text{Percent recovery} = \frac{\text{spiked result} - \text{unspiked result}}{\text{spike added}} \times 100$$

3. Method blank

Method blank results are assessed to determine the existence and magnitude of contamination. Guidelines for evaluating blank results and specific actions to be taken are identified in U.S. EPA (1988a,b). Sample results will not be corrected by subtracting a blank value.

4. Laboratory control sample

Bias of these measurements will be calculated as the ratio of the measured value to the referenced value:

$$\text{Percent recovery} = \frac{\text{measured value}}{\text{referenced value}} \times 100$$

5. Completeness

Completeness will be measured for each set of data received by dividing the number of valid (i.e., accepted) measurements actually obtained by the number of measurements that were planned:

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

To be considered complete, the data set should also contain all QC check analyses that verify the accuracy (precision and bias) of the results.

2.15 CORRECTIVE ACTIONS

Major problems that could arise during field or laboratory operations, predetermined corrective actions for these problems, and the individual responsible for each corrective action are identified in this section.

One purpose of any QA program is to identify nonconformance as quickly as possible. A nonconformance event is defined as any event that does not follow defined methods, procedures, or protocols, or any occurrence that may affect the quality of the data or study. A QA program should have a corrective action plan and should provide feedback to appropriate management authority defining how all nonconformance events were addressed and corrected.

Corrective actions fall into two categories: 1) handling of analytical or equipment malfunctions, and 2) handling of nonconformance or noncompliance with the QA requirements that have been established. During field and laboratory operations, the supervisor is responsible for correcting equipment malfunctions. All corrective measures taken should be documented (e.g., a written standard operating procedure for the corrective action) and, if required, an alteration checklist should be completed.

Corrective action procedures should be described for each project and include the following elements:

- Procedures for corrective actions when predetermined limits for data acceptability are exceeded (see DQO discussion in Section 2.3)
- For each measurement system, the individual responsible for initiating the corrective action and the individual responsible for approving the corrective action.

Corrective actions for field procedures should be described in a separate section from the corrective actions that would apply to the data or laboratory analysis. Corrective actions may be initiated as a result of other QA activities including performance audits, system audits, interlaboratory/interfield comparison studies, and QA program audits. An example of a corrective actions checklist is provided in Appendix A.

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2.16 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The process of assuring data quality does not end with the data review. A report summarizing the sampling event (see Appendix H) and the QA review of the analytical data package should be prepared, samples should be properly stored or disposed of, and laboratory data should be archived in a storage file or database. Technical interpretation of the data begins after the QA review has been completed. Once data interpretation is complete, the results of the project should be carefully examined to determine how closely the original project goals and objectives were met. QA reviews are particularly useful for providing data users with a written record of data concerns and a documented rationale for why certain data were accepted as estimates or were rejected.

QA project plans provide a mechanism for periodic reporting to management on the performance of measurement systems and data quality. At a minimum, these reports should include:

- Periodic assessment of measurement data accuracy (precision and bias) and completeness
- Results of performance and system audits
- Significant QA problems and recommended solutions.

The individuals responsible for preparing the periodic reports should be identified. The final report for each project should include a separate QA section that summarizes data quality information contained in the periodic reports. These reports may be prepared by the project manager if a brief evaluation was conducted, or by QA specialists if a detailed review was requested by the project manager.

2.16.1 Preparing Basic Quality Assurance Reports

Basic QA reports should summarize all conclusions concerning data acceptability and should note significant QA problems that were found. The table of contents for a basic QA report should include the following:

- **Data summary**—The data summary section should discuss the number of samples collected, the laboratory(s) that analyzed the samples, and a summary of the data that were qualified during the QA review.
- **Holding times**—The holding time section should briefly discuss the holding time requirements and holding time exceedances.

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- **Analytical methods**—The analytical methods section should briefly describe the methods of analysis, any departures from the methods, and any calibration or instrument-specific QC criteria exceedances.
- **Accuracy**—The accuracy section should include a discussion of QC criteria and exceedances for 1) analytical bias (surrogate compound, laboratory control sample, matrix spike, and reference material recoveries) and 2) precision of matrix replicates (and matrix spike duplicates for organic compounds.
- **Method blanks**—The method blank section should include a brief discussion of method blank QC criteria and exceedances.

QA reviews are usually included as appendices to technical project reports. In any case, the QA review becomes part of the documented project file, which also includes the original data package and any computer files used in data compilation and analysis.

2.16.2 Preparing Detailed Quality Assurance Reports

Depending on the project objectives, a more detailed QA report may be desired. An example of a detailed QA review for a metals data package is provided in Appendix F. In addition to the sections outlined for the basic QA report, the detailed QA report should also include:

- **Introduction**—The introduction should give a brief overview of the purpose of data collection and brief summaries of how the samples were collected and processed in the field.
- **Sample set description**—The sample set section should describe the number of samples sent to each laboratory, including the number of field blanks, field replicates, SRMs, and interlaboratory split samples.
- **Sample delivery group description**—The sample delivery group section should briefly describe how the samples were sorted by the analytical laboratories (how many sample delivery groups were returned by the laboratory), and whether or not the QC criteria were performed at the correct frequency for each sample delivery group.
- **Field QC summary**—The field QC section should discuss the evaluation of the field blank and replicate results for the sample survey.

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- **Interlaboratory comparison**—The interlaboratory section, where applicable, should describe the evaluation of the split samples as compared to the corresponding samples analyzed by the contract laboratory.
- **Field results description**—The field results section, where applicable, should present tabular summaries of all data with appropriate qualifiers.

For organic analyses, a discussion of the results of instrument tuning (if applicable), instrument calibration analyses, internal standard performance (if applicable), and summation of any factors that could effect overall data quality (e.g., system degradation) should also be included in the detailed QA report.

2.17 REFERENCES

References cited in the QA project plan should be provided at the end of the plan.

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4. GLOSSARY

Accuracy	The ability to obtain precisely a nonbiased (true) value. Accuracy as used in this document is the combined measure of precision and bias (see footnote at beginning of Section 2).
Acid Volatile Sulfide	The sulfides removed from sediment by cold acid extraction, consisting mainly of H_2S and FeS. AVS is a possible predictive tool for divalent metal sediment toxicity.
Analyte	The specific component measured in a chemical analysis.
Bias	Deviation of the measurement from the true value. Usually expressed as the percent recovery of a known amount of a chemical added to a sample at the start of a chemical analysis. Bias (along with precision) is a component of the overall accuracy of a system.
Bioaccumulation	The accumulation of contaminants in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, pore water, or dredged material.
Bioassay	A bioassay is a test using a biological system. It involves exposing an organism to a test material and determining a response. There are two major types of bioassays differentiated by response: **toxicity tests** which measure an effect (e.g., acute toxicity, sublethal/chronic toxicity) and **bioaccumulation tests** which measure a phenomenon (e.g., the uptake of contaminants into tissues).
Bioconcentration Factor	The degree to which an organism uptakes a substance from water.

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Blanks	QC samples that are processed with the samples but contain only reagents. They are used to obtain the response of an analysis in the absence of a sample, including assessment of contamination from sources external to the sample.
Calibration	The systematic determination of the relationship of the response of the measurement system to the concentration of the analyte of interest. Instrument calibration performed before any samples are analyzed is called the **initial calibration**. Subsequent checks on the instrument calibration performed throughout the analyses of samples are called **continuing calibration**.
Chromatography	The process of selectively separating a mixture into its component compounds. The compounds are measured and presented graphically in the form of a **chromatogram** and digitally as a **quantification report**.
Cleanup	The process of removing certain components from sample extracts, performed to improve instrument sensitivity
Comparability	Reflects the confidence with which one data set can be compared with others and the expression of results consistent with other organizations reporting similar data. Comparability of analytical procedures also implies using analytical methodologies that produce results comparable in terms of precision, bias, and effective range of calibration.
Completeness	A measure of the amount of valid data *obtained* vs. the amount of data originally *intended* to be collected.
Confined Disposal Facility	A diked area, either in-water or upland, used to contain dredged material.
Contaminant	A chemical or biological substance in a form that can be incorporated into, onto, or be ingested by and that harms aquatic organisms, consumers of aquatic organisms, or users of the aquatic environment, and includes but is not limited to the

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substances on the 307(a)(1) list of toxic pollutants promulgated on January 31, 1978 (43 *Federal Register* 4109).

Control Limit — A value for data from the analysis of QC checks indicating that a system or a method is not performing normally and that an appropriate corrective action should be taken. When control limits are exceeded, analyses should be halted; samples analyzed since the last QC sample may need reanalysis.

Control Sediment — A sediment used to confirm the biological acceptability of the test conditions and to help verify the health of the organisms during the test. Control sediment is essentially free of contaminants and compatible with the biological needs of the test organisms such that it has no discernable influence on the response being measured in the test. Test procedures are conducted with the control sediment in the same way as the reference sediment and dredged material. Control sediment may be the sediment from which the test organisms are collected or a laboratory sediment. Excessive mortality in the control sediment indicates a problem with the test conditions or organisms, and can invalidate the results of the corresponding dredged material test.

Data Package — The results of chemical analyses completed by a laboratory, compiled, printed out, and presented to the agency or individual requesting the analyses. The data package should include chromatograms, calculations, and tuning and calibration summaries, where appropriate. Also included in the data package may be computer disks, magnetic tape, or other forms of electronically stored data.

Data Quality Indicators — Surrogate spike recoveries, matrix spike recoveries, analytical values obtained for blanks, standard reference material, and performance evaluation samples for each parameter in each matrix.

Data Quality Objectives (DQOs) — Qualitative and quantitative statements of the overall uncertainty that a decision maker is willing to accept in results or decisions derived from

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environmental data. DQOs provide the framework for planning environmental data operations consistent with the data user's needs.

Detector — A device used in conjunction with an analytical instrument to determine the components of a sample.

Digestion — A process used prior to analysis that breaks down samples using acids (or bases). The end product is called a digestate. Other chemicals, called **matrix modifiers**, may be added to improve the final digestate.

Disposal Site — That portion of inland or ocean where specific disposal activities are permitted. It consists of a bottom surface area and any overlying volume of water.

Dredged Material — Material excavated or dredged from waters of the United States. A general discussion of the nature of dredged material is provided by Engler et al. (1991).

Dredged Material Discharge — Any addition of dredged material into waters of the United States, including: open water discharges; discharges from unconfined disposal operations (such as beach nourishment or other beneficial uses); discharges from confined disposal facilities which enter waters of the United States (such as effluent, surface runoff, or leachate); and overflow from dredge hoppers, scows, or other transport vessels.

Elutriate — Material prepared from the sediment dilution water and used for chemical analyses and toxicity testing.

Evaluation — The process of judging data in order to reach a decision.

Extraction — A chemical or mechanical procedure to remove semivolatile organic compounds from a sample matrix. The end product of extraction is called an **extract**.

Interference — Unwanted elements or compounds in a sample

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that have properties similar to those of the chemical of interest and that collectively cause unacceptable levels of bias in the results of a measurement or in sensitive measurements. Unless removed by an appropriate cleanup procedure, the interferant is carried along with the chemical of interest through the analytical procedure.

Ion — An atom or group of atoms that carries a positive or negative electric charge as a result of having lost or gained one or more electrons.

Matrix — The sample material (e.g., water, sediment, tissue) in which the chemicals of interest are found. Matrix refers to the physical structure of a sample and how chemicals are bound within this structure. At a gross level, tissue is one kind of sample matrix and soil is another. At a finer level, a sediment sample of silty sand containing large amounts of calcium carbonate from the shells of aquatic organisms represents a different sample matrix than a sediment sample of clayey silt containing a large amount of organic carbon from decaying vegetation.

Matrix Effects — Matrix effects are physical or chemical interactions between the sample material and the chemical of interest that can bias chemical measurements in either a negative or positive direction. Because matrix effects can vary from sample to sample and are often not well understood, they are a major source of variability in chemical analyses.

Matrix Spike Samples — QC check samples created by adding known amounts of chemicals of interest to actual samples, usually prior to extraction or digestion. Analysis of matrix spikes and matrix spike duplicates will provide an indication of bias due to matrix effects and an estimation of the precision of the results.

Metals — A group of naturally occurring elements. Certain metals (such as mercury, lead, nickel, zinc, and cadmium) can be of environmental concern when they are released to the environment in unnaturally high amounts. This group usually includes the metalloid arsenic.

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Organic Compounds	Carbon-based substances commonly produced by animals or plants. **Organic chemicals** are chemical compounds based on carbon chains or rings and also containing hydrogen with or without oxygen, nitrogen, or other elements. Organic chemicals may be produced naturally by plants and animals or processed artificially using various chemical reactions.
Performance Audit	Audit of a laboratory's performance by testing a standard reference material. The test results are evaluated by the auditor.
Precision	The ability to replicate a value; the degree to which observations or measurements of the same property, usually obtained under similar conditions, conform to themselves. Usually expressed as standard deviation, variance, or range. Precision, along with bias, is a component of the overall accuracy of a system.
Quality Assurance	The total integrated program for assuring the reliability of data. A system for integrating the quality planning, quality control, quality assessment, and quality improvement efforts to meet user requirements and defined standards of quality with a stated level of confidence.
Quality Assurance Management Plan	A detailed document specifying guidelines and procedures to assure data quality at the program level (i.e., multiple projects).
Quality Assurance Project Plan	A detailed, project-specific document specifying guidelines and procedures to assure data quality during data collection, analysis, and reporting.
Quality Control	The overall system of technical activities for obtaining prescribed standards of performance in the monitoring and measurement process to meet user requirements.
Quality Control Checks	Blanks, replicates, and other samples used to assess the overall analytical system and to evaluate the performances of individual analytical instruments or the technicians that operate them.

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Reference Materials — Materials or substances with well-characterized properties that are useful for assessing the accuracy of an analysis and comparing analytical performances among laboratories.

Reference Sediment — A sediment that serves as a point of comparison to identify potential effects of contaminants in the dredged material (see *Inland* and *Ocean Testing* manuals for further discussion).

Replicates — One of several identical samples. When two separate samples are taken from the same station, or when one sample is split into two separate samples and analyzed, these samples are called **duplicates**. When three identical samples are analyzed, these samples are called **triplicates**.

Representativeness — The degree to which sample data depict an existing environmental condition; a measure of the total variability associated with sampling and measuring that includes the two major error components: systematic error (bias) and random error. Sampling representativeness is accomplished through proper selection of sampling locations and sampling techniques, and collection of sufficient number of samples.

Sediment — Material, such as sand, silt, or clay, suspended in or settled on the bottom of a water body. The term *dredged material* refers to material which has been dredged from a water body (see definition of dredged material), while the term *sediment* refers to material in a water body prior to the dredging process.

Semivolatile Organic Compound — An organic compound with moderate vapor pressure that can be extracted from samples using organic solvents and analyzed by gas chromatography.

Spectrometry — The use of spectrographic techniques for deriving the physical constants of materials. Four basic forms of spectrometry commonly used are atomic absorption spectrometry (AA), inductively coupled plasma-atomic emission spectrometry (ICP) for metals, and ultraviolet spectrometry (UV) and

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fluorescence emission or excitation spectrometry for organic compounds.

Spiked Method Blanks

Method blanks to which known amounts of surrogate compounds and analytes have been spiked. Such samples are useful to verify acceptable method performance prior to and during routine analysis of samples containing organic compounds. Also known as check standards in some methods; independently prepared standards used to check for bias and to estimate the precision of measurements.

Standard Operating Procedure

A written document which details an operation, analysis, or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks.

Standard Reference Material

Standard reference materials are certified reference materials containing precise concentrations of chemicals, accurately determined by a variety of technically valid procedures.

Statement of Work

A contract addendum used as a legally binding agreement between the individual or organization requesting an analysis and the individual, laboratory, or organization performing the actual tasks.

Surrogate Spike Compounds

Compounds with characteristics similar to those of compounds of interest that are added to a sample prior to extraction. They are used to estimate the recovery of organic compounds in a sample.

Target Detection Limit (TDL)

A performance goal set by consensus between the lowest, technically feasible, detection limit for routine analytical methods and available regulatory criteria or guidelines for evaluating dredged material. The TDL is, therefore, equal to or greater than the lowest amount of a chemical that can be reliably detected based on the variability of the blank response of routine analytical methods. However, the reliability of a chemical measurement generally increases as the concentration increases. Analytical costs may also be lower at higher detection limits. For these reasons, a TDL is

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typically set at not less than 10 times lower than available dredged material guidelines for potential biological effects associated with sediment chemical contamination.

Tests/Testing — Specific procedures which generate biological, chemical, and/or physical data to be used in evaluations. The data are usually quantitative but may be qualitative (e.g., taste, odor, organism behavior).

Toxicity Test — A **bioassay** which measures an effect (e.g., acute toxicity, sublethal/chronic toxicity). Not a **bioaccumulation test** (see definition of **bioassay**).

Volatile Organic Compound — An organic compound with a high vapor pressure that tends to evaporate readily from a sample.

Warning Limit — A value indicating that data from the analysis of QC checks are subject to qualification before they can be used in a project. When two or more sequential QC results fall outside of the warning limits, a systematic problem is indicated.

Water Quality Standard — A law or regulation that consists of the beneficial designated use or uses of a water body, the numeric and narrative water quality criteria that are necessary to protect the use or uses of that particular water body, and an anti-degradation statement.

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APPENDIX A

Example QA/QC Checklists, Forms, and Records

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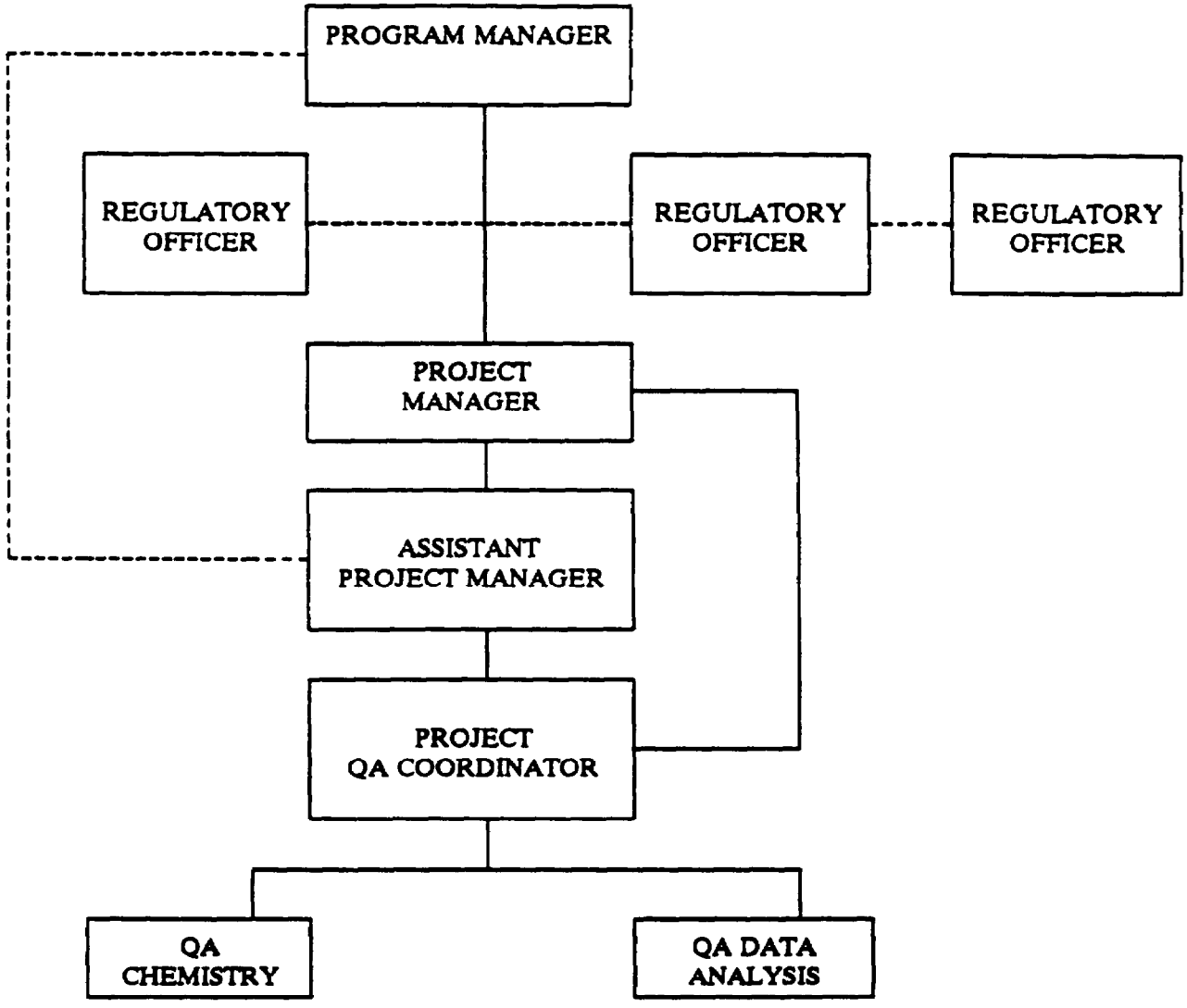
QA PROGRAM ORGANIZATION FLOW DIAGRAM



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EXAMPLE DATA QUALITY OBJECTIVES FOR ACCURACY AND COMPLETENESS

Variable	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method	Reference	Maximum Holding Time
Volatiles	Sediment	µg/kg	10	±50%	±30%	99%	Purge & Trap/GC-MS	EPA abc/x-cc-yy(1975)	14 days
Grain Size	Sediment	Percent	0.01	—	±5%	99%	Sieve & Pipet		Undetermined

ALTERATION CHECKLIST

Sample Program Identification: _____

Material to be Sampled: _____

Measurement Parameter: _____

Standard Procedure for Analysis: _____

_____

Reference: _____

_____

_____

Variation from Standard Procedure: _____

_____

_____

Reason for Variation: _____

_____

_____

Resultant Change in Field Sampling Procedure: _____

_____

_____

Special Equipment, Material, or Personnel Required: _____

_____

_____

Author's Name: _____ Date: _____

Approval: _____ Title: _____

Date: _____

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CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
SAMPLERS: *(Signature)*	

STA. NO.	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	ANALYSIS						REMARKS

Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received for Laboratory by: *(Signature)*	Date / Time	Remarks	

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

FIELD TRACKING REPORT FORM

W/O No. _____ Page _____

FIELD TRACKING REPORT: _____-_____
(LOC-SN)

FIELD SAMPLE CODE (FSC)	BRIEF DESCRIPTION	DATE	TIME	SAMPLER

LABORATORY TRACKING REPORT FORM

W/O No. _____ Page _____

LABORATORY TRACKING REPORT: _____-_____
(LOC-SN)

FRACTION CODE	X	PREP/ANAL REQUIRED	RESPONSIBLE INDIVIDUAL	DATE DELIVERED	DATE COMPLETED

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GENERAL SAMPLE LABEL

(NAME OF SAMPLING ORGANIZATION)

PROJECT: _____

DATE: _____

TIME: _____

SAMPLE ID NO.: _____

MEDIA: _____

STATION NUMBER: _____

DEPTH: _____

PRESERVATION: _____

ANALYSES TO BE PERFORMED: _____

SAMPLED BY: _____

LAB NO.: _____

REMARKS: _____

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STATION LOCATION LOG

DATE: _____

PROJECT: _____

STATION LOCATION: _____

DESCRIPTION OF SAMPLES COLLECTED: _____

SPC ZONE: _____(N/S) EAST: _____ NORTH: _____

_____

LOCATION:

Bottom Depth: _____ (ft) _____ (m) Tide: ± _____ (m) MLLW: _____ (ft) _____ (m)

LORAN C: LOP1 _____ LOP2 _____

Variable Radar Range: _____

_____

_____

Visual Fixes: (Note: Please tape any drawings to back of this sheet)

_____

_____

_____

Photos - Roll: _____ Pictures: _____

PID Reading (range): _____

Comments: _____

_____

_____

RECORDER: _____ SIGNATURE: _____ ORG. CORE _____ DATE: _____

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SYSTEMS AUDIT CHECKLIST

SAMPLE PROGRAM IDENTIFICATION: _____

SAMPLING DATES: _____

MATERIAL TO BE SAMPLED: _____

MEASUREMENT PARAMETER: _____

SAMPLING AND MONITORING EQUIPMENT IN USE:

_____

_____

_____

_____

AUDIT PROCEDURES AND FREQUENCY: _____

_____

_____

_____

FIELD CALIBRATION PROCEDURES AND FREQUENCY: _____

_____

_____

SIGNATURE OF QA COORDINATOR: _____

DATE: _____

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CORRECTIVE ACTIONS CHECKLIST

SAMPLE PROGRAM IDENTIFICATION: _____

SAMPLING DATES: _____

MATERIAL TO BE SAMPLED: _____

MEASUREMENT PARAMETER: _____

ACCEPTABLE DATA RANGE:

_____

CORRECTIVE ACTIONS INITIATED BY: _____

TITLE: _____

DATE: _____

PROBLEM AREAS REQUIRING CORRECTIVE ACTION: _____

_____

_____

_____

MEASURES TO CORRECT PROBLEMS: _____

_____

_____

MEANS OF DETECTING PROBLEMS (FIELD OBSERVATIONS, SYSTEMS AUDIT, ETC): _____

_____

_____

APPROVAL FOR CORRECTIVE ACTIONS: _____

TITLE: _____

SIGNATURE: _____

DATE: _____

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APPENDIX B

Example Statement of Work for the Laboratory

PREFACE

This appendix contains a generic statement of work for the analysis of most chemicals in the most commonly analyzed sample matrices.

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STATEMENT OF WORK

The following tasks shall be performed by _____ as extensions to work identified as part of Contract No. ____ between Contractor and _____.

SUMMARY OF ANALYSES AND SERVICES

The Laboratory shall perform quantitative analyses for the analytes listed in Table 1 on sediment, water, and tissue samples collected from in and around _____. The analyses shall be conducted according to _____ sampling and analysis plan (SAP), the project work plan, and _____.

SAMPLE DELIVERY AND STORAGE

Sampling will begin approximately _____, and continue for a period of approximately _____. Contractor will provide samples to the Laboratory no earlier than _____. Table 2 summarizes the maximum number of samples the Laboratory could receive each month and the associated analyses. The actual number of samples that will be delivered to the Laboratory may vary from these estimates.

Samples will be sent from the site to the Laboratory's facilities via United Parcel Service or equivalent carrier. Contractor may choose to use the Laboratory's courier service if the Laboratory provides such a service. Contractor will coordinate with the Laboratory for final disposition of the samples after analysis. All samples shall be maintained under strict chain of custody at all times, including documentation of any transfers among facilities.

METHODS

The Laboratory shall perform the analyses according to the specified _____, or other Contractor-specified protocols. Table 1 provides a list of specific method references, holding times, and data quality objectives.

The Laboratory shall promptly notify the Contractor Quality Assurance and Quality Control (QA/QC) Coordinator prior to any deviation from these methods. Further, the Laboratory shall immediately notify the Contractor QA/QC Coordinator as soon as it becomes apparent that the data quality objectives cannot be met for a set of samples.

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TABLE B-1. SUMMARY OF ANALYSES AND DATA QUALITY OBJECTIVES

Analyte	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method Reference	Holding Time (days)
Organic Analyses								
TCL[a] semivolatile organic compounds	Solids	µg/kg						
	Water	µg/L						
	Tissue	µg/kg						
TCL volatile organic compounds	Solids	µg/kg						
	Water	µg/L						
	Tissue	µg/kg						
TCL pesticides and PCBs[b]	Solids	µg/kg						
	Water	µg/L						
	Tissue	µg/kg						
Lipids	Tissue	µg/kg						
Metals Analyses								
Copper	Solids	µg/kg						
	Water	µg/L						
Mercury	Solids	µg/kg						
	Water	µg/L						
	Tissue	µg/kg						
TAL[c] metals	Solids	µg/kg						
	Water	µg/L						
	Tissue	µg/kg						
Conventional and Nutrient-Related Analyses								
Acid-volatile sulfide	Solids	µmoles/g						
Total organic carbon	Solids	% carbon						
	Water	mg/L						
Dissolved organic carbon	Water	mg/L						

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TABLE B-1. (cont.)

Analyte	Matrix	Units	Target Detection Limit	Bias (%)	Precision (%)	Completeness (%)	Method Reference	Holding Time (days)
Physical Analyses								
Grain size	Solids	g dry wt.						
Percent moisture	Solids	% moisture						
Total suspended solids	Water	mg/L						

[a] Target compound list.
[b] Polychlorinated biphenyl.
[c] Target analyte list.

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TABLE B-2. ESTIMATED MAXIMUM NUMBER OF SAMPLES BY MONTH AND ANALYTE TYPE

	(date) Maximum			(date) Maximum			(date) Maximum			(date) Maximum			Total Maximum		
Analyte	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue	Solids	Water	Tissue
Organic Analyses															
TCL[a] semivolatile organic compounds															
TCL volatile organic compounds															
TCL pesticides and PCBs[b]															
Lipids															
Metals Analyses															
Copper															
Mercury															
TAL[c] metals															
Conventional and Nutrient-Related Analyses															
Acid-volatile sulfide															
Total inorganic carbon															
Dissolved organic carbon															
Physical Analyses															
Grain size															
Percent moisture															
Total suspended solids															

[a] Target compound list.
[b] Polychlorinated biphenyl.
[c] Target analyte list.

QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

The Laboratory shall implement the following procedures to assess quality during sample analysis:

- **Calibration Verification**—Initial calibration of instruments shall be performed at the start of the project and when any ongoing calibration does not meet control criteria. The number of points used in the initial calibration is defined in each analytical method (e.g., Contract Laboratory Program [CLP]). Ongoing calibration verification shall be performed as specified in the analytical methods to monitor instrument performance. In the event that an ongoing calibration is out of control, analysis of project samples shall be suspended until the source of the control failure is either eliminated or reduced to within control specifications. Any project samples analyzed while the instrument was out of control shall be reanalyzed at Laboratory's expense.

- **Surrogate Spike Compounds**—The Laboratory shall spike all project samples to be analyzed for organic compounds with appropriate surrogate compounds as defined in the analytical methods (e.g., CLP). Recoveries determined using these surrogate compounds shall be reported by the Laboratory; however, the Laboratory shall not correct sample results using these recoveries.

- **Method Blanks**—The Laboratory shall not apply blank corrections to original data. For organic analyses, a minimum of 1 method blank shall be analyzed for every extraction batch, or 1 for every 20 samples, whichever is more frequent. For metals and conventional analyses, 1 method blank shall be analyzed for every digestion batch, or 1 for every 20 samples, whichever is more frequent.

- **Matrix Spike Samples**—For organic analyses and metals, the Laboratory shall analyze a minimum of 1 matrix spike for each group of samples extracted or digested, or 1 for every 20 samples, whichever is more frequent. For organic analyses, 1 matrix spike duplicate shall either be analyzed for each group of samples extracted or for every 20 samples, whichever is more frequent.

- **Laboratory Control Samples**—When available, the Laboratory shall use laboratory control samples (LCS). For metals and applicable conventional parameters, 1 LCS shall either be analyzed for every digestion batch or for every 20 samples, whichever is more frequent. The source of the LCS must be included in the data package.

- **Laboratory Duplicates**—The Laboratory shall perform duplicate analyses as indicators of laboratory precision. For metals analyses (except mercury) and conventional analyses, the Laboratory shall analyze 1 laboratory duplicate either for every digestion batch or for every 20 samples, whichever is more frequent.

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- **Sample Container Preparation**—Sample containers shall be prepared by the Laboratory and delivered to the project site, as required. Sampling personnel shall discard any containers that have visible signs of dirt or contamination. Documentation of the preparation of sample containers shall be prepared, signed, and dated by Laboratory personnel and included with the sample container shipment.

DELIVERABLES

The Laboratory shall report results that are supported by sufficient backup data and quality assurance results to enable reviewers to conclusively determine the quality of the data. The data and supporting documents shall be provided to the Contractor QA/QC Coordinator. The Laboratory shall not divulge outside of Contractor any data or other information obtained or generated by the Laboratory with respect to the work specified herein. Data reporting requirements are summarized below.

Laboratory Data Reports

All data reports shall include the following:

A. General

1. A cover letter documenting all sample preparation and analytical protocols used and explaining any variance from protocols contained in the appropriate EPA statement of work (SOW) or this SOW.

2. Copies of completed chain-of-custody records and sample analysis request forms.

3. A cross-referenced table of Contractor and Laboratory identification numbers, and full explanation of all data qualifier symbols in accordance with the appropriate EPA SOW.

4. Tabulated results in units specified in the appropriate EPA SOW or this SOW.

5. A table of sample preparation data, including initial weights or volumes of samples, final dilution volumes, and digestion or preparation reagents. Data must be grouped by preparation date and include the identity of all quality control checks associated with each preparation batch. If subsets of a large number of samples are prepared or digested at separate times, then each sample subset is defined as a batch. Data provided in this table must be sufficient to unequivocally match each field sample with the corresponding quality control check samples.

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B. Quality Control Results

1. For the analyses of inorganic compounds, the following summary results should be tabulated in the format of the appropriate indicated EPA form:

   a. Initial and ongoing calibration verifications

   b. Initial and ongoing calibration blanks and preparation blanks

   c. Inductively coupled plasma-atomic emission spectrometry (ICP) interference checks

   d. Matrix spike sample recoveries

   e. Duplicate samples

   f. Laboratory control sample recoveries

   g. Method of standard additions, if performed

   h. ICP serial dilution

   i. Mercury holding times, if performed

   j. Instrument detection limits

   k. ICP interelemental correction factors

   l. ICP linear ranges.

2. For all other analyses, the following tabulated summaries of all quality control checks for each analyte should be included:

   a. Initial and ongoing calibration verifications

   b. Initial and ongoing calibration blanks and preparation blanks

   c. Matrix spike sample recoveries

   d. Duplicate samples

   e. Independent standards.

C. Original Data

1. Legible photocopies of all original data, including Laboratory notebook pages, computer printouts, and stripcharts, with sufficient information to unequivocally identify the following:

   a. Calibration and ongoing calibration results

   b. Surrogate spike compound recoveries

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c. Samples and all dilutions

d. Results of all method blanks

e. Results of all matrix spikes and matrix spike duplicates

f. Results and origin of LCS analyses

g. Results of Laboratory duplicates and triplicates

h. Origin of all reference materials

i. Any instrument adjustments or apparent anomalies on the measurement record.

2. The following information should be shown on the first page of each set of original data sheets pertaining to a particular protocol (e.g., ICP computer printout):

   a. A statement documenting the analyte(s) and the exact protocol used

   b. The date of analysis

   c. Typed name and signature of the analyst.

3. Copies of all sample container preparation documentation.

D. Electronic Deliverables

All data reported on the EPA forms must also be submitted as a diskette deliverable. The data should be in Format A (on an MS-DOS diskette), as defined by the SOW.

E. Other Information

Although not required as a deliverable for every data package, the following documentation must be available at the request of the Contractor QA/QC Coordinator as part of the Laboratory's standard QA/QC procedures:

- All original data
- Sample receipt and storage logbooks
- Record of sample holding time
- Storage temperature logbooks
- Conductivity of distilled/deionized water
- Analytical balance annual and routine (Class S weights) calibration logbooks

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- Standard preparation and tracking logbooks, including purity of chemicals used to prepare standards
- Instrument calibration protocols and service record logbooks, including preventive maintenance
- Evidence of spot-checking of data handling
- In-house quality control charts.

TURNAROUND TIME

Schedules for delivery of results may vary, but shall not exceed a turnaround time of __ calendar days. Generally, a turnaround time of __ days will be desired. For data that are delivered late, the Laboratory will be subject to, at the discretion of the Contractor, a penalty of __ percent per calendar day for each day the data are late up to a maximum of __ percent of the total cost of the analyses.

PROGRESS REPORTS, PROBLEM NOTIFICATION, AND PROJECT AUDITS

A verbal progress report to the Contractor QA/QC Coordinator is required each week for the duration of the project. Immediate notification of the Contractor QA/QC Coordinator is required when the Laboratory identifies a problem that could prevent all QA/QC requirements or data quality objectives, including required detection limits, to be met for the final data. Contractor may conduct onsite audits of the Laboratory's facilities during the period of analysis to assess implementation of QA/QC requirements. The Laboratory shall maintain records to support an audit of the technical quality of all analyses and shall provide all such records to Contractor upon request.

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APPENDIX C

Description of Calibration, Quality Control Checks, and Widely Used Analytical Methods

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DESCRIPTION OF CALIBRATION, QUALITY CONTROL SAMPLES, AND WIDELY USED ANALYTICAL METHODS

INTRODUCTION

The relative importance, rationale, and recommended frequency of calibration and each of the quality control samples are discussed in the following sections. A summary of the major considerations in applying these procedures is provided in the main text (see Section 2.7).

The concepts of calibration and quality control samples apply to dozens of analytical methods that are currently used by laboratory technicians. Selection of appropriate methods for particular types of analyses is based on the list of chemicals for analysis and the required detection limits. Some of the widely used analytical methods are described below, along with technical issues that should be considered when choosing individual methods.

CALIBRATION

Calibration of analytical instruments is a critical element of quality control because the procedures used for calibration will determine both the accuracy and precision of analytical results. Gas chromatography/mass spectrometry, or any other analytical technique, measures the magnitude of an unknown concentration of an analyte relative to a known concentration of the analyte or a similar analyte in a standard. Such relative measurements are meaningless unless the responsiveness of the analytical instrument can be determined over a range of analyte concentrations. Through calibration, this level of responsiveness can be determined. The relationship between response and concentration is generally expressed as an analytical curve. For the analysis of organic compounds in samples, response factors (RFs) for analytes relative to standards at various concentrations may be established from this analytical curve. The degree with which incremental concentrations of an analyte produce constant increments of response is called *linearity*.

Guidelines for instrument calibration must be included in the statement of work for the laboratory performing the analysis. Examples of these guidelines are given in *Methods for Chemical Analysis of Water and Wastes* (U.S. EPA 1983). Project managers should ensure that the statement of work addresses the following points:

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- Instruments should be calibrated at the beginning of the project before any samples are analyzed, after each major disruption in analytical procedures, and whenever action limits are exceeded for certain samples. This type of calibration is called the *initial calibration* of the instrument. Through initial calibration, an analytical curve based on the absorbance, emission intensity, or other measured characteristics of known standards can be established. Data from subsequent analyses are considered valid as long as the values fall within the linear range of this curve.

- In some analytical programs, the accuracy of the initial calibration is verified and documented for every analyte by analyzing U.S. Environmental Protection Agency (EPA) quality control solutions immediately following the initial calibration. If immediate verification is not required, then the verification may be conducted after several samples have been analyzed. When a certified solution of an analyte is not available from EPA or any other source, analyses should be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. When measurements for the certified components exceed the action limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the recalibration verified.

- The validity of the original calibration curve should be confirmed throughout the analyses of samples. This process is called *continuing calibration*. However, unless required by a specific method, the continuing calibration results should not be used to quantify sample results (use the average response from the initial calibration instead). For gas chromatography/mass spectrometry (GC/MS) analyses of samples containing organic compounds, calibration should be checked at the beginning of each work shift, at least once every 12 hours (or every 10–12 analyses, whichever is more frequent), and after the last sample analysis of each work shift. For gas chromatography/electron capture detection analyses, calibration should be checked at the beginning of each shift, every 6 hours (or every 6 samples, whichever is less frequent), and after the last sample analysis of each shift.

- For analyses with inductively coupled argon plasma emission spectrometry and atomic absorption spectrometry, all work should be performed using continuing calibration. A procedure for conducting these calibrations is outlined in EPA's Contract Laboratory Program statement of work for inorganic chemicals (U.S. EPA 1990e). Frequency of continuing calibration of these instruments is 10 percent of the samples or every 2 hours during an analysis run, whichever is more frequent.

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QUALITY CONTROL SAMPLES

Blanks

Blanks are quality control samples that are processed with the samples but contain only reagents. They are used to obtain the response of an analysis in the absence of a sample, including assessment of contamination from sources external to the sample. Contamination can arise from sources such as the reagents themselves, sample or reagent containers, and equipment used for sampling, sample storage, and analysis. The types of analytical blanks used to identify each of these potential sources of contamination are described below:

- **Method blanks** (also called preparation blanks or reagent blanks) are used to identify any contamination that may have been contributed by laboratories during sample preparation. A method blank should be required for each batch of samples prepared for analysis, except in the case of volatile organic analyses (VOAs), in which case, method blanks should be analyzed at least once every 12 hours. Because method blanks are usually included in the cost of sample analysis, they should not place an additional cost burden on a project.

- **Bottle blanks** are used to determine whether sample containers are sources of contamination. One bottle blank should be prepared for each lot of sample containers. Large increases in the contaminant level for the bottle blank compared with the method blank indicate a potential container problem. Laboratories usually provide clean containers for performing bottle blank analyses at no additional cost. For most sampling efforts, precleaned containers from a chemical supply company can be obtained at reasonable cost. The use of precleaned bottles may eliminate the need to have bottle blanks analyzed.

- **Transport blanks** (also called trip blanks) are used to detect contamination arising during sample shipping, handling, and storage. These blanks are taken from clean containers filled with deionized water, transported to the field, and stored and shipped with the samples. One transport blank should be included with each shipping container. A contaminant level for the transport blank that greatly exceeds the contaminant level of the method blank indicates a potential field handling, container, or storage problem. Transport blanks are important only for projects involving analysis of volatile organic compounds, which may migrate from one container to another.

- **Field equipment blanks** (also called decontamination checks) are used to detect contamination arising from field sampling equipment. At least one field equipment blank should be required for each medium that is sampled during a sampling effort.

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Matrix Spikes

Matrix spike samples are used to provide an indication of the bias due to matrix effects and an estimation of the precision of results. They can also provide indications of how tightly an analyte is bound to its matrix, such as soil or tissue. Matrix spike samples are created by adding known amounts of chemicals of interest to actual samples, prior to extraction and usually prior to digestion. The addition of these chemicals is commonly called spiking. The matrix spike is analyzed using the same analytical procedure used for samples. The results are then compared with the results from the analysis of a replicate, unspiked sample. In this way the effect of the particular sample matrix on the recovery of chemicals of concern can be evaluated. By spiking and analyzing the sample after digestion, an analyst can determine whether spike analysis results have been affected by matrix binding or by sample preparation procedures. This postdigestion spiking is only used for metals analyses.

Matrix spike samples should include a wide range of chemical types. For example, a matrix spike sample for analysis of semivolatile organic compounds may include spiking with three neutral compounds, two organic acid compounds, and two organic base compounds. Ideally, samples should be spiked either at approximately 5 times the expected chemical concentration in a sample or at 5 times the target detection limit, whichever is higher. Spiking at this concentration reduces the possibility for any increase in random error during the matrix spike analysis and eliminates any masking of interferences at representative chemical concentrations.

One matrix spike sample and one matrix spike duplicate sample should be analyzed for every set of twenty or fewer samples or with each sample preparation lot. If 20 or more samples are submitted, 1 matrix spike duplicate pair should be run for each set of 20 samples. Analysis of matrix spikes and matrix spike duplicates is often performed to assess the precision and bias of one set of results.

Surrogate Spikes

Surrogate spike compounds can be used to estimate the recovery of organic compounds in a sample. Surrogates are compounds with characteristics similar to those of compounds of interest that are added to a sample before it undergoes the process of extraction. Surrogates should be compounds that are not expected to be present in the samples, but they should have characteristics similar to the compounds of concern. Compounds labeled with stable isotopes (that is, where normal carbon or hydrogen atoms in the molecule have been replaced with isotopes of carbon or hydrogen) are commonly used as surrogates. However, all surrogates need not be isotopically labeled. They need only be compounds that are physically and chemically similar to the chemicals of interest. For example, dibromooctafluorobiphenyl is used by some laboratories as a surrogate for polychlorinated biphenyls (PCBs), although this compound is not identical in structure to a PCB.

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Because surrogate compounds are the only means of checking method performance on a sample by sample basis, they should be used whenever possible. A minimum of five surrogate spikes (three neutral and two acid compounds) should be added to each sample when analyzing for semivolatile organic compounds. These surrogate spikes should cover a wide range of compound classes. At least three surrogate compounds should be used for the analysis of volatile organic compounds, and at least one surrogate compound should be used in each extracted sample as a check on recovery of pesticides. A separate surrogate compound should be used in each extracted sample to check the recovery of PCB mixtures.

Check Standards

Check standards contain known amounts of analyte and are analyzed along with the samples. Check standard results are used to indicate bias due to sample preparation and/or calibration and to control precision.

Laboratory Control Samples

Laboratory control samples are check standards used to assess precision in the analytical procedures for metals. Like reference materials, these samples can be acquired from EPA. Often they are routinely analyzed by the laboratory at no extra cost.

Spiked Method Blanks

In certain organic methods, surrogate spikes are added to the check standards; these quality control samples are called spiked method blanks. The different compounds and their required amounts are specified in EPA's guidelines for the Contract Laboratory Program (U.S. EPA 1990d,e) and other regional guidelines. Such analyses are useful to verify acceptable method performance prior to and during routine analysis of samples containing organic compounds. Spiked method blanks do not take into account sample matrix effects, but can be used to identify basic problems in procedural steps. Spiked method blanks can also be used to provide minimum recovery data when no suitable reference material is available or when sample size is insufficient for matrix spikes. A spiked method blank should be analyzed whenever a method is used for the first time in a project and each time that a method is modified. In these instances, analysis of the spiked method blank should take place before analysis of any samples.

Reference Materials

Reference materials are substances with well-characterized properties that are useful for assessing the bias of an analysis and auditing analytical performances among laboratories. SRMs are certified reference materials containing precise concentrations of chemicals,

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accurately determined by a variety of technically valid procedures, and are issued by the National Institute of Standards and Technology. Currently, SRMs are not available for the physical measurements or all pollutants in sediments; however, where possible, available SRMs or other regional reference materials that have been repeatedly tested should be analyzed with every 20 samples processed. Further information on SRMs is provided in the main text (see Section 2.11.2).

Replicates

Replicates are two or more identical samples that are analyzed to provide an estimate of the overall precision of sampling or analytical procedures. When two separate samples are taken from the same field station, or when one sample is split into two separate samples, these replicate samples are specifically called *duplicates*. Duplicates are usually sufficient when using an analytical procedure that is well proven in the laboratory. Analyzing three replicate samples (called *triplicates*) yields more meaningful statistical measures of variability than analyzing duplicate samples. However, statistically combining the variance of duplicate sample results across several sets of duplicates is also an effective way of evaluating variability.

Replicate samples are commonly used for the following purposes:

- **Analytical (or laboratory) replicates** measure the precision of sample analyses. To prepare analytical replicates, the sample is homogenized by the laboratory and divided into two subsamples. The subsamples are then independently analyzed. If five or fewer samples are submitted for analysis, a minimum of one analytical replicate is recommended, the exact number to be determined by the project manager. If more than 5 but less than 20 samples are submitted, at least 1 analytical replicate should be analyzed. A general rule is 1 analytical replicate for every batch of up to 20 samples analyzed together (e.g., U.S. EPA 1990d).

- **Field replicates** measure sampling variability. These samples are collected at the same time and location as other samples and are submitted for analysis along with the other samples. Field replicates should be coordinated with analysis of laboratory replicates so that both sampling variability and analytical variability can be measured for the same station. The project manager or coordinator usually determines the frequency with which field replicates are collected and sent to the laboratory. If funds are limited, a single laboratory replicate to measure analytical variability is preferred over a field replicate.

- **Blind replicates** are samples submitted to the laboratory without the laboratory's prior knowledge. Data from these blind replicates can be used to detect potential laboratory bias when compared with data from the analysis of analytical replicates. In this manner, blind replicates can serve

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as laboratory quality control samples. However, the results for these samples are subject to errors introduced by the process of splitting the sample and by preservation, transportation, and storage procedures as well as analytical errors. Analysis of 1 set of blind replicates should be performed whenever 20 or more samples are submitted. At least one triplicate set is recommended for analysis of more than 20 samples.

COMMON ANALYTICAL METHODS

Gas Chromatography

Gas chromatography is a technique used to separate a complex mixture of organic materials into its components (for example, an extract of oil or smoke, which may contain hundreds, even thousands, of compounds). To do this, the sample extract is injected into a heated chamber, in which the mixture of compounds is concentrated at the head of a separating column. The mixture is then carried through the column by an inert gas (called the *mobile phase*). As the column is heated, the analytes pass through absorbent materials (called the *stationary phase*). Different analytes move at different rates and appear one after another, along with any interfering substances for a particular analyte, at the effluent end of the column. Here they are measured by a *detector*. The detector sends information as an electronic signal to an integrator, chart recorder, or computer. The signals are then interpreted and presented graphically in the form of a *chromatogram* and digitally as a *quantification report*.

Using the chromatogram and the digital information contained in the quantification report, many analytes contained in the sample can be accurately identified and quantified. Several different gas chromatograph/detector combinations are commonly used for the analysis of volatile and semivolatile organic compounds, which include pesticides and PCBs. Three of these combinations are described in the following sections.

Gas Chromatography/Mass Spectrometry

GC/MS enables positive identification of a compound that has eluted from a gas chromatographic column. In the GC/MS chamber, separated compounds are bombarded by electrons and broken into characteristic fragments called *ions*. The mass of the charged ions (i.e., their molecular weight) can be sensed by a detector that accumulates data on ionization current over a wide range of masses. The more ions of a particular mass, the greater the ionization current that is recorded for that mass. At any one time, the relative intensity of this current over all the different masses recorded for a particular compound gives rise to its mass spectrum (Figure C-1). The pattern of fragmentation ions in a mass spectrum is used to distinguish one compound from another. In addition, the intensity of the current recorded for one characteristic ion over time gives rise to its mass chromatogram, which is used to quantify the concentration of the analyte as it

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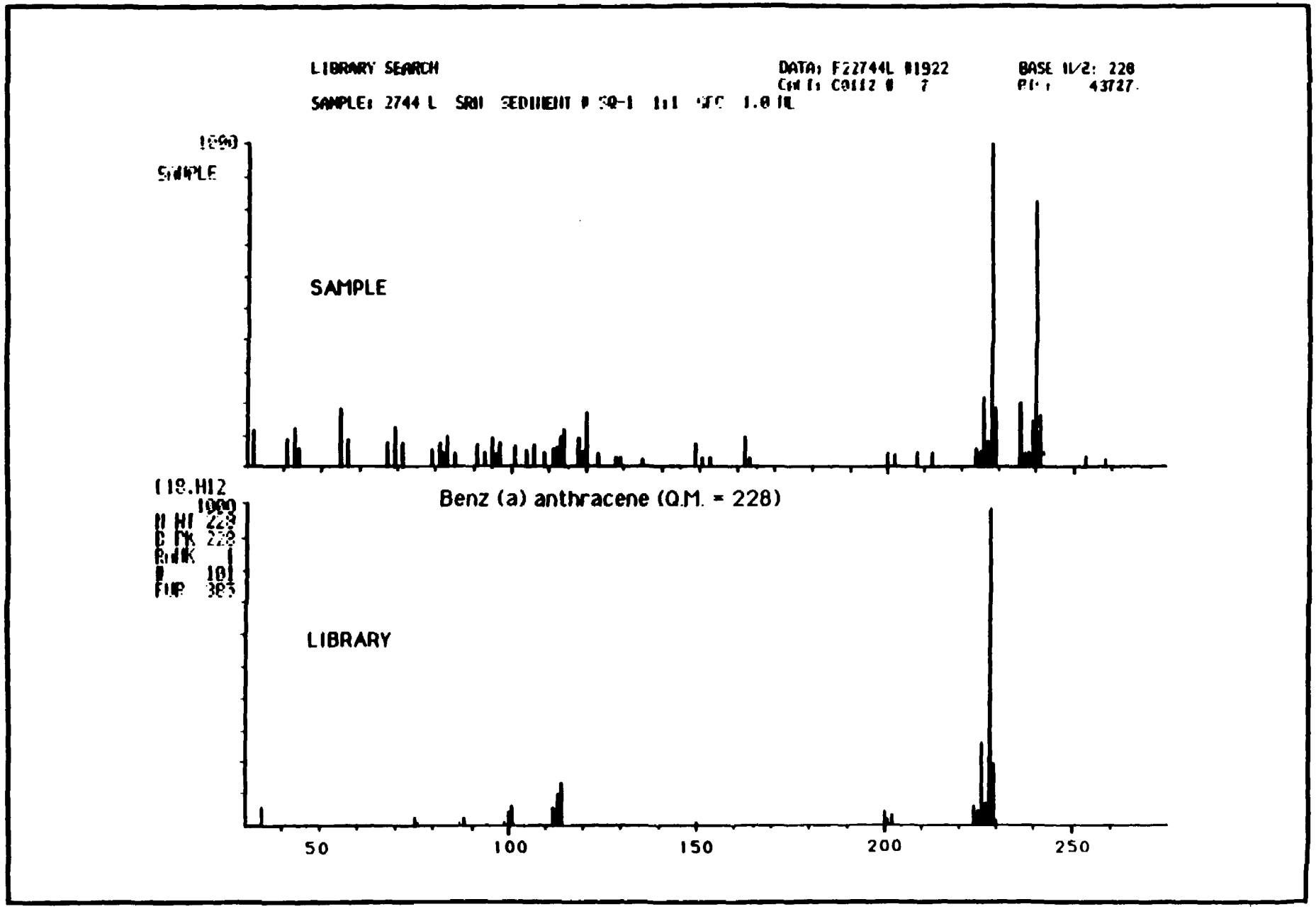

Figure C-1. Example mass spectrum for benz(a)anthracene identified in a sample sediment extract (upper) and authentic spectrum stored in computerized GC/MS library (lower).

elutes from the gas chromatograph. This characteristic ion is called the *quantification ion*. The mass chromatograms for all ions detected can be superimposed into a reconstructed ion chromatogram (RIC), also called a total ion chromatogram. The RIC is a graphic display of the total ionization current resulting from all mass fragments for all compounds detected from the start to the finish of the analysis. The RIC can be compared with the chromatograms produced by other detectors and provides an indication of the relative composition of components in the sample mixture analyzed by GC/MS. The mass spectrometer is a selective detector that allows for the positive identification of many compounds. Other kinds of detectors may be more sensitive in detecting PCBs and other chlorinated compounds.

Gas Chromatography/Electron Capture Detection

Gas chromatography/electron capture detection (GC/ECD) is useful for detecting analytes such as pesticides, PCBs, and other similarly structured chemical compounds that contain chlorine. The ECD measures the total concentration of a chemical in a sample, but it cannot distinguish one individual chemical from others. Verification of individual chemicals is accomplished by comparing the order in which the chemicals appear (called the *elution order*) and the time that passed before they appeared (called the *retention time*) with the elution orders and retention times of certain analytical standards. The identity of a chemical is verified when the elution orders and retention times match on two columns of different stationary phases. This verification technique, called *dual dissimilar column confirmation*, is useful because two chemicals that may have the same elution orders and retention times on one column will have different characteristics on the second column.

Gas Chromatography/Flame Ionization Detection

Gas chromatography/flame ionization detection (GC/FID) can be used to detect organic compounds that can be converted to ions during exposure to flame. This kind of detector is especially sensitive to molecules that contain carbon and hydrogen, just as the GC/ECD is especially sensitive to molecules containing chlorine. Because the GC/FID, like the GC/ECD, cannot distinguish between individual chemicals, dual dissimilar column confirmation must also be performed for each sample analyzed. Related detectors that use flame for analyzing organic samples include the nitrogen flame ionization detector (NFID), which is especially sensitive to nitrogen- and phosphorus-containing molecules, and the flame photometric detector (FPD), which is especially sensitive to organophosphorus pesticides and other compounds containing sulfur.

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PACKED VS. CAPILLARY COLUMNS

Different kinds of separating columns will yield different results. Packed columns have been used routinely in the past for the analysis of PCBs, pesticides, and volatile organic compounds. Packed columns produce chromatograms of fairly low resolution, although the results may be reproducible (i.e., precise). However, a large quantity of the sample extract can be analyzed without overloading the instrument. More exacting analysis is afforded by either megabore capillary or fused silica capillary columns. Pesticides and PCBs can now be routinely analyzed using megabore columns. Analysis of volatile organic compounds can be conducted on capillary columns. However, because the entire sample purge is used for volatile analyses, a packed column with high loading capacity may still be preferred if high resolution is not essential. If project results are dependent on detailed recognition of contaminant mixtures (as is the case with PCBs and toxaphene), laboratories equipped with capillary columns should be selected to perform analytical tasks.

High Pressure Liquid Chromatography

Like gas chromatography, high pressure liquid chromatography (HPLC) is a technique used to separate a complex mixture into its component compounds. The compounds are carried as a liquid through solid absorbent phases and are sensed at the effluent end of the column by a specialized detector sensitive to, for example, ultraviolet, fluorescent, or infrared signals. This technique (described in EPA's laboratory manual *Test Methods for Evaluating Solid Waste* [U.S. EPA 1986a) is useful for analyzing polycyclic aromatic hydrocarbon (PAH) compounds in samples because many interferents on other instruments do not emit ultraviolet or fluorescent spectra, thereby increasing the sensitivity of the ultraviolet/fluorescent detector to many PAH compounds. However, some compounds of interest also do not emit these characteristic spectra. It is for this reason that EPA's Contract Laboratory Program statement of work for organic analysis recommends GC/MS over HPLC using ultraviolet/fluorescent detectors. However, HPLC can be useful as a way to screen samples for PAH contamination. Because it removes some interferents and separates the sample into components that can be individually collected and analyzed, HPLC can also be used as a powerful cleanup technique.

Atomic Absorption Spectrometry

Two basic methods of spectrometry are commonly used to identify and measure concentrations of metals in a sample. Using the first method, atomic absorption spectrometry, the digested sample is first vaporized and then exposed to a light source emitting a spectrum characteristic of the target analyte. A portion of the light is absorbed by the analyte in the sample. The remaining light is measured by a photoelectric detector and assigned a numerical value. Because the intensity of light absorbed by the sample is proportional to the quantity of the target analyte present in the light's path,

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this value represents the concentration of a metal in the sample. Several different forms of atomic absorption are frequently used:

- Graphite furnace atomic absorption spectrometry (GFAA) determinations are completed as single element analyses. With this technique, sample digestates are vaporized in an electrically heated graphite furnace. The furnace is designed to gradually heat the digestates in several stages, allowing an experienced analyst to remove unwanted matrix components and select the optimum final temperature for the metal being analyzed. The major advantage of this technique is that it affords extremely low detection limits, which are particularly essential in the analysis of arsenic, cadmium, selenium, or lead. Samples must be relatively clean for GFAA to produce usable data.

- Hydride generation atomic absorption (HGAA) spectrometry uses a chemical reaction to separate arsenic or selenium selectively from a sample digestate. This technique removes these two elements from the sample matrix, minimizing interferences and improving instrument sensitivity.

- Cold vapor atomic absorption (CVAA) spectrometry uses a chemical reaction to release mercury from the digestate as a vapor, which is then analyzed by atomic absorption. This method should be used whenever analysis of mercury in samples is required.

- Flame atomic absorption (FLAA) spectrometry determinations are normally completed as single element analyses, following exposure of the vaporized samples to either a nitrous oxide/acetylene or air/acetylene flame. Data produced using this technique are relatively free of interferents, however instrument sensitivity is not as great as with other forms of atomic absorption.

Inductively Coupled Plasma-Atomic Emission Spectrometry

The second widely used and cost-effective form of spectrometry is inductively coupled plasma-atomic emission spectrometry (ICP). Using ICP, the digested sample is first turned into an aerosol, then subjected to extremely high temperatures within the instrument. The high temperature ionizes the atoms, which produce ionic emission spectra uniquely characteristic of specific metals. The wavelengths of these spectra can then be used to identify one or many different metals in the sample, while the intensity of light can be used to determine metals concentrations.

The primary advantage of ICP is that it allows simultaneous or rapid sequential determination of many different metals, reducing the time and cost of individual metals analyses. The primary disadvantage of ICP, however, is its lower degree of sensitivity. The detection limit associated with ICP analysis is often higher than the detection limit that can be obtained through the use of a graphite furnace or several other forms of atomic

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absorption spectrometry. Although all ICP instruments use high-resolution optics and background corrections to minimize interferences, analysis for traces of metals in the presence of a large excess of a single metal can be difficult. Spectrometric data are reliable only if the analyte concentrations in the digestate are 5–10 times greater than the instrument detection limit. When concentrations are lower than this value for ICP analysis (as is often the case, for example, with samples containing arsenic or lead), then GFAA should be used. A relatively new method of detection is the use of combined inductively coupled plasma-mass spectrometry (ICP/MS), which not only allows for simultaneous determination of many different metals, but can also achieve lower detection limits comparable to those using graphite furnace techniques.

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APPENDIX D

Example Standard Operating Procedures

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General Standard Operating Procedures

STANDARD OPERATING PROCEDURE
SAMPLE PACKAGING AND SHIPPING

For samples collected during field operations that will be classified as "environmental." Specific sample packaging and shipping requirements are described below.

ENVIRONMENTAL SAMPLES

All samples identified as Environmental Samples should be packaged and/or shipped utilizing the following procedures.

Packaging

1. Place samples into a strong container, such as a lined cooler or a U.S. Department of Transportation (DOT)-approved fiberboard box. The inside of the container should be lined with a polyethylene bag. Wrap glass jars with bubble-pack and surround the samples with noncombustible, absorbent, cushioning material for stability during transport.

2. Seal the large polyethylene bag with two chain-of-custody seals.

3. Place the laboratory/sampling (including chain-of-custody) paperwork in a large envelope and tape it to the inside lid of the shipping container (see Shipping Papers).

4. Close and seal the outside container with several chain-of-custody seals. Tape it shut using fiberglass tape.

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Marking/Labeling

1. Use abbreviations only where specified.

2. Place the following information, either hand-printed or in label form, on the outside container:

   - Laboratory name and address

   - Return name and address.

3. Print "Environmental Samples" and "This End Up" clearly on top of the shipping container. Put upward pointing arrows on all four sides of the container. No other marking or labeling is required.

Shipping Papers

No DOT shipping papers are required. The following sample custody and analytical laboratory request forms should accompany the sample shipment. These documents should be taped to the inside lid of the outside sample container:

- Chain-of-custody form

- Sample analytical request form

- Sample packing list.

See the quality assurance project plan for procedures in filling out these forms.

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STANDARD OPERATING PROCEDURE

EQUIPMENT DECONTAMINATION

The purpose of this standard operating procedure (SOP) is to define decontamination procedures for field equipment used for collecting soil, sediment, and water samples. Techniques for ridding equipment of both metals and organic contaminants are discussed. Sampling equipment is decontaminated between each sampling event to avoid cross contamination of samples and to help maintain a healthy working environment. Protective clothing is worn by all field technicians during sampling and decontamination as described in the health and safety plan.

It is the responsibility of the field sampling coordinator to assure that proper decontamination procedures are followed and that all waste materials produced by decontamination are properly managed. It is the responsibility of the project safety officer to draft and enforce safety measures that provide the best protection for all persons involved directly with sampling or decontamination. All subcontractors (e.g., drilling contractors) are required to follow the decontamination procedures specified in the contract, the health and safety plan, and this SOP. Individuals involved in sampling and/or decontamination are responsible for maintaining a clean working environment and ensuring that contaminants are not introduced to the environment.

All equipment will be decontaminated using a series of washes and rinses designed to remove materials of interest without leaving residues that will in any way interfere with analysis of the samples taken with that equipment. In addition, the decontamination site will be set up at a location separate from the sampling area in order to isolate these two activities.

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Field equipment blanks will be taken at a frequency of 5 percent of samples and sent to the laboratory(s) for analysis along with the regular samples. These blanks will serve as a quality assurance indicator of possible cross contamination of samples. When feasible, samples to be taken with the same equipment will be taken in order from lowest to highest suspected contaminant levels to minimize the chances of cross contamination.

The following is a list of materials that are required on site to support decontamination. The quantity and actual use of each item will be dependent on the overall size and nature of the sampling effort.

- Cleaning liquids and dispensers: soap and/or phosphate free detergent solutions, tap water, methanol, 10 percent nitric acid, distilled/deionized water
- Personal safety gear as defined in the project health and safety plan
- Chemical-free paper towels and/or tissues
- Powder-free disposable latex gloves
- Waste storage containers: drums, boxes, plastic bags
- Plastic ground cloth on which to lay clean equipment
- Cleaning containers: plastic and/or galvanized steel tubs and buckets
- Cleaning brushes with non-contaminating stiff bristles
- Steam cleaning apparatus (supplied by drilling contractor).

The materials used in decontamination activities are located a minimum of 15–30 feet downwind of the sampling site as designated by the task leader. Decontamination will be carried out before moving to the next sampling site to avoid transporting contaminants.

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PROCEDURES

Regardless of the type of contamination that requires removal, the basic steps involved are the same. Procedures unique to organic, metal, and organic/metal combined contamination are discussed in their respective sections that follow.

Step 1: Gross Removal of Material

Steam Cleaning

Depending on the availability of apparatus (e.g., drilling operations), steam cleaning combined with brushing is the preferred method of initial material removal. Using steam alone introduces little further contamination, and is a very efficient way of removing materials. Equipment such as spatulas, split spoons, and drill flights are placed in and/or suspended over tubs that catch contaminated wash waters for proper disposal.

Detergent Wash

In cases where steam apparatus is not available, a phosphate free detergent wash and tap water rinse may be used. A detergent bath is formulated in a tub large enough to hold the equipment to be washed leaving enough volume to hold the tap water rinses. All material is brushed from the equipment into the tub. The equipment is rinsed with tap water while suspended over the wash tub. Because detergents can contain low levels of interfering contaminants for both organic and metals analysis, the thoroughness of the final rinse in this step is of utmost importance. When the analyte levels in the samples to be taken by the decontaminated equipment are suspected to be very low (e.g., background level), it is recommended that the detergent wash be replaced by a distilled water wash or steam cleaning when available, followed by a decontamination equipment blank as described below.

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Step 2: Specific Contaminant Removal

Organic Contaminants

For removal of general organic contaminants, the solvent of choice is methanol because a) it dissolves all contaminants of concern and b) it is miscible with water which means it can be removed with a water rinse. The equipment is suspended over a tub and rinsed from the top down with high purity methanol delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Metal Contaminants

Metals require acid solvents for efficient removal. Nitric acid is the acid of choice because of its ability to dissolve all of the metals of concern. The equipment is suspended over a tub and rinsed from the top down with 10 percent nitric acid delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Combined Organic/Metals Contaminants

When equipment will be used to take samples that will be analyzed for both metal and organic constituents, the acid rinse is performed followed by the methanol rinse, each as described above. Due to the difficulty in obtaining organics free acids, and the ease of obtaining metals free methanol, the order of the two rinses must not be reversed.

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Step 3: Final Distilled/Deionized Water Rinse

A final rinse with distilled/deionized water is carried out last to remove the contaminant specific solvents (i.e., nitric acid and/or methanol). Because these solvents may themselves interfere with sample analyses, this step is very important and must be carried out thoroughly. The equipment is suspended over a waste tub, and rinsed from the top down with distilled/deionized water delivered by pump or squirt bottle, depending on equipment size. In the case of metals decontamination, a simple pH monitoring technique (e.g., pH paper) may be used to monitor rinse water in determining rinse completion.

Step 4: Air Dry

Before an equipment blank is taken, the equipment is laid out on a clean plastic ground cloth and allowed to dry. The equipment should be protected from gross contamination during the drying process.

Equipment Blanks

Equipment blanks are taken between selected samplings as described in the Sampling and Analysis Plan. Equipment is rinsed with distilled water that is subsequently collected in a sample container. The rinsate sample is then labeled and shipped as a blind sample to the laboratory(s) with regular samples. One blank is created in this way for each analysis to be performed on samples taken with this equipment unless otherwise stated in the quality assurance plan. The equipment should be protected from contamination between the time the blank is taken and the time the next sample is collected.

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Specific Analytical Standard Operating Procedures

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ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR COLUMN CHROMATOGRAPHY OF SEMIVOLATILE ORGANIC ANALYTES IN SEDIMENT AND TISSUE EXTRACTS
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the preparation of columns for the cleanup and chemical class separation of semi-volatile organic compounds from marine samples. The extract fractions will be analyzed by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

9.5-mm ID X 45-cm glass chromatography column with 200 ml reservoir

Apparatus for determining weight
- Top-loading balance capable of weighing to 0.01 g

Turbo-Vap (Zymark) apparatus, with heated water bath maintained at 25-35° C
- Glass Turbo-Vap flasks, 200 ml
- Nitrogen gas, compressed, 99.9% pure

Tumbler, ball-mill

Glass graduated cylinders, 100- and 500-ml

Glass beakers, 50-ml

Borosilicate glass vials with Teflon-lined screw caps, 2-ml

Micropipets, solvent rinsed or muffled at 400°C

Reagents
- Pentane, pesticide grade or equivalent
- Methylene Chloride (CH_2Cl_2), pesticide grade or equivalent
- Hexane, pesticide grade or equivalent
- Heptane, pesticide grade or equivalent
- Deionized water, pentane-extracted

BioSil A silicic acid, 100-200 mesh
Glass wool, silanized

3.0 METHODS

3.1 Silica gel preparation

3.1.1 Approximately 150 grams of fully activated silica gel is accurately weighed and transferred to a glass jar.

3.1.2 The silica gel is deactivated by adding 7.5% (weight basis) of pentane-extracted deionized water. The water is weighed accurately and an appropriate amount is added dropwise, ~ 1 ml at a time, to the silica gel. After each water addition, the jar is hand-shaken vigorously.

3.1.3 The glass jar is then placed on a ball-mill tumbler and allowed to tumble overnight.

3.1.4 After tumbling, the jar is removed from the tumbler. The silica gel is stored tightly sealed in the jar at room temperature until use.

3.2 Column preparation

3.2.1 The glass columns are set up in ring stands in a fume hood.

3.2.2 Glass wool, sufficient to create a 1 cm thick plug in the column is placed into the reservoir of the column. A glass rod is used to push the glass wool to the bottom of the column.

3.2.3 11.5 g of the 7.5% deactivated silica gel is weighed out in a beaker. Approximately 30 ml of CH_2Cl_2 is added to the beaker to form a slurry. The slurry is then carefully poured into the column. The beaker is rinsed with additional CH_2Cl_2, as are the inner walls of the reservoir to ensure all silica is introduced to the column. The total volume of CH_2Cl_2 should be approximately 50 ml.

3.2.4 The column is allowed to drip, and the eluate is collected and discarded. When the level of the CH_2Cl_2 just reaches the top of the silica gel, 50 ml of pentane is slowly added to the column. This eluate is also collected and discarded.

3.3 Chemical class separations

3.3.1 The sample extract is introduced to the column just as the pentane rinse

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level reaches the silica gel. The vial is then rinsed with an additional 1 ml of pentane which is also introduced to the column just before the silica gel is exposed. The eluate is collected in a clean round bottom flask.

3.3.2 As the sample rinse level reaches the silica gel, 55 ml of pentane is added to the column. The eluate is collected as the F-1 fraction in a clean Turbo-Vap flask.

3.3.3 As the pentane level reaches the top of the silica, 36 ml of 70:30 pentane:methylene chloride is introduced to the column. The F-2 fraction is collected in a separate Turbo-Vap flask from the F-1 fraction. After collection, the flasks are kept tightly capped with aluminum foil. At no time should the column flow rate exceed 6 ml/min.

3.3.4 After the F-2 fraction has been collected from the column, the flasks are placed in the Turbo-Vap. The apparatus is turned on and Nitrogen gas is introduced to the flasks. The solvent is reduced to approximately 1 ml. The samples are then solvent-exchanged to heptane and concentrated to about 1 ml.

3.3.5 The fractions are then transferred to borosilicate glass vials fitted with Teflon-lined screw caps for storage until analysis.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

4.1 Silica Gel Testing

4.1.1 Silica Gel is verified to separate compound classes using the silica gel testing SOP.

4.2 Method Blanks

4.2.1 Method (procedural) blanks are included in each sample set to provide an estimate of contamination from the reagents.

4.3 Internal Standard Recovery

4.3.1 PCB103 is added to final column fractions to calculate recovery of the internal standard.

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ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR ANALYSIS OF PAHs BY GC/MS
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard procedure for analyzing marine environmental samples for PAHs using GC/MS in electron impact/positive ion mode.

2.0 EQUIPMENT

HP Model 5890 Series II Gas Chromatograph
HP Model 5971A Mass Selective Detector
HP Model 7673 Autosampler
HP MS Chemstation (DOS Series) Software
IBM Compatible Personal Computer

3.0 OPERATION

A. Instrument Parameters

Column: 60 m x 0.25 mm ID x 0.25 um DB-5 (J&W Scientific)
Carrier: Helium at 25 psi; 0.8-1.0 ml/min
Injector: 270 degrees C; splitless mode, purge on at 0.8 min
Interface: 300 degrees C; direct, source 200 degrees C
Temperature Program: 1 min, 40 deg; 20 deg/min to 120 deg; 10 deg/min to 310 deg and hold 16 min. This is suitable for Polycyclic Aromatic Hydrocarbons.
MS Parameters: Set by Autotune using PFTBA as the calibration compound; Manual Tune is then used to force the 131 and 219 abundances to 20 to 40 percent of the 69 base peak; the electron multiplier is then set to meet the requirements of the particular method. This procedure is done in a series of loops, as new parameter settings for a specific lens will affect the behavior of the others.

B. Daily Performance Checks

1) Adequate DFTPP spectrum (see attached criteria), based on a 50 ng injection.
2) Calibration Check - results for a mid-level standard must be within 25 percent of the true value for a single target compound; the average error for all compounds in the method must be less than 15 percent.

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C. Calibration

The calibration method is a 5 point, internal standard, least squares fit, forced through the origin. The levels are chosen to cover a range from 4 to 10 times the instrument detection limit for the lowest point, up to the point at which saturation and/or non-linear behavior is observed. For PAHs in marine sediment or tissue, the current levels are 1.0, 5.0, 10.0, 15.0, and 20.0 ng/ul. Acceptance criteria for each level are the same as listed for the daily check.

D. Sample Analysis

A 250 uL aliquot of the sample extract is blown down to 20-25 uL with nitrogen or helium. If required, an internal injection standard is added (4-chloro-p-terphenyl). Once the daily performance checks are satisfied, the extracts are queued up on the autosampler. Periodic solvent blanks, standards, etc. are inserted at the judgement of the analyst.

E. Identification

Compounds are identified by monitoring a characteristic ion within a 12 second retention time window. Additional ions may be monitored at the discretion of the analyst. Confirmation is obtained by inspection of the full mass spectrum.

4.0 QUALITY ASSURANCE

A. Standard Reference Materials, Blanks, Calibration Checks

Standard reference materials are prepared along with each batch of samples. Calibration standards are verified with independently prepared control standards.

B. Method Detection Limits

Method detection limits are determined independently for a given sample matrix. Instrument detection limits are generally in the 6-10 pg per injection range, which usually corresponds to a 3-5 ng/g (ppb) method detection limit range in samples.

5.0 TROUBLESHOOTING AND MAINTENANCE

On a daily basis, the injection port and liner are cleaned; the septum and glass wool in the liner are changed. It is periodically necessary to break off the first few inches of the column (this is done daily for heavy workloads of dirty samples; compounds most affected are the high molecular weight compounds).

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DFTPP ACCEPTANCE CRITERIA (by CLP 3/90)

Mass	Abundance
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Less than mass 443
442	40-60% of mass 198
443	17-23% of mass 442

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ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR GAS CHROMATOGRAPHIC ANALYSIS OF PCBs AND CHLORINATED PESTICIDES
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard procedure for analyzing marine environmental samples for polychlorinated biphenyls (PCBs) and chlorinated hydrocarbon pesticides using gas chromatography and electron capture detectors.

2.0 EQUIPMENT USED

Hewlett Packard 5890 Gas Chromatographs equipped with electron capture detectors (Ni 63), automatic samplers, 30 m DB-5 fused silica capillary columns (0.25 μ film thickness, 0.25 mm i.d.). Perkin-Elmer/Nelson software (ACCESS*CHROM) provides for collection and storage of raw chromatographic data, and for selection and quantitation of analyte peaks. Ultra high purity helium and 95/5% Argon/Methane gases are used as the carrier and auxiliary gas respectively.

3.0 OPERATION

3.1 Instrument checks made prior to data collection

3.1.1 Gas supply

3.1.1.1 Check gas cylinder pressures. Replace tank if pressure is less than 100 psig.

3.1.1.2 Check head pressure gauge on front panel of instrument. Gauge should read 18 psig; adjust to correct setting if reading is high; check for leaks if pressure is low. This setting provides for a carrier gas flow of approximately 1.5 ml/min.

3.1.1.3 Replace injection port septum. Check septum nut and column fittings for leaks with leak detector and tighten as necessary.

3.1.1.4 Check the auxiliary gas flow. A flow of 35 ml/min is required.

3.1.1.5 Check septum purge and split flows. Adjust to 1 and 35 ml/min, respectively, as necessary.

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3.1.2 Instrument output signal

3.1.2.1 Display the analog output signal from the detector on the LED panel of the GC. Record the value in the instrument log book, and check for consistency with previous readings. On instruments with dual detectors, ensure the signal is correctly assigned to the detector selected for the analysis.

3.1.3 Instrument operating parameters

3.1.3.1 Temperature programs and run times are stored as workfiles in each GC's integrator. The following conditions are required for the analysis of PCBs and pesticides:

Injection port temperature	275°C
Detector temperature	325°C
Initial column temperature	100°C
Initial hold time	1 min
Rate 1	5°C/min
Ramp 1 final temperature	140°C
Ramp 1 hold time	1 min
Rate 2	1.5°C/min
Ramp 2 final temperature	230°C
Ramp 2 hold time	20 min
Rate 3	10°C/min
Final column temperature	300°C
Final hold time	5 min
Stop time	100 min
Injection port purge open time	1 min

3.1.3.2 Load an appropriate workfile into the integrator.

3.1.3.3 Enter the autosampler parameters into the integrator via Option 11. Indicate which injection port is being used, the number and positions of the samples in the autosampler tray, the number of injections per bottle, and the amount injected (1 ul).

3.1.3.4 Check the signal assignments and levels again. If they are correct, store the workfile in the integrator.

3.2 Data system setup

3.2.1 Scheduling of standards and samples

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3.2.1.1 Setting up the instrument queue is accomplished by following instructions laid out in the Perkin-Elmer Nelson manual.

3.2.1.2 Order the samples, standards, and rinses according to the following guidelines:

-place hexane rinses before and after standards
-bracket groups of no more than five (5) samples with standards.
-arrange multiple level standards so that a high and a low standard precede as well as follow samples
-procedural and field blanks should be run prior to samples to minimize risk of carryover contamination.

3.2.1.3 Type in sample weight and internal standard amounts for each sample to be used in final concentration calculations. Double check all manually entered values for accuracy.

3.3 Instrument startup and data collection

3.3.1 After the instrument has been scheduled, arrange the samples and standards to be run in the autosampler trays. Check the order for accuracy against a copy of the queue. Load the trays into the autosampler.

3.3.2 Visually recheck tank regulator gauges and instrument settings to ensure proper settings.

3.3.3 Start GC operation and data collection by pressing 'start' on the integrator.

3.4 Peak identification and quantitation

3.4.1 Peak identification is accomplished by automated routines. Identifications are based on comparison of retention times of actual standards to unknown peaks. Multilevel standards are calibrated to generate a linear regression curve of response according to the manufacturer's instructions. After a calibration curve has been generated, the samples are analyzed. Analytes are quantitated based on the peak areas for the analytes and internal standard, the amount of the internal standard, and the response factors generated from the calibration curve. Chromatograms and data reports are generated for each sample and standard.

4.0 QUALITY ASSURANCE

4.1 Chromatograms of standards are compared to posted references. Peak identifications, resolution and shapes are inspected. Calculated standard amounts are checked for accuracy and documented. Other abnormalities, such as spurious or extra peaks, rising or falling baselines, and negative spiking are examined. Response factors

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and overall instrument response are compared to previous runs and documented. Blanks are checked for the presence of interferences or analytes of interest. Unknown samples are compared to standards to verify peak identifications.

5.0 TROUBLESHOOTING

5.1 Refer to the ERLN GC Troubleshooting notebook, the manufacturer's manuals, or to experienced personnel for guidance in troubleshooting the GCs.

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ERLN CHEMISTRY GROUP STANDARD OPERATING PROCEDURE FOR INSTRUMENTAL ANALYSIS OF METALS IN SEDIMENT AND TISSUE EXTRACTS

1.0 OBJECTIVES

The objective of this document is to outline the proper sample preparation and instrumental parameters for the analysis of trace metals in marine sediment or tissue acid digests.

2.0 MATERIALS AND EQUIPMENT

Atomic Absorption Spectrometer or Inductively Coupled Plasma Atomic Emission Spectrometer

Reagent grade Instra-Analyzed concentrated HNO_3 for trace metal analysis (diluted to 2M concentration)

3.0 METHODS

3.1 Standard Calibration

3.1.1 Estimate or determine the range of concentrations that exist within the sample analytes. This may require scanning several samples prior to standard calibration in order to approximate the range of absorbances (AA) or emission intensities (ICP) produced from the samples.

3.1.2 Prepare multiple calibration standards that bracket the expected range of sample analyte concentrations. The composition of the standard matrices (i.e. acid strength and salt content) should match that in the samples as closely as possible.

3.1.3 Analyze the standards and calculate calibration equations by regression (linear or polynomial) of standard concentrations against measured standard absorbances or intensities.

3.2 Sample Dilutions

3.2.1 In section 3.1 the expected range of sample concentrations is determined. If sample concentrations exceed the upper limit of the chosen analytical technique, then the sample analytes will need to be diluted to fall within the range of standard concentrations. Sample diluent should be of the same acid composition and strength present in the sample analytes (Keep close record of the sample dilutions so that raw analytical concentrations can be dilution-corrected).

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4.0 ANALYSIS

4.1 Sample Analysis (Unknown Concentrations)

4.1.1 Analyze the samples and record the absorbances (AA) or emission intensities (ICP).

4.1.2 Triplicate readings should be made for every element.

4.1.3 After approximately 10 (AA) or 20 (ICP) samples, several calibration standards should be re-analyzed to determine instrumental drift.

4.2 Concentration Calculation

4.2.1 Calculate sample concentrations by applying the calibration equation obtained from the standard curve to the measured sample signals (absorbances or intensities). Calculate the mean and standard deviation of the individually calculated sample concentrations.

4.3 Dilution Correction

4.3.1 Calculated analyte concentrations must be dilution- corrected to obtain the true metal concentration present in the sample. The analyte concentration, in ug/ml, is converted to ug/g dry sample by inputing the sample prep. information into the following equation:

$$\text{Sed. Conc. (ug/g dry sed.)} = \frac{\text{Analyte conc.(ug/ml)} \times \text{Acid volume (ml.)}}{\text{dry sed. wt. (g)}}$$

5.0 QUALITY CONTROL

5.1 Determination of Analytical Accuracy (Calibration check)

5.1.1 Analyze several standards as unknown samples to check the accuracy of the standard curve regression. Recoveries should be within 10% of the standard concentration.

5.1.2 Analyze a solution of known and/or certified concentration, prepared independently from the calibration standards, to determine the daily analytical fluctuation. Recoveries should be within 10% of the certified concentration.

5.2 Standard Additions (Spike Additions)

5.2.1 Standard additions are required to investigate instrumental interferences arising from differing sample solution matrices.

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5.2.2 Select a sample whose concentrations can be matched fairly closely with a dilution of a calibration standard.

5.2.3 Prepare an acid spike (a dilution of a calibration standard) in the same acid matrix as the samples. Try to match spike concentrations as closely as possible with the sample chosen.

5.2.4 Prepare a sample spike by removing a second sample aliquot and adding the same amount of calibration standard as was used in the acid spike. The total volume of sample spike should also be equal to the total volume of acid used in the acid spike.

5.2.5 Analyze the sample, acid spike and sample spike as unknown samples.

5.2.6 Calculate the spike recovery using the following equation:

$$R(\%) = \frac{C_{SAMPLE\ SPIKE} - C_{SAMPLE}}{C_{ACID\ SPIKE}}$$

5.2.7 Acceptable spike recoveries fall between 80-120%

5.2.8 One out of every 20 samples should be chosen for a standard addition.

6.0 DETECTION LIMITS

6.1 Instrument Detection Limits

6.1.1 Instrument detection limits are determined as the concentration equivalent to a signal three times the standard deviation of a blank. The limits should either be determined previously for given instrumental conditions or as part of the instrumental data analysis, and should be comparable to those listed below:

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	ICP (ug/ml)	GFAA (ug/L)
Cu	.020	1.0
Zn	.005	0.1
Cr	.020	1.0
Pb	.050	3.0
Ni	.050	2.0
Mn	.010	0.5
Fe	.020	2.0
Cd	.005	0.5
Al	.075	
Sn	.050	2.0
Sb	.100	2.0
As	.100	2.0
Ag	.020	0.5

6.1.2 Sample Detection Limits, assuming a dry weight of 2 grams and a total volume of 50 mls. (ie. sediment ultrasonic extraction method), are 25 times higher than the instrument D.L.'s. Method detection limits should be calculated following the rigorous statistical procedure detailed in 40 CFR Part 136.

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ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR SEDIMENT EXTRACTION OF SEMIVOLATILE ORGANIC ANALYTES
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the extraction of semi-volatile organic compounds from marine sediment samples. The extracts will be further cleaned up by silica gel chromatography procedures prior to analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

Apparatus for homogenizing sediment
- Wrist-action shaker
  - 100 ml glass centrifuge tubes

Apparatus for determining weight and dry weight
- Top-loading balance capable of weighing to 0.01 g
- Aluminum weighing pans
- Stainless steel spatula

Drying oven maintained at 105-120°C

Turbo-Vap (Zymark) apparatus, with heated water maintained at 25-35°C
- Nitrogen gas, compressed, 99.9% pure
- Glass Turbo-Vap flasks, 200 ml

Glass graduated cylinders, 100- and 500-ml

Erlenmeyer flasks, 250 ml

Microliter syringes or micropipets, solvent rinsed

Borosilicate glass vials with Teflon-lined screw caps, 2-ml

Reagents
- Methylene chloride, pesticide grade or equivalent
- Deionized water, pentane-extracted
- Acetone, pesticide grade or equivalent
- Sodium sulfate-anhydrous, reagent grade. Heated to 400°C for at least 4 hours, then cooled and stored in a tightly sealed glass container at room temperature.
- Internal Standards, to be added to each sample prior to extraction.

3.0 METHODS

3.1 Find the correct caps for each centrifuge tube to be used by filling them with

approximately 25 mls of methylene chloride, putting the caps on and rolling the tube on the lab bench on a paper towel and look for leaks. Once the correct tubes and caps have been matched, weigh approximately 10.0 g of homogenized sample into a solvent rinsed centrifuge tube. Homogenization is accomplished by physical mixing of the sediment with stainless steel or Teflon coated utensils, or by a polyethylene propeller attached to an electric drill. The amount of sample may be adjusted based on expected contaminant concentrations or detection limits required. Weigh approximately 2.0 grams into a preweighed aluminum pan for dry/wet determination.

3.2 Add Internal Standards as required: CB198 for PCB analysis, 2,5-dichloro-m-terphenyl for pesticides, and d12 Benzo(a)anthracene/ d10 Phenanthrene mix for PAHs. The amount of IS added is dependent on the expected contaminant concentrations and should be equivalent to those concentrations.

3.3 Add 30 g Sodium sulfate and mix with a teflon coated spatula very well. Then add 50 ml 20:80 acetone:methylene chloride.

3.4 Seal the centrifuge tubes with teflon tape and caps, and shake ~15 hrs. (overnight). Shake tubes at approximately a 60° angle, at an intensity setting of "5". Centrifuge for 20 minutes at 1750 rpm and pour off the supernatant into an erlenmeyer flask.

3.5 Add 50 ml of 20:80 acetone:methylene chloride, seal and shake as above for ~6 hrs. Centrifuge for 20 minutes at 1750 rpm and add the supernatant to the erlenmeyer flask. Add some additional sodium sulfate to the combined extracts to ensure all water is excluded.

3.6 Gravity filter the extract through a pre-rinsed (methylene chloride) glass fiber filter. Rinse the erlenmeyer 2 x with methylene chloride, and the filter itself once. Collect the filtrate in a clean rinsed 200 ml Turbo-Vap tube. Place the flask into the Turbo-Vap apparatus, and turn on the unit. Open the valve on the nitrogen tank and adjust the regulator to ensure a pressure of 15 psi. Reduce the sample volume to approximately 1 ml, with solvent exchange to pentane.

3.9 Adjust the volume to 1 ml with hexane.

3.10 Fractionate the sample following the Column Chromatography SOP.

4.0 OPTIONAL CLEANUP PROCEDURES

Activated copper powder (activated by the addition of 8 M hydrochloric acid and rinsed with the following solvents in succession: deionized water, methanol, methylene chloride, and hexane) may be added to the extract to remove any free elemental sulfur. The copper is added until the formation of black copper sulfide no longer occurs.

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5.0 QUALITY ASSURANCE/QUALITY CONTROL

5.1 Standard Reference Materials

5.1.1 A certified SRM is prepared with each batch of samples to validate analytical recovery. Results are compared to certified concentrations and corrective action is required if the accuracy is outside of the required specifications.

5.1.2 SRMs should be prepared in the exact same manner as the unknowns.

5.2 Analytical Reproducibility

5.2.1 Replicate samples should be prepared to assess the reproducibility of the extraction procedure.

5.2.2 For every batch of samples, one sample should be chosen to extract and analyze in triplicate. Deviation between replicate samples should be <30%.

5.3 Procedural Blanks

5.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify the absence of contamination of the method.

5.3.2 Trace amounts of analytes in the blanks (less than three times the method detection limit) may be ignored and have no effect on the subsequent sample analyses, but samples should be rejected if significant concentrations (greater than five times the MDL) are present in procedural blanks.

5.3.3 One blank should be prepared for each batch of samples (minimum frequency of 5%).

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ERLN CHEMISTRY GROUP STANDARD OPERATING PROCEDURE FOR DIGESTION OF MARINE ORGANISM SAMPLES FOR METALS ANALYSIS

1.0 OBJECTIVES

The objective of this document is to establish the standard operating procedure for the total digestion of marine tissue samples. Sample extracts are routinely analyzed by Flame Atomic Absorption Spectrometry (FAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

2.0 MATERIALS AND EQUIPMENT

Top-loading balance (0.01 gram precision)
Vacuum Freeze Dryer
CEM Microwave Digestion System (Including 100 ml. Teflon vessel liners and pressure control capability)
50 ml. class A volumetric flasks
60 ml. polyethylene screw-cap bottles
Instra-Analyzed grade concentrated HNO_3 for trace metal analysis (70-71 %)
Hydrogen Peroxide - H_2O_2 (30%)
Vacuum filtering apparatus with Whatman 42 filter paper

3.0 METHODS

3.1 Sample Preparation

3.1.1 Organism samples should be thawed, and handled only with plastic or stainless steel utensils. Where neccessary, organism tissues should be homogenized. If chromium or nickel is to be analyzed in the samples, the homogenizer tip should be constructed of titanium to avoid contamination of sample tissues.

3.1.2 Obtain the tare weight of labeled, acid-washed 100 ml. Teflon microwave digestion vessel liners.

3.1.3 Weigh approximately 3-5 grams wet tissue into each vessel (~0.5 grams dry). Obtain the wet gross weight of each tube.

3.1.4 Freeze dry samples and obtain the dry gross weight for each sample. Subtract the tare weight and record the weight of dry tissue in each tube.

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3.2 Closed Vessel Microwave Digestion (1st Stage)

3.2.1 Add 10 ml. of concentrated HNO_3 (70-71 %) to each digestion vessel.

3.2.2 Make sure the tissue sample is fully saturated and allow to sit for a minimum of 1 hour, or until all foaming subsides.

3.2.3 Place each liner into a microwave vessel.

3.2.4 Insert a pressure relief membrane into each cap assembly and place on top of the vessels. (use the modified cap assembly for the vessel to be used for pressure monitoring)

3.2.5 Place a top on each vessel and hand tighten.

3.2.6 Place the vessels into the carousel.

3.2.7 Insert a vent tube into each vessel, place the free end in the center trap, then place the carousel into the oven.

3.2.8 Connect the pressure sensing line to the modified cap assembly. (make sure the valve on the side of the oven is in the "neutral" position)

3.2.9 Program the oven following the parameters below:

STAGE	1	2	3	4	5
%POWER	85	85	85	85	85
PSI	20	40	85	150	190
TIME	15:00	15:00	15:00	15:00	15:00
TAP	5:00	5:00	5:00	5:00	5:00
FAN SPEED	100	100	100	100	100

** Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.2.10 After completion of the program, allow the pressure in the control vessel to drop below 20 PSI, then manually vent the control vessel, remove the pressure sensing line and place the carousel into the fume hood.

3.3 Closed Vessel Microwave Digestion (2nd Stage)

3.3.1 Manually vent each vessel, remove the caps and add 2 ml. of 30% H_2O_2.

3.3.2 Allow the reaction to subside, then reassemble the vessels as described in

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sections 3.2.4-3.2.6.

3.3.3 Place the carousel into the oven and reconnect the pressure sensing line to the control vessel. Check to ensure the exhaust fan is operating.

3.3.5 Program the oven following the parameters below:

STAGE	1	2
%POWER	85	100
PSI	100	100
TIME	15:00	15:00
TAP	5:00	5:00
FAN SPEED	100	100

** Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.3.6 Although the oven is automated, individual tissue samples will react differently, so all steps should be monitored in case venting should occur. If venting does occur, remove the vented vessels and lower the power accordingly.

3.3.7 After completion of the program, allow the vessels to cool in the oven until the pressure in the control vessel is below 20 PSI.

3.3.8 Manually vent the control vessel, then remove the carousel and place in a fume hood until the liquid reaches room temperature.

3.3.9 Remove the vent tubes and manually vent the remaining vessels.

3.4 Sample Filtration

3.4.1 Remove the tops and rinse the lids with deionized water, catching the rinse in the vessel liner.

3.4.2 Add ~15 ml. of deionized water to each vessel.

3.4.3 Using plastic tweezers, place a sheet of Whatman 42 filter paper in a vacuum filtration funnel and wet the paper with 2M HNO_3.

3.4.4 Place a 60 ml. acid-cleaned polyethylene bottle and vacuum gasket under the filter funnel and apply vacuum.

3.4.5 Filter the digested sample through the paper and collect the filtrate in the

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bottle.

3.4.6 Rinse the digestion vessel with deionized water, filter and collect the filtrate in the bottle.

3.4.7 Pour the combined filtrates into a 50 ml. acid-cleaned volumetric flask, and dilute to the mark with deionized water.

3.4.8 Shake the solution thoroughly and transfer back to the acid-cleaned 60 ml. polyethylene bottle. Label the bottle appropriately.

4.0 QUALITY ASSURANCE

4.1 Standard Reference Materials (SRM)

4.1.1 A certified SRM should be prepared with every batch of samples to validate analytical recovery.

4.1.2 SRMs should be prepared in the exact manner as the unknown samples, including drying, even if the material is already dry.

4.1.3 The frequency of SRM preparation should be approximately 1 for every 20 unknown samples prepared.

4.1.4 The outlined extraction technique should yield close to 100% recoveries for organism SRMs, as outlined in the ERLN QA/QC guidelines.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the digestion procedure.

4.2.2 For every 20 samples prepared, one sample should be chosen to digest and analyze in triplicate. The relative standard deviation between replicate analyses should be <20%.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify that contaminants are not present in the reagents and that no contamination has occurred throughout the procedure.

4.3.2 Trace amounts of metals in the blanks can be subtracted from subsequent sample analyses (blank subtraction), but a sample batch should be rejected if concentrations in the blank are >10% of "average" sample concentrations.

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4.3.3 One procedural blank should be prepared for every 20 samples extracted.

ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR TOTAL DIGESTION OF SEDIMENT SAMPLES

1.0 OBJECTIVES

The objective of this document is to establish the standard operating procedure for the total digestion of bulk sediments. Sample digests are routinely analyzed by Flame Atomic Absorption Spectrometry (FAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP).

2.0 MATERIALS AND EQUIPMENT

Top-loading balance (0.01 gram precision)
Vacuum Freeze Dryer
CEM Microwave Digestion System (Including 100 ml. Teflon digestion vessel liners with pressure control capability)
Protective Clothing (Polyethylene apron, Neoprene gloves, Safety goggles, Face shield)
100 ml. class A volumetric flasks
125 ml. polyethylene screw-cap bottles
Instra-Analyzed grade concentrated HNO_3 for trace metal analysis (70-71 %)
Reagent grade concentrated HF (49%)
Reagent grade concentrated HCL (36.5-38%)
Boric Acid (5%) prepared from H_3BO_3 crystals
Deionized water

3.0 METHODS

3.1 Sample Preparation

3.1.1 Sediment samples should be thawed and homogenized with plastic or stainless steel utensils.

3.1.2 Obtain the tare weight of labeled, acid-washed 100 ml. Teflon microwave digestion vessels liners.

3.1.3 Weigh approximately 1.5 grams wet sediment into each vessel (~0.5 grams dry). Obtain the wet gross weight of each liner.

3.1.4 Freeze dry samples and obtain the dry gross weight for each sample. Subtract the tare weight and record the weight of dry sediment in each liner.

3.2 Microwave digestion

** NOTE- Be sure to wear proper safety clothing when working with the concentrated HF.

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3.2.1 Add 5 ml. of concentrated HNO_3 (70-71 %), 4 ml. of concentrated HF (49%) and 1 ml. concentrated HCl (36.5-38%) to the vessel liners.

3.2.2 Make sure the sediment is fully saturated and allow to sit for a minimum of 1 hour.

3.2.3 Place the liners into their corresponding vessels.

3.2.4 Insert a rupture membrane into each lid and secure into place with a cap. Do not overtighten.

3.2.5 Place the vessels into the carousel.

3.2.6 Insert a vent tube into each vessel and place the free end into the center trap.

3.2.7 Attach the pressure sensing line to thhe control vessel, making sure the lever on the side of the oven is in the "neutral" position.

3.2.8 Program the oven following the parameters below:

STAGE	1	2
%POWER	100	100
PSI	120	150
TIME	30:00	15:00
TAP	20:00	10:00
FAN SPEED	100	100

**Note - Power settings are for 12 vessels. If a different # of vessels is desired, subtract or add 5% power per vessel.

3.2.9 Although the oven is automated, individual sediments will react differently, so all steps should be monitored in case venting should occur. If venting does occur, remove the vented vessels and lower the power accordingly.

3.2.10 When the program is finished, allow the pressure in the control vessel to drop below 20 PSI.

3.2.11 Manually vent the control vessel, detach the pressure sensing line and place the carousel in a fume hood.

3.2.12 Remove the vent tubes and vent the remaining vessels manually.

3.2.13 In a fume hood, remove the caps and rinse the lids with deionized water, catching the rinse in the vessel liner.

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3.2.14 Add 30 ml. of 5% Boric acid to each sample.

3.3 Sample Filtration (This step may not be necessary)

3.3.1 Add ~15 ml. of deionized water to each vessel.

3.4.2 Using plastic tweezers, place a sheet of Whatman 42 filter paper in a vacuum filtration funnel and wet the paper with 2M HNO_3.

3.3.3 Place a 120 ml. acid-cleaned polyethylene bottle and vacuum gasket under the filter funnel and apply vacuum.

3.3.4 Filter the digested sample through the paper and collect the filtrate in the bottle.

3.3.5 Rinse the digestion vessel with deionized water, filter and collect the filtrate in the bottle.

3.3.6 Pour the combined filtrates into a 100 ml. acid-cleaned volumetric flask, and dilute to the mark with deionized water.

3.3.7 Shake the solution thoroughly and transfer back to the acid-cleaned 120 ml. polyethylene bottle. Label the bottle appropriately.

3.4 Sample Dilution (Required only if filtration step was omitted)

3.4.1 Transfer the contents of the vessel liner to a clean 100 ml. volumetric flask and rinse the vessel with deionized water, also adding the rinse to the flask.

3.4.2 Dilute to the volume mark with deionized water.

3.4.3 Shake the extracts thoroughly and transfer into acid-cleaned 125 ml. polyethylene screw-cap bottles.

3.4.4 Label the bottles appropriately and store at room temperature until analysis.

4.0 QUALITY ASSURANCE

4.1 Standard Reference Materials (SRMs)

4.1.1 A certified SRM should be prepared with every batch of samples to validate analytical recovery.

4.1.2 SRMs should be prepared in the exact manner as the unknown samples, including drying, even if the material is already dry.

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4.1.3 The frequency of SRM preparation should be approximately 1 for every 20 unknown samples prepared.

4.1.4 The outlined extraction technique should yield close to 100% recoveries for sediment SRMs.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the digestion procedure.

4.2.2 For every 20 samples prepared, one sample should be chosen to digest and analyze in triplicate. The relative standard deviation between replicate analyses should be <20%.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire digestion procedure to verify that contaminants are not present in the reagents and that contamination has not occurred throughout the procedure.

4.3.2 Trace amounts of metals in the blanks can be subtracted from subsequent sample analyses (blank subtraction), but a sample batch should be rejected if concentrations in the blank are >10% of "average" sample concentrations.

4.3.3 One procedural blank should be prepared for every 20 samples digested.

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ERLN CHEMISTRY GROUP
STANDARD OPERATING PROCEDURE FOR TISSUE EXTRACTION OF SEMIVOLATILE ORGANIC ANALYTES
(REVISED FEBRUARY 1993)

1.0 OBJECTIVES

The objective of this document is to define the standard operating procedure for the extraction of semi-volatile organic compounds from marine tissue samples. The extracts will be further cleaned up by silica gel chromatography procedures prior to analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS).

2.0 MATERIALS AND EQUIPMENT

Apparatus for homogenizing tissue
- Brinkman Polytron
- 100- or 150-ml glass centrifuge tubes

Apparatus for determining weight and dry weight
- Top-loading balance capable of weighing to 0.01 g
- Aluminum weighing pans
- Stainless steel spatula

Drying oven maintained at 105-120°C

Turbo-Vap (Zymark) apparatus, with heated water bath maintained at 25-35° C
- Nitrogen gas, compressed, 99.9% pure
- Glass Turbo-vap flasks, 200 ml

Glass graduated cylinders, 100- and 500-ml
Glass separatory funnels, 1 L.
Glass erlenmeyer flasks, 250 and 500 ml.
Borosilicate glass vials with Teflon-lined screw caps, 2-ml

Microliter syringes or micropipets, solvent rinsed

Reagents
- Pentane, pesticide grade or equivalent
- Acetonitrile, pesticide grade or equivalent
- Deionized water, pentane-extracted
- Sodium sulfate-anhydrous, reagent grade. Heated to 400°C for at least 4 hours, then cooled and stored in a tightly-sealed glass container at room

temperature.

Internal Standards, to be added to each sample prior to extraction.

3.0 METHODS

3.1 Weigh approximately 10.0 g of sample into a solvent rinsed centrifuge tube. Weigh approximately 1.0 gram into a preweighed aluminum pan for dry/wet determination.

3.2 Add Internal Standards as required: CB198 for PCB analysis, 2,5-dichloro-m-terphenyl for pesticides, and d12 Benzo(a)Anthracene and d10 Phenanthrene mix for PAHs. The amount of IS added is dependent on the expected contaminant concentrations and should be equivalent to those concentrations.

3.3 Add 50 ml acetonitrile.

3.4 Polytron the samples for 20 seconds, at a speed setting of ~ 5. Centrifuge for 10 minutes at 1750 rpm and pour off the supernatant into a separatory funnel containing 500 ml pentane extracted deionized water (DI). Repeat this step two more times.

3.5 Back extract the DI/ACETONITRILE phase in the separatory funnel with 3 X 50 ml pentane. After each addition of pentane has been shaken, draw off the bottom layer into a 500 ml erlenmeyer flask. Decant the Pentane layer into a 250 ml erlenmeyer flask by pouring it out the top of the separatory funnel. This way the transfer of water into the pentane extract will be avoided.

3.6 Transfer the water layer from the 500 ml erlenmeyer flask back into the separatory funnel for every addition of pentane. Rinse the 500 ml flask 3 x with Pentane and add the rinses to the separatory funnel.

3.7 Combine the pentane extracts and dry over Sodium Sulfate.

3.8 Transfer the sample to a 200 ml Turbo-Vap flask. Rinse the flask 3 x with pentane and add the rinses to the flask. Place the flask into the Turbo-Vap apparatus, and turn on the unit. Open the valve on the nitrogen tank and set the regulator to ensure a pressure of 15 psig is reaching the Turbo-Vap unit. Reduce the volume of sample to approximately 1 ml.

3.9 Adjust the volume to 1.0 ml with pentane. Remove 0.1 ml of sample into a preweighed aluminum pan for lipid weight determination. Allow it to dry at room temperature for at least 24 hours. Record the weight of the pan plus the sample.

3.10 Fractionate the sample following the Column Chromatography SOP.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

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4.1 Standard Reference Materials

4.1.1 A certified SRM is prepared with each batch of samples to validate analytical recovery. Analytical results should then be compared to the certified concentrations. Corrective action is required if the required accuracy goals are not met.

4.1.2 SRMs should be prepared in the exact same manner as the unknowns.

4.2 Analytical Reproducibility

4.2.1 Replicate samples should be prepared to assess the reproducibility of the extraction procedure.

4.2.2 For every batch of samples, one sample should be chosen to extract and analyze in triplicate. Deviation between replicate samples should be <30%.

4.3 Procedural Blanks

4.3.1 Procedural blanks should be carried throughout the entire extraction procedure to verify the absence of contamination of the method.

4.3.2 Trace amounts of analytes in the blanks (less than three times the method detection limit) may be ignored and have no effect on the subsequent sample analyses, but samples should be rejected if significant concentrations (greater than five times the MDL) are present in procedural blanks.

4.3.3 One blank should be prepared for each batch of samples (minimum frequency 5%).

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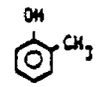
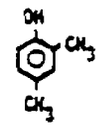
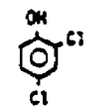
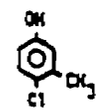
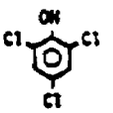
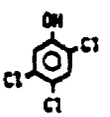
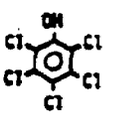
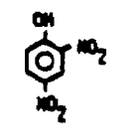
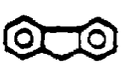
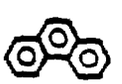
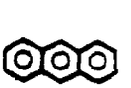
APPENDIX E

EPA Priority Pollutants and Additional Hazardous Substance List Compounds

CHEMICAL STRUCTURES AND MOLECULAR WEIGHTS OF U.S. EPA
PRIORITY POLLUTANT AND ADDITIONAL HAZARDOUS SUBSTANCE LIST COMPOUNDS

	EPA #	Compound	Structure	mw
PHENOLS				
a	65	phenol	a	94
b	HSL	2-methylphenol	b 	108
c	HSL	4-methylphenol	c	108
d	34	2,4-dimethylphenol	d 	122
SUBSTITUTED PHENOLS				
a	24	2-chlorophenol	a	126
b	31	2,4-dichlorophenol	b 	163
c	22	4-chloro-3-methylphenol	c 	143
d	21	2,4,6-trichlorophenol	d 	198
e	HSL	2,4,5-trichlorophenol	e 	198
f	64	pentachlorophenol	f 	266
g	57	2-nitrophenol	g	139
h	59	2,4-dinitrophenol	h 	184
LOW MOLECULAR WEIGHT AROMATICS				
a	55	naphthalene	a	128
b	77	acenaphthylene	b	152
c	1	acenaphthene	c	154
d	80	fluorene	d 	116
e	81	phenanthrene	e 	178
f	78	anthracene	f 	178

EPA # - EPA priority pollutant number defined for toxic pollutants in 40 CFR 401.15 that are a subset of the hazardous substances listed in Appendix VIII of 40 CFR 261.

mw - molecular weight of an organic compound.

HSL - hazardous substance list.

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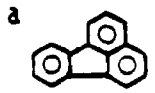
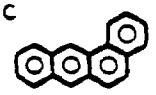
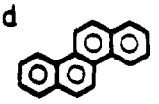
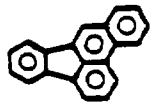
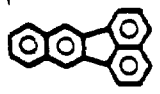
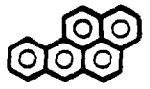
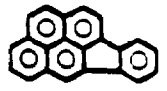
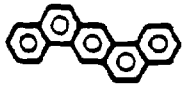
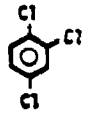
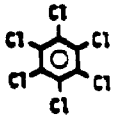
	EPA #	Compound	Structure	mw
HIGH MOLECULAR WEIGHT PAH				
a	39	fluoranthene		202
b	84	pyrene		202
c	72	benzo(a)anthracene		228
d	76	chrysene		228
e	74	benzo(b)fluoranthene		252
f	75	benzo(k)fluoranthene		252
g	73	benzo(a)pyrene		252
h	83	indeno(1,2,3-c,d)pyrene		276
i	82	dibenzo(a,h)anthracene		278
j	79	benzo(g,h,i)perylene		276
CHLORINATED AROMATIC HYDROCARBONS				
a	26	1,3-dichlorobenzene		147
b	27	1,4-dichlorobenzene		147
c	25	1,2-dichlorobenzene		147
d	8	1,2,4-trichlorobenzene		181
e	20	2-chloronaphthalene		163
f	9	hexachlorobenzene		285

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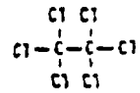
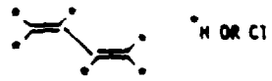
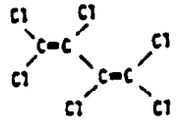
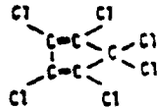
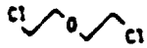
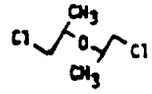
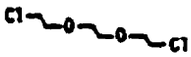
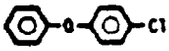
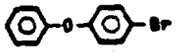
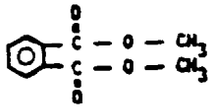
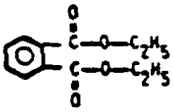
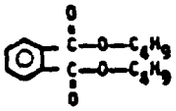
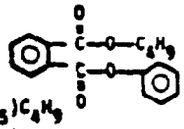
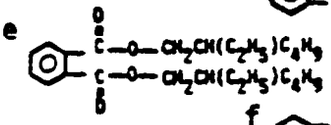
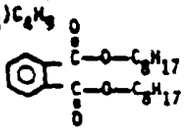
	EPA #	Compound	Stucture	mw
CHLORINATED ALIPHATIC HYDROCARBONS				
a	12	hexachloroethane	a 	168
b	xx	trichlorobutadiene isomers	b,c,d: 	158
c	xx	tetrachlorobutadiene isomers		192
d	xx	pentachlorobutadiene isomers		226
e	52	hexachlorobutadiene	e 	261
f	53	hexachlorocyclopentadiene	f 	273
HALOGENATED ETHERS				
a	18	bis(2-chloroethyl)ether	a 	143
b	42	bis(2-chloroisopropyl)ether	b 	171
c	43	bis(2-chloroethoxy)methane	c 	173
d	40	4-chlorophenyl phenyl ether	d 	204
e	41	4-bromophenyl phenyl ether	e 	249
PHTHALATES				
a	71	dimethyl phthalate	a 	194
b	70	diethyl phthalate	b 	222
c	68	di-n-butyl phthalate	c 	278
d	67	butylbenzylphthalate	d 	312
e	66	bis(2-ethylhexyl) phthalate	e 	391
f	69	di-n-octylphthalate	f 	391

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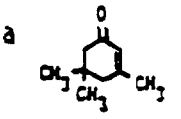
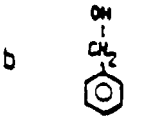
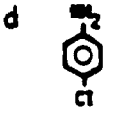
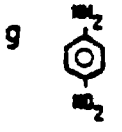
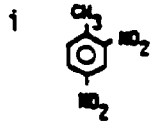
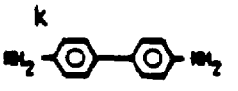
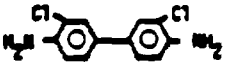
	EPA #	Compound	Structure	mw
MISCELLANEOUS OXYGENATED COMPOUNDS				
a	54	isophorone		138
b	HSL	benzyl alcohol		108
c	HSL	benzoic acid		122
d	129	2,3,7,8-tetrachlorodibenzo-p-dioxin		322
e	HSL	dibenzofuran		168
ORGANONITROGEN COMPOUNDS				
a	HSL	aniline		98
b	56	nitrobenzene		123
c	63	N-nitroso-di-n-propylamine		130
d	HSL	4-chloroaniline		128
e	HSL	2-nitroaniline		138
f	HSL	3-nitroaniline		138
g	HSL	4-nitroaniline		138
h	36	2,6-dinitrotoluene		182
i	35	2,4-dinitrotoluene		182
j	62	N-nitrosodiphenylamine		198
k	5	benzidine		184
l	28	3,3'-dichlorobenzidine		253

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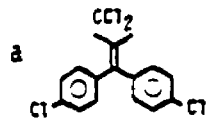
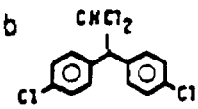
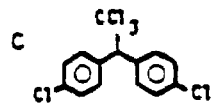
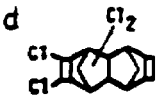
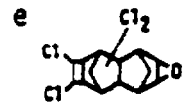
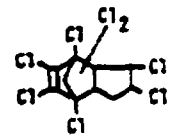
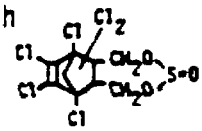
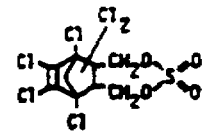
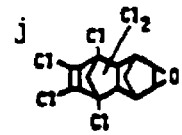
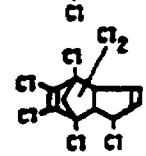
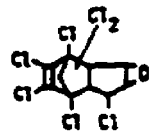
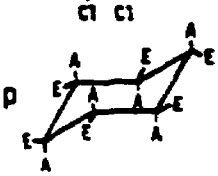
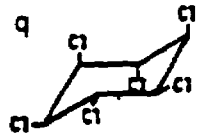
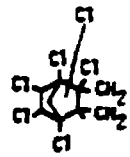
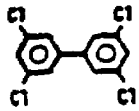
	EPA #	Compound	Structure	mw
PESTICIDES				
a	93	p,p'-DDE		318
b	94	p,p'-DDD		320
c	92	p,p'-DDT		356
d	89	aldrin		365
e	90	dieldrin		381
f	91	chlordane		410
g	95	alpha-endosulfan *		407
h	96	beta-endosulfan		407
i	97	endosulfan sulfate		423
j	98	endrin		381
k	99	endrin aldehyde	STRUCTURE NOT SHOWN	381
l	100	heptachlor		373
m	101	heptachlorepoxide		389
n	102	alpha-HCH	 A = AXIAL; E = EQUATORIAL; α - HCH: 4 EQUATORIAL Cl; β - HCH: 6 EQUATORIAL Cl; δ - HCH: 5 EQUATORIAL Cl	290
o	103	beta-HCH		
p	104	delta-HCH		
q	105	gamma-HCH	 3 EQUATORIAL Cl, 3 AXIAL Cl	290
r	113	toxaphene	 (MANY COMPONENTS, APPROXIMATE FORMULA)	
PCBs				
a	106	Aroclor 1242	 REPRESENTATIVE FORMULA	
b	110	Aroclor 1248		
c	107	Aroclor 1254		
d	111	Aroclor 1260		

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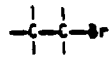
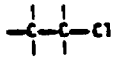
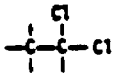
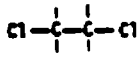
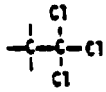
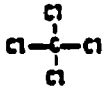
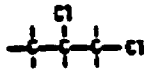
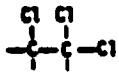
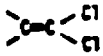
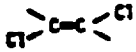
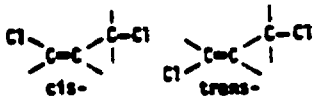
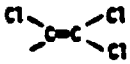
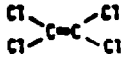
	EPA #	Compound	Structure	mw
VOLATILE HALOGENATED ALKANES				
a	45	chloromethane	a	50.6
b	46	bromoethane	b 	109
c	16	chloroethane	c 	64.5
d	44	methylene chloride	d	85
e	13	1,1'-dichloroethane	e 	99
f	23	chloroform	f	119
g	10	1,2-dichloroethane	g 	99
h	11	1,1,1-trichloroethane	h 	133
i	6	carbon tetrachloride	i 	154
j	48	bromodichloromethane	j	164
k	32	1,2-dichloropropane	k 	133
l	51	chlorodibromomethane	l	208
m	14	1,1,2-trichloroethane	m 	133
n	47	bromoform	n	253
o	15	1,1,2,2-tetrachloroethane	o	168
VOLATILE HALOGENATED ALKENES				
a	88	vinyl chloride	a	62.5
b	29	1,1'-dichloroethene	b 	97
c	30	trans-1,2-dichloroethene	c 	97
d	33	cis- and trans-1,3-dichloropropene	d  cis- trans-	111
e	87	trichloroethene	e 	131
f	85	tetrachloroethene	f 	166

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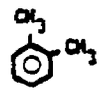
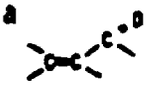
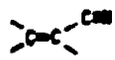
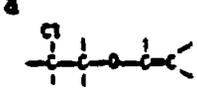
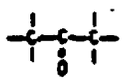
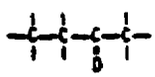
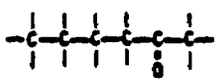
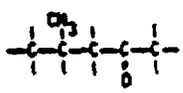
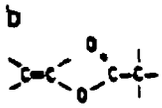
	EPA #	Compound	Structure	mw
VOLATILE AROMATIC HYDROCARBONS				
a	4	benzene	a	78
b	86	toluene	b	92
c	38	ethylbenzene	c	106
d	HSL	styrene	d	104
e	NSL	total xylenes	e  e.g. AND OTHER ISOMERS	106
VOLATILE CHLORINATED AROMATIC HYDROCARBONS				
a	7	chlorobenzene	a	112
VOLATILE UNSATURATED CARBONYL COMPOUNDS				
a	2	acrolein	a 	56
b	3	acrylonitrile	b 	53
VOLATILE ETHERS				
a	19	2-chloroethylvinylether	a 	106
VOLATILE KETONES				
a	HSL	acetone	a 	58
b	HSL	2-butanone	b 	72
c	HSL	2-hexanone	c 	100
d	HSL	4-methyl-2-pentanone	d 	100
MISCELLANEOUS VOLATILE COMPOUNDS				
a	HSL	carbon disulfide	a S=C=S	76
b	HSL	vinyl acetate	b 	86

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APPENDIX F

Example Quality Assurance Reports

PREFACE

The following examples of detailed quality assurance (QA) reviews for a metals data package and a polychlorinated biphenyl (PCB) data package demonstrate the kind of information provided by QA specialists. The sections of these example reports address each of the components of a QA review discussed in Section 2.16 in the main text of this document.

These reviews were conducted in accordance with EPA Contract Laboratory Program procedures. QA reviews for other programs may use alternative criteria for evaluation and different detection limits. For example, the target detection limits discussed for dredging programs differ from the detection limits described in this QA review.

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QUALITY ASSURANCE REVIEW OF METALS IN WATER SAMPLES

INTRODUCTION

This report documents the results of a quality assurance review of analytical data for metals in water samples from Project X. This quality assurance report is provided in support of the quality assurance project plan for this project.

All laboratory analyses were performed by Analysis Laboratory in City, State. All samples were analyzed in accordance with the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program Statement of Work for Inorganic Analyses (U.S. EPA 1987). Data validation was performed according to EPA's *Laboratory Data Validation: Functional Guidelines for Evaluating Inorganics Analyses* (U.S. EPA 1988).

The quality assurance review included examination and validation of the following laboratory data:

- Sample digestion and extraction logs
- All instrument printouts, except for mercury (the instrument printout was not available from the laboratory)
- Instrument calibration and calibration verification procedures and results
- Sample holding times and custody records
- Manual data transcriptions and computer algorithms.

Data qualifiers were assigned as necessary during this review. Following the validation procedures, data quality was assessed with respect to accuracy, precision, and completeness. All qualifier codes used in this report are defined in Table F-1.

QUALITY ASSURANCE REVIEW

Overall Case Assessment

All data for metals in the five water samples are acceptable as qualified in this review for the uses specified in the quality assurance project plan except for the matrix spike result for silver, which was rejected. Data for all samples analyzed for cadmium, calcium, lead, mercury, silver, and zinc are acceptable as estimates. Data qualified as *J* (estimated) are

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TABLE F-1. DATA QUALIFIER CODES

Qualifiers Applied During Quality Assurance Review

U The analyte was not present above the level of the associated value. The associated numerical value indicates the approximate concentration necessary to detect the analyte in this sample.

J The analyte was positively identified, but the associated numerical value may not be consistent with the amount actually present in the field sample. The data should be seriously considered for decision-making and are usable for many purposes.

UJ The analyte was not present above the level of the associated numerical value. The associated numerical value may not accurately or precisely represent the concentration necessary to detect the analyte in this sample.

R The data are unusable for all purposes. The presence or absence of the analyte has not been verified. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

Qualifiers Applied During Laboratory Validation[a]

E The reported value is estimated because of the presence of interference. This qualifier is commonly used when the serial dilution result for analyses by inductively coupled plasma-atomic emission spectrometry (ICP) does not meet control limits.

M Duplicate injection precision was not met.

N Predigestion matrix recovery was not within control limits.

S The reported value was determined by the method of standard additions (MSA). The associated value is as reliable as unqualified results.

W The postdigestion spike recovery for GFAA[b] analysis was not within control limits (85–115 percent), and the sample absorbance was less than 50 percent of the spike absorbance.

***** Duplicate analysis was not within control limits.

+ The reported value was determined by MSA. The correlation coefficient for MSA is < 0.995.

[a] Adapted from U.S. EPA (1987).

[b] Graphite furnace atomic absorption spectrometry.

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acceptable, but a greater degree of uncertainty is associated with these values than with unqualified data.

The matrix spike result for silver was rejected because the postdigestion spike recovery (58 percent) was well below the EPA Contract Laboratory Program (CLP) control limit (85- to 115-percent recovery). Analysis of the sample by the method of standard additions (MSA) is required in this case, but was not performed.

Calcium values received *J* qualifiers because the CLP control limit (U.S. EPA 1987) was exceeded slightly for the serial dilution sample analyzed by inductively coupled plasma-atomic emission spectrometry (ICP). Reported results may be underestimated by approximately 10 percent.

Cadmium and lead results received *J* qualifiers because CLP control limits for matrix spike recoveries and for duplicate analyses were exceeded. In addition, the result for lead in Sample 2 was restated as undetected (*U*) at the reported concentration because the associated digestion blank was contaminated. Cadmium and lead data should be considered order-of-magnitude estimates.

Mercury results were qualified *J* because the matrix spike recovery was below the CLP control limit. These results may be 100–200 percent higher than reported.

A *J* qualifier was applied to silver results because recovery of silver was poor for the laboratory control sample (LCS). Silver results may be approximately 100 percent higher than reported. Additional individual results were qualified *J* because the correlation coefficient for the results determined by MSA did not meet the CLP control limit of 0.995

The overall data quality achieved by the laboratory for analyses completed by ICP (Table F-2) is typical for metals analyses in water samples. The overall data quality for analyses by graphite furnace atomic absorption (GFAA) is typical for arsenic, chromium, and silver. Data quality for cadmium, lead, and mercury is less than may be expected for these analytes in similar samples. Data quality may have been affected by unstable instrument performance.

Completeness

A complete data package was submitted by the laboratory for five water samples, one matrix duplicate and one matrix spike, and one laboratory control sample and one method blank for each digestion batch. A list of analytes is included in Table F-2. During the quality assurance review, 33 results were qualified *J* as discussed above. Data completeness for metals was 100 percent of total requested analytes.

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TABLE F-2. ANALYTICAL METHODS AND INSTRUMENT DETECTION LIMITS

Analyte	Method of Analysis	Instrument Detection Limit (µg/L)
Aluminum	ICP[a]	55
Arsenic	GFAA[b]	5
Cadmium	GFAA	5
Calcium	ICP	28
Chromium	GFAA	10
Copper	ICP	11
Iron	ICP	9.6
Lead	GFAA	5
Magnesium	ICP	140
Manganese	ICP	1.8
Mercury	CVAA[c]	0.2
Nickel	ICP	18
Silver	GFAA	5
Zinc	ICP	4

[a] Inductively coupled plasma-atomic emission spectrometry.

[b] Graphite furnace atomic absorption spectrometry.

[c] Cold vapor atomic absorption spectrometry.

[d] Manual spectrophotometry.

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Holding Times

Holding times required by EPA CLP protocols were met for all metals analyses.

Analytical Methods

All sample digestion and analysis procedures, instrument calibration procedures, and quality control checks conformed to EPA CLP requirements except as noted below.

Sample Preparation and Analysis

Water samples were digested according to requirements specified for CLP (U.S. EPA 1987). Sample digestates were analyzed by ICP, GFAA, and cold vapor atomic absorption spectrometry (CVAA), as indicated in Table F-2. Multiple digestions were prepared for Samples 1 and 2 and the duplicate and the spike of Sample 2, because unacceptably high levels of lead were present in the second preparation blank and because volumes of digestate were initially insufficient for all analyses. A preparation blank and a laboratory control sample were digested and analyzed with each batch. Only lead and arsenic results were obtained from the second and third digestion batches. Results for all applicable quality control samples, except the method blank for lead for the third digestion group, were provided on the appropriate CLP forms by the laboratory or were added during the quality assurance review.

Instrument Calibration

Instrument calibration was completed according to EPA CLP protocols (U.S. EPA 1987). Four calibration standards and one blank were used for all analyses by GFAA. The correlation coefficient of a least squares linear regression met the CLP control limit of ≥0.995 in all cases except one. The correlation coefficient was 0.993 for the initial calibration for analysis of cadmium in Samples 3 and 5. Consequently, the cadmium results for these samples were qualified *J*.

ICP instruments were calibrated according to manufacturer instructions, using one standard and one blank. A low-level standard was used to verify accuracy of the calibration curve at low analyte concentrations for all metals except mercury and aluminum.

Initial (ICV) and continuing (CCV) calibration check standards and initial (ICB) and continuing (CCB) calibration blanks were analyzed immediately after instrument calibration, after every 10 samples or more frequently, and at the conclusion of each analytical run, with the following exception: no CCV/CCB pair was analyzed at the conclusion of the ICP run. However, only interference check samples were analyzed after the final CCV/CCB pair, and data quality was not affected. Results for all CCVs fell within 90–110 percent of the expected value (80–120 percent for mercury), as required

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by EPA CLP. Instrument calibration remained within control limits for all samples thorughout each sample run and for all other analytes.

Instrument-Specific Quality Control Procedures

ICP—A serial dilution sample is required by EPA CLP protocols to check for matrix interference in samples analyzed by ICP. All samples analyzed by ICP were diluted to one fifth of their initial concentration to bring manganese concentrations within the linear range of the ICP. The laboratory chose to report the results of diluted Sample 3 on CLP Form 9, *ICP Serial Dilutions*. A further serial dilution was required by CLP protocols to obtain a diluted result for manganese, but was not performed. Results of the serial dilution for iron, magnesium, nickel, and zinc were within the CLP control limit of 10-percent difference from the undiluted result. The results for aluminum and copper were not applicable because the undiluted concentration of these metals was not sufficiently high. The result for calcium (11-percent difference) exceeded control limits, with the diluted result (corrected for dilution) exceeding the undiluted result. All calcium data were qualified *E* by the laboratory and *J* during the quality assurance review. Reported calcium results may have a small negative bias of approximately 10 percent due to matrix interference.

Interference check samples (ICSs) were analyzed at the beginning and end of the ICP sample run to check for interference by other metals. Results met CLP control limits in all cases. To extend the linear range of the ICP to accommodate the high analyte concentrations present in the ICSs, a second calibration curve was obtained for some of the ICS analytes using higher standards than were used for the sample analyses. The analytical wavelength and all instrument parameters remained the same. Calibration was verified at the higher calibration curve as well. Data relating to the higher calibration curve were labeled "secondary lines" in the original data.

GFAA—Quality control procedures for GFAA analyses included duplicate injection of all samples and analysis of a postdigestion analytical spike with each sample. Results of duplicate injections were spot-checked at a frequency of approximately 10 percent. All examined duplicate injection results agreed within 20-percent coefficient of variation, as required by CLP protocols.

Recoveries of the analytical spike for numerous samples and analytes did not meet CLP control limits of 85–115 percent. In most cases, these data were qualified *W* (analytical spike recovery did not meet control limits and sample absorbance is less than 50 percent of spike absorbance) by the laboratory, or MSA was used to analyze the samples as required by CLP protocols. Sample results obtained by MSA were qualified *S* by the laboratory if the correlation coefficient obtained with the MSA results was ≥0.995. Results qualified *S* are reliable and are not considered to be estimates. Sample results obtained by MSA with correlation coefficients <0.995 were qualified + by the laboratory and *J* during the quality assurance review. These results are estimates.

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A systematic calculation error was made by the laboratory for all sample results obtained by MSA. The error consisted of the misassignment of axes to the sample concentration values and to the instrument response values, resulting in an incorrect value for the slope of the instrument response per added concentration and consequently for the analyte concentration in the sample. Results obtained with a poor correlation coefficient showed the greatest magnitude in the error. All results were corrected during quality assurance review.

Several errors were made by the laboratory in following the CLP sample analysis sequence for analyses by GFAA. The analytical spike recoveries of silver and lead in the first method blank (122- and 119-percent recovery, respectively) exceeded CLP control limits (85–115 percent). According to U.S. EPA (1987), the problems should have been corrected and acceptable results should have been generated for the method blank prior to sample analysis. A qualifier (*E*) was applied to the silver result for Sample 5 (the only result not obtained by MSA) by the laboratory because of the high analytical spike recovery from the blank, but was removed during the quality assurance review because data qualification is not automatically warranted in this case. All samples results for lead from the first digestion group were obtained by MSA and were not qualified by the laboratory or during the quality assurance review.

The matrix spike samples for lead and silver should have been analyzed by MSA because the analytical spike recoveries were low (74- and 58-percent recovery, respectively) for these analytes. The initial sample and duplicate (Sample 2) for silver were analyzed by MSA. The spike results for silver and lead are estimates.

The analytical spike recovery for lead in Sample 3 was 34 percent. This sample should have been diluted and reanalyzed (U.S. EPA 1987); however, MSA was performed instead. Samples 2 (duplicate), 5, and 6 were analyzed by MSA for arsenic and had correlation coefficients below the control limit. These samples should have been reanalyzed, but were not. The correlation coefficient for arsenic by MSA in Sample 2 (duplicate) was 0.909, well below the control limit of 0.995, and the curve generated by the standard additions was exponential in appearance. This result (45.5 µg/L) was rejected during the quality assurance review because of the poor correlation coefficient, and the initial result (26.2 µg/L) was accepted as an estimate.

Detection Limits

All reported instrument detection limits (IDLs) were below or equal to the CLP contract-required detection limits (CRDLs) (Table F-2). The IDL for lead by GFAA was omitted from CLP Form 11, but was subsequently provided by the laboratory. The IDLs reported for GFAA analytes were estimated by laboratory personnel based on their experience with the instrument and were not determined statistically as required by CLP protocols (U.S. EPA 1987). Data were not qualified for this omission. Based on the quality assurance

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review of original laboratory data, in the reviewer's judgment the laboratory estimates of detection limits tended to be high. Use of statistically determined detection limits may result in lower values than the reported IDL in many cases.

Accuracy

The laboratory performed one LCS analysis (using a commercially available standard prepared specifically for CLP analyses) and one predigestion matrix spike analysis (Sample 1 for mercury, and Sample 2 for all other analytes). Recovery of all analytes except silver from the LCS ranged from 84 to 112 percent. Silver recovery was 52 percent (Table F-3). CLP control limits for metals in the LCS are 80- to 120-percent recovery (except for silver, which has no contractual control limit [U.S. EPA 1987]). All results for silver were qualified *J* during the quality assurance review because of the poor LCS recovery (U.S. EPA 1988).

Predigestion matrix spike recovery was within control limits (75–125 percent; U.S. EPA 1987) for all metals except cadmium, lead, mercury, and silver (Table F-4). Results for cadmium and lead (194- and 261-percent recovery, respectively) were greater than the control limit, and all sample results greater than the IDL were qualified *J* during the quality assurance review (U.S. EPA 1988). Only Sample 2 was not qualified for cadmium because none was detected. The spike results for both lead and cadmium are questionable because the matrix duplicate results for Sample 2 exceeded control limits, so a reliable sample concentration is not available. The spike sample result for lead is also questionable because the sample should have been analyzed by MSA, but was not. In addition, at least one method blank for lead was contaminated (as discussed in the *Blanks* section); nonsystematic lead contamination may also have contributed to the poor replicability of the duplicates and the high spike recovery for lead. All data were qualified as estimated despite the uncertainty in the matrix spike results because the magnitude of the control limit exceedance was large for both analytes.

All mercury data were qualified *J* during the quality assurance review because predigestion spike recoveries (40 and 39 percent, respectively) were much lower than control limits. Recovery for a postdigestion mercury spike analyzed for Sample 1 was 38 percent, similar to the predigestion spike result. This result indicates that a matrix interference at the spectrophotometer was probably responsible for poor recovery. Reported results for mercury may be lower than the actual sample concentrations.

The matrix spike result reported for silver was lower than the result reported for the unspiked sample. The analytical spike result of the matrix spike sample was low (58-percent recovery), and therefore the matrix spike sample should have been analyzed by MSA, but was not. The original and duplicate Sample 2 were both analyzed by MSA. The matrix spike result for silver was rejected during the quality assurance review. The matrix spike result for chromium was not applicable because the sample concentration exceeded 4 times the spike concentration. The magnitude of the precision error (the control limit is ≤20 relative percent difference [RPD]) may be significant with respect to

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TABLE F-3. PERCENT RECOVERY FOR METALS IN LABORATORY CONTROL SAMPLE

Analyte	Percent Recovery[a]
Aluminum	98
Arsenic	105
Cadmium	112
Calcium	99
Chromium	109
Copper	101
Iron	99
Lead	98
Magnesium	99, 84, 93
Manganese	100
Mercury	111
Nickel	97
Silver	52
Zinc	98

[a] Percent recovery = $\frac{\text{measured value}}{\text{true value}} \times 100.$

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TABLE F-4. MATRIX SPIKE RECOVERY FOR METALS IN SAMPLE 2

Analyte	Sample Result (µg/L)	Spike Added (µg/L)	Percent Recovery[a]
Aluminum	310	2,000	97
Arsenic	25	40	89
Cadmium	5 *U*[b]	5	194
Calcium	--	--	NR[c]
Chromium	69	10	NA[d]
Copper	27	250	103
Iron	7,090	1,000	77
Lead	29	20	261
Magnesium	--	--	NR
Manganese	6,560	500	76
Mercury[e]	0.2 *U*	1.0	40
Nickel	180	500	106
Silver	28 *R*[f]	10	--[f]
Zinc	180	500	95

[a] Percent recovery = $\frac{\text{spiked result} - \text{unspiked result}}{\text{spike added}} \times 100.$

[b] *U* - the analyte was not detected at the indicated concentration.

[c] A matrix spike was not required for this analyte (U.S. EPA 1987).

[d] The result is not applicable because the sample concentration is greater than 4 times the spike concentration.

[e] Sample 1 was spiked for mercury only.

[f] *R* - the spike sample result was rejected; the result is not meaningful.

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the spike concentration in this situation, and spike recovery results cannot be clearly interpreted. Assessment of analytical accuracy was based on the LCS for both silver and chromium.

Precision

Duplicate subsamples of Sample 2 for all metals and Sample 1 for mercury only were analyzed by the laboratory. Results are summarized in Table F-5. All results except cadmium and lead were within the control limit of 25 RPD (for sample results >5 times the CRDL) or ± the CRDL (for results ≤5 times the CRDL) specified by the EPA. A qualifier (*) was applied to all cadmium and lead values by the laboratory or during the quality assurance review to indicate EPA CLP duplicate control limit exceedance, and all cadmium and lead values were qualified *J* during the quality assurance review.

The result for arsenic for Sample 2 (duplicate) as obtained by MSA and reported by the laboratory was rejected during the quality assurance review, but the result obtained initially by direct comparison to the instrument calibration curve was accepted as estimated (details in the *Calibration* section). The latter value was well within control limits, and the former value exceeded the control limit by less than 1 µg/L. The data qualifier (*) applied by the laboratory to the arsenic value for Sample 2 was removed during the quality assurance review. No arsenic data were qualified *J*.

Blanks

A method blank and several calibration blanks were analyzed with the samples for each metal. No contaminant was found in any method blank with one exception: lead was present (6.1 µg/L) in the method blank prepared with the second digestion batch. Results for Sample 2 and the duplicate and spike samples for Sample 2 were reported from this digestion batch. Sample 2 was qualified *U* (undetected at the reported concentration) during the quality assurance review because the sample result (29.4 µg/L) was <5 times the concentration in the method blank (U.S. EPA 1988). According to the laboratory worksheets for lead, the method blank prepared with the third digestion batch also contained lead (105 µg/L); however, data corresponding to this result were absent from the instrument printout, and the result was not entered onto the appropriate CLP form. The entry on the worksheet was apparently a transcription error, and no result is available for this method blank. The result reported for Sample 1 was obtained from this digestion batch and was qualified *J* during the quality assurance review.

Several results for CCBs exceeded the detection limits for calcium, manganese, and zinc. However, all associated sample results exceeded 5 times the concentration of the respective analyte found in any CCB, and were therefore not significant with respect to the expected analytical variability of sample results. No sample results were qualified as a result of detected analyte concentrations in associated CCBs.

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TABLE F-5. DUPLICATE ANALYSIS RESULTS FOR METALS IN SAMPLE 2

Analyte	Sample Result (µg/L)	Duplicate Result (µg/L)	Control Limit[a]	Relative Percent Difference[b]
Aluminum	310	308	200	--
Arsenic	25	26	10	--
Cadmium	5 *U*[c]	17	5*[d]	--
Calcium	184,000	180,000	--	2
Chromium	69	78	--	--
Copper	27	29	15	--
Iron	7,100	6,700	--	8
Lead	29	47	--	46*
Magnesium	200,000	190,000	--	3
Manganese	6,600	6,400	--	2
Mercury[e]	0.2 *U*	0.2 *U*	0.2	--
Nickel	180	190	40	--
Silver	28	31	10	--
Zinc	180	190	--	3

[a] For results less than 5 times the CRDL, the difference between replicate sample results must be ≤ the CRDL.

[b] $RPD = \frac{|\text{sample} - \text{duplicate}|}{(\text{sample} + \text{duplicate})/2}$.

[c] *U* - the analyte was not detected at the indicated concentration.

[d] Results followed by "*" exceed CLP control limits.

[e] Sample 1 was analyzed in duplicate for mercury only.

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U.S. EPA. 1987. U.S. EPA Contract Laboratory Program statement of work for inorganics analysis, multi-media, multi-concentration. SOW No. 788. U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA. 1988. Laboratory data validation: functional guidelines for evaluating inorganics analyses. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

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QUALITY ASSURANCE REVIEW OF POLYCHLORINATED BIPHENYLS IN SEDIMENT

INTRODUCTION

This report documents the results of a quality assurance review of data for polychlorinated biphenyls (PCBs) in sediment samples as part of the sediment characterization of the Project Y site. The sampling and analysis plan (SAP) and the quality assurance project plan (QAPP) are described in the study proposal.

All laboratory analyses were performed by the laboratory in accordance with procedures specified in the SAP. Sample analyses were performed using modified versions of U.S. Environmental Protection Agency (EPA) SW-846 Method 8080 (U.S. EPA 1986); the modifications are detailed in the laboratory statement of work (SOW). Data validation was performed in accordance with the U.S. EPA (1988) functional guidelines for evaluating organic compound analyses, guidelines established in U.S. EPA (1986) SW-846 Method 8080, the data quality objectives specified in the SAP, and the requirements specified in the laboratory SOW.

The quality assurance review included examination and validation of the following data:

- Sample holding times and chain-of-custody records
- Initial and continuing calibration analyses, including calculations by least squares linear regression
- Reported detection limits
- Method blank analyses
- Matrix spike and matrix spike duplicate recoveries
- Surrogate compound recoveries
- All reported sample results, including verification of quantification, examination of chromatograms, and PCB identification.

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OVERALL CASE ASSESSMENT

The results of the quality assurance review for the analysis of PCBs in the 64 sediment samples are presented below in two sections. These sections address completeness of the data package and the qualifiers assigned to individual measurements.

Summary of Completeness

A complete data package was submitted by the laboratory for 64 sediment samples, 4 method blanks, 4 matrix spikes, and 4 matrix spike duplicates. Data completeness is 100 percent of the total requested analyses; no results were rejected.

Summary of Data Qualifications

The results of analyses for PCBs in the 64 sediment samples associated with this project are acceptable for the intended purposes specified in the SAP. Some data were assigned a *J* qualifier to indicate that the values reported are estimates. The data are acceptable, but have a greater degree of uncertainty than nonqualified data.

A summary of the technical factors resulting in the qualification of the PCB data is as follows:

- The laboratory did not fully establish linearity for the initial calibration near the lower end of the standard curve. Demonstration of linearity near the lower end of the curve is important for validating to demonstrate the limits of detection and practical quantification limits specified in the laboratory SOW.
- The laboratory quantified all sample results using a single-point standard (i.e., the continuing calibration standard). However, quantification using a single-point standard is only acceptable if linearity is established throughout the calibration range in the initial calibration.
- The criterion for continuing calibration was not met for three of the eight total standard analyses.
- Surrogate recoveries for 13 samples did not meet quality control limits; the associated data were qualified as estimates.

In addition, all PCB values were recalculated because coeluting chromatographic peaks were used by the laboratory to identify PCBs; therefore, the peak heights used for quantification resulted in biased values. The recalculated values were typically one-half of the original concentrations reported by the laboratory. In addition, the laboratory occasionally incorrectly identified and reported results for specific PCBs. During the quality assurance review, these data were corrected.

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A complete discussion of the results of the data validation and specific problems identified during the quality assurance review is provided below.

HOLDING TIMES

All storage conditions and sample holding times were properly met by the laboratory. The holding time requirements for PCB analyses specified in the SAP are as follows:

- All samples must be shipped on ice to the laboratory and stored at −18°C until sample extractions are performed
- Sample extracts must be analyzed within 40 days
- Sediment samples must be kept frozen and extracted within 6 months from the date and time of sample collection.

The 64 sediment samples were collected between _____ and _____; the samples were received at _____ on _____. Samples were extracted between _____ and _____, and the sample extracts were analyzed between _____ and _____.

ANALYTICAL METHODS

Samples were analyzed for PCBs using a modified version of U.S. EPA (1986) SW-846 Method 8080. The modifications are specified in the SAP and the laboratory SOW and include the following:

- Larger sample size for extraction (i.e., approximately 100 grams, wet weight)
- In addition to the Contract Laboratory Program (CLP) surrogate compound dibutylchlorendate (DBC), the use of an additional surrogate compound (4,4'-dibromooctafluorobiphenyl [DBOFB]) to monitor recovery on a sample-by-sample basis
- Sample extract cleanup procedures as required using alumina column chromatography by EPA Method 3610, florisil column chromatography by EPA Method 3620, and elemental sulfur cleanup by EPA Method 3660
- Megabore capillary gas chromatography/electron capture detection (GC/EC-D) analysis to enhance resolution and reduce potential interferences
- Use of a multipoint calibration for all Aroclor® mixtures and analysis of a check standard of 0.1 ng (on-column) for verification of instrument sensitivity to assess the validity of the required detection limits.

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The laboratory generally performed the recommended modifications. Florisil column chromatography was used for a limited number of samples. EPA Method 3660 (mercury cleanup) and a sulfuric acid cleanup step were used to remove elemental sulfur; the sulfuric acid cleanup step was used on all samples associated with this project. The use of sulfuric acid was approved by the project manager during sample processing.

CALIBRATION

The results of all initial and continuing instrument calibrations performed by the laboratory are generally acceptable. Specific problems identified during this quality assurance review are discussed in the section below.

Instrument calibration is performed to establish and ensure that the chromatographic system is capable of producing acceptable and reliable analytical data. An initial calibration is performed prior to sample analysis to establish the linearity of the chromatographic system, including demonstrating that all target compounds can be detected. Continuing calibrations are performed to verify that instrument performance is stable and reproducible on a day-to-day basis. The initial and continuing calibrations are to be performed according to procedures established by CLP protocols and modified in the SAP and the laboratory SOW.

A detailed description of the results for initial and continuing calibrations is presented below.

Initial Calibration

The laboratory performed an initial three-point calibration using concentrations of 0.4, 1.0, and 5.0 ng (on-column) for the five Aroclor® mixtures (Aroclor® 1016, 1221, 1232, 1248, and 1260). A five-point initial calibration (0.4, 1.0, 2.0, 3.0, and 5.0 ng) was performed for PCB 1242 and PCB 1254.

Linearity of the initial calibration to zero concentration is assumed when the percent relative standard deviation (RSD) of the calibration factors is ≤20 percent over the entire calibration range (U.S. EPA 1986). Additionally, the correlation coefficients (r^2) generated by least squares linear regression should be greater than 0.9950 to demonstrate linearity.

The laboratory calculated the r^2 values for the initial calibrations using the sum of all chromatographic peaks that were integrated (i.e., from the first peak integrated, the injection peak, to the last peak integrated) to perform the calculations. Only the chromatographic peaks representative of a specific PCB mixture should be used for performing these calculations. Therefore, all standard chromatograms were reviewed during the quality assurance review and the r^2 values were recalculated.

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The recalculated results generated using least squares linear regression indicate that linearity through the origin was not established. While linearity through the origin is not uncommon for this type of analysis, most PCB concentrations that were recalculated are in this low concentration range. Therefore, the results for PCBs were assigned a *J* qualifier to indicate estimated values.

Continuing Calibration

The number of continuing calibrations is acceptable; however, the frequency of calibrations is not acceptable. The data were not qualified for unacceptable frequency of antimony calibration because of the numerous other problems identified and discussed in other sections of this report.

The criteria for acceptable continuing calibration require that the calibration factors for all target compounds have a difference of ≤15 percent from the average calibration factor calculated for the associated initial calibration (U.S. EPA 1986). The 15-percent difference value is required for results calculated using the chromatographic column that is used for quantitative purposes. In addition, the percent difference of the calibration factors calculated for the chromatographic column used for confirmation must be ≤20 percent (U.S. EPA 1986). If the criteria for the percent differences are not met, then a new initial calibration sequence must be prepared.

The laboratory performed 8 continuing calibration analyses during the analysis of the 64 sediment samples. The criteria for continuing calibration were not met for three of eight calibrations performed (ranging from 32- to 92-percent difference). In addition, the laboratory typically performed continuing calibrations at the end of a given daily analytical sequence or the calibrations were clustered together.

METHOD BLANK ANALYSIS

Method blank analysis is performed to determine the extent of laboratory contamination of samples. The four method blank analyses for this project are acceptable; PCBs were not detected.

ACCURACY

Accuracy of the analytical results is expressed in terms of the bias and precision of measurements. Bias is assessed by evaluating the recoveries of the surrogate compounds and the matrix spike recoveries calculated for sample analyses. Precision is assessed by evaluating the differences between duplicate matrix spike analyses. These results are presented below.

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Surrogate Compound Recoveries

The surrogate compound recoveries reported for the 64 sediment sample analyzed are acceptable, except 13 surrogate recoveries did not meet the quality control limits and the associated data are accepted as estimates. The data quality objective for acceptable recovery for surrogate recovery is 100±50 percent.

The recoveries for DBC ranged from 0 to 160 percent, with an average recovery of 70 percent. The recoveries for DBOFB ranged from 0 to 128 percent, with an average recovery of 71 percent. Thirteen surrogate recoveries exceeded the quality control limits; four recoveries were reported at zero percent, and nine recoveries were less than 50 percent but greater than zero percent. No data were rejected because only one unacceptable surrogate recovery was reported for a given sample and the other surrogate recovery value was acceptable. The values for PCBs reported in these samples were assigned a *J* qualifier to indicate the values are estimates.

Matrix Spike Recoveries

The results for the matrix spike recoveries are acceptable for the four sets of duplicate matrix spike analyses that were performed, except for three results that are acceptable as estimates. All matrix spike analyses were performed using Aroclor® 1254 and the samples chosen by the laboratory for the matrix spikes had detectable amounts of PCBs.

The criteria for acceptable matrix spike recovery is 100±50 percent. All recoveries were recalculated during the quality assurance review. The recalculated matrix spike recoveries ranged from 0 to 90 percent. Only three results did not meet the quality control limits. No data were rejected in accordance with procedures detailed by EPA CLP protocols (U.S. EPA 1988).

PRECISION

Two of the four total relative percent difference (RPD) values did not meet the quality control criteria for precision. Precision is expressed as the RPD between the recoveries of the matrix spike and the matrix spike duplicate analyses performed on a sample. The quality control criterion for precision is ±50 percent. The RPDs calculated from the duplicate matrix spike recoveries ranged from 13 to 90 percent.

IDENTIFICATION OF COMPOUNDS

All chromatograms were examined during the quality assurance review to verify that PCB identifications and confirmations (where applicable) are correct. The confirmation of the PCB identification during the quality assurance review focuses on false positives. However, PCBs reported as not detected are also evaluated to investigate the possibility of false negatives. Confirmation of possible false negatives is addressed by reviewing

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other factors relating to analytical sensitivity (e.g., detection limits, instrument linearity, and analytical recovery).

Either Aroclor® 1254 or Aroclor® 1260, or a mixture of the two, was identified in 55 of 64 samples associated with this study. Absolute identification for the presence of Aroclors® 1254 or 1260 could not be confirmed during the quality assurance review because all chromatograms generated with the confirmational chromatographic column drifted off scale (i.e., 100 percent, full-scale deflection). Additional sample dilutions were not performed for these samples. Therefore, results generated using data obtained from only one chromatographic column were used to perform quantification and identify the PCBs. As a result, all results were assigned a *J* qualifier to indicate the values reported are estimates.

COMPOUND QUANTIFICATION AND REPORTED DETECTION LIMITS

All quantifications performed by the laboratory were corrected during the quality assurance review. The laboratory had not accounted for coeluting peaks when Aroclors® 1254 and 1260 were present in a given sample; the inclusion of coeluting peaks resulted in biased values. Quantification of the reported data and the reported detection limits were recalculated to ensure all results are accurate and consistent with the requirements established in U.S. EPA (1986) SW-846 Method 8080, the SAP, and the laboratory SOW.

During the quality assurance review, chromatographic peaks characteristic to each PCB mixture were chosen to check quantifications and their identity. The heights of selected integrated peaks for a specific PCB mixture used for calibration were summed to recalculate the r^2 values, and concentrations of PCBs detected in the samples were recalculated using least squares linear regression. The results for PCBs quantitated in the samples were typically one-half of the values originally reported by the laboratory; all results were assigned a *J* qualifier to indicate estimated values.

The laboratory reported limits of detection of 5 µg/kg (wet-weight basis) for Aroclors® 1016, 1254, and 1260 and 10 µg/kg (wet-weight basis) for Aroclors® 1221, 1232, 1242, and 1248 in most samples. Overall, the laboratory reported limits of detection that range from 5 to 100 µg/kg (all values are adjusted for dilutions that may have been performed).

REFERENCES

U.S. EPA. 1986. Test methods for evaluating solid waste (SW-846): physical/chemical methods. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA. 1988. Laboratory data validation: functional guidelines for evaluating organics analyses. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

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APPENDIX G

Analytical/Environmental Laboratory Audit Standard Operating Procedure

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ANALYTICAL/ENVIRONMENTAL LABORATORY AUDIT STANDARD OPERATING PROCEDURE

1. PURPOSE AND INTRODUCTION

The purpose of this standard operating procedure (SOP) is to provide guidance to EZ Consultants (EZ) staff in auditing analytical or environmental testing laboratories. The audit requires evaluation of information collected during the review of laboratory documents, performance of site interviews, and observation of normal laboratory operations. Basic procedures for arranging and performing a site visit are provided, as well as a checklist for items to be considered during the audit process, and an evaluation guide. Portions of the audit checklist form (Attachment 1) are based upon laboratory evaluation checksheets developed by the U.S. EPA Industrial Technology Division.

There are two typical reasons why an audit is requested to be performed: to determine the capability of a laboratory to perform (future) testing for EZ; or to evaluate the quality of data submitted, usually on behalf of a third party. The SOP outlined below is applicable in both cases.

2. AUDITOR QUALIFICATIONS

The auditor should have the technical experience necessary to perform the audit, i.e., familiarity with the analytical methods of interest, instrumentation used, standard QA practices, and general good laboratory practices. The auditor should also be familiar with this SOP.

3. REQUEST FOR AUDIT

A staff member desiring a laboratory audit be performed can contact the EZ chemistry group and request an auditor be assigned for this task.

4. CLARIFICATION OF AUDIT OBJECTIVES

The auditor should consult the staff member requesting the audit to determine the purpose of the audit and the rigor with which the audit must be performed. The extent of the audit and the intensity of scrutiny will vary, according to the type of laboratory, analyses,

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and type of project which are involved. The auditor should get clear direction from the individual requesting the audit to determine the intensity of review which is desired. Information necessary to make this decision include:

- Reason for audit
- Rigorousness of the data requirements
- Type of project for which data are (to be) collected
- Analytical methods required.

5. ESTIMATE OF AUDIT COSTS

The labor costs involved for the audit will depend on the intensity of the audit, which in turn depends upon factors such as the following:

- Type and size of project involved
- Type of laboratory involved
- Rigorousness of information requirements
- Required analytical methods
- Size and organization of the laboratory
- Accessibility of documents for review
- Type of audit report necessary.

For a rough estimate, the audit of a small, subcontract laboratory with 10 staff members, producing standard CLP data packages for inorganics, with all necessary documents available in the EZ contract files would take approximately 18 hours of the auditor's time: eight hours for audit preparation, four hours for the site visit (excluding travel), and six hours for evaluation and report generation. Additional labor costs would include clerical, word processing, and editing staff time. Other direct costs such as travel expenses and computer time would also need to be included.

6. PREPARATION FOR THE AUDIT

6.1 Identification of Laboratory Contact Person

If a laboratory (which will be) performing analyses for EZ is to be audited, then the auditor should contact the laboratory directly. Usually the best person with whom to establish contact is the technical director or lab manager, if such a position exists.

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If the laboratory to be audited is (or will be) performing analyses for a third party, that party should first be contacted, and their assistance should be enlisted to establish contact with the laboratory.

6.2 Initial Discussion with Laboratory Management

Initiate preliminary discussions with the laboratory contact person to:

- Obtain a profile of laboratory, e.g., what types of samples and analyses are handled, what clients are served, what level and types of services are available, how lab is managed, identification of the managerial chain, management's overall philosophy of quality, type of quality program in place.
- Identify the primary concerns, e.g., potential or perceived problems, perceived strengths.
- Identify the expectations, e.g., reason for desiring an audit, expected use of the outcome.
- Identify any problems the laboratory may have with EZ.

If at all possible, do not take an adversarial attitude, but instead try to foster a cooperative relationship with the laboratory. This is especially important when there have been previous problems or concerns regarding the quality of data produced by the laboratory. It is much easier to obtain necessary information and to resolve problems if an open, cooperative relationship can be established for the audit process.

6.3 Pre-Site Visit Activities

- Review the audit checklist form (Attachment 1): determine what information will be necessary to complete the form and prepare for the site visit. The topics generally covered during the site visit include organization and personnel training, client requests, sample receipt and storage areas, sample preparation areas, general laboratory facilities, documents, standards, procedures, instrumentation, quality control, data review, data management, and report generation.
- Collect relevant information: gather applicable laboratory or project documents which will be helpful in filling out portions of the audit checklist in advance, or aid in completing the audit report. Such documents could include the laboratory statement of qualifications (SOQ), statement of work (SOW), contract or bid package, relevant analytical or sampling methods, EPA or state performance evaluations performed within the past year, and the laboratory QA/QC manual. If the laboratory is currently under contract with EZ, or a third party for whom EZ is performing the audit, obtain the applicable documents from our contract files or

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from the third party. If the laboratory is being considered for performance of future work, obtain copies of the documents from the laboratory, if possible.

- Review the assembled information and begin filling out the audit checklist form following the instructions in Section 8. Make notes of additional questions regarding the laboratory which will need to be answered. Note that the audit checklist form (Attachment 1) contains general guidelines for laboratories testing hazardous materials, therefore, not all of the questions may be applicable. The audit procedure will proceed more quickly if those sections which are not applicable are marked with "N/A" in advance.

6.4 Schedule of the Site Visit

Remind the laboratory contact person of the purpose of the audit when you make the arrangements for a site visit. Since the most useful information can be gained while the laboratory is operating under typical conditions, only two to three days' advance warning should be allowed prior to the site visit. This should allow enough time for the laboratory to arrange that key individuals are available for site interviews.

It is helpful to the laboratory staff if the auditor provides the laboratory with information on the audit and explains how the site visit will be conducted. See Section 7 for a typical agenda for a site visit. Information which should be discussed in making arrangements for the site visit should include:

- Purpose of the audit (e.g., potential contract, resolution of problems)
- Estimate of time the site visit will take (typically, three to four hours for a small laboratory performing one type of analysis)
- Areas of the laboratory to be audited
- Topics to be covered during the site visit (e.g., organization and personnel training, client requests, sample receipt and storage areas, sample tracking, sample preparation areas, general laboratory facilities, documents, standards, procedures, instrumentation, quality control, data review, data management, and report generation)
- Staff requested to be available to the auditor during the site visit (e.g., lab manager or director, QA/QC officer, sample management supervisor, sample custodian, sample processing supervisor, inorganic and/or organic section supervisors, bench chemists and technicians, data management); there should be a specific laboratory staff member identified to provide information on each of the topics listed above

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- Documents requested to be available to the auditor during the site visit (e.g., QA program documents, policies and procedures, manuals, control charts, corrective action reports)
- Proposed site visit schedule (see Section 7 for a typical schedule)
- Specific problems, if any.

7. PERFORMANCE OF THE SITE VISIT

It is important to perform the site visit in a professional, efficient manner, and to minimize disruption of the normal laboratory activities. Try to have a cooperative attitude, and emphasize that this site visit is an information gathering activity that may provide helpful information to their organization as well. Do not make critical remarks or point out flaws, but include such remarks in written notes. One way to conduct a site visit is as follows:

- Initial briefing: meet the key personnel (managers and supervisors) in the laboratory as a group and briefly explain the purpose of the audit. Have one of the laboratory staff present a general overview of the laboratory organization and capabilities, and introduce personnel. Ask that a history be presented on a sample, beginning with the initial request for analysis, receipt of the sample from the client, through internal procedures and analysis, generation of data and submittal of the final data report to the client. Set the format for this initial briefing with the laboratory contact person prior to the site visit. Try to arrange to keep this initial briefing to approximately half an hour.
- Document review: have arrangements made ahead of time for an opportunity to review the laboratory documents you requested be available. This can be done at this point, during the interview, or near the end of the interview, just prior to the final briefing.
- Observation of the various areas of the laboratory: make arrangements ahead of time with the laboratory contact person to visit each area of interest in the laboratory to make observations. Cover each of the applicable topics on the audit checklist. Follow the sample history, as presented earlier by the laboratory. The audit checklist is organized to facilitate this task.
- Information gathering: collect information on the audit checklist as the site visit progresses. Make checks in the appropriate places, or write in the information necessary for each question as responses are given. It is difficult to remember all the information provided, and is important to be as accurate as possible in recording responses at the time they are provided.

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If possible, arrange to speak with bench level technicians and analysts during the observation process. Specific instructions for filling out the audit checklist are provided in Section 8.

- Final briefing: meet with the key personnel, or at a minimum with the laboratory director or QA manager, at the end of the interviews to ask any questions which may not have been answered. If additional information is necessary, ask that it be forwarded. Since it is not possible to tell the laboratory at this time whether the audit was passed or not, because a detailed review of the information provided on the checklist will be required, make no comment on whether the laboratory has passed the audit. However, give an indication of when the laboratory may expect an audit report, and to whom this report will be made available. Always thank the laboratory staff for their time and for allowing you to disrupt their schedules.

8. USE OF THE AUDIT CHECKLIST FORM

The audit checklist form (Attachment 1) provides general guideline questions for laboratories performing hazardous materials analysis. The EZ chemistry group leader should be consulted by the auditor, if it is felt that a project-specific form must be generated.

The checklist is divided into several sections:

- Organization and Personnel
- Sample Receipt and Storage Area
- Sample Preparation Area/Facilities
- Instrumentation
- Quality Control
- Data Handling and Review
- QC Manual Checklist
- Summary.

It is assumed that appropriate staff (who have been previously identified) will be made available to the auditor to answer the questions in each of these sections. Make checks in the appropriate boxes, or write in the information necessary for each question as the answers are provided. Do not make critical remarks or point out flaws, but include such information in written notes. Either write all notes on the checklist form or attach notes to the form. Ask to inspect documents, when appropriate, to verify answers.

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9. USE OF THE AUDIT SCORING GUIDELINES

Once the site visit has been completed and any additional information has been provided to the auditor, the evaluation of the laboratory can be completed.

Point distributions for each response which can be answered "yes" or "no" are given in the scoring guideline in Attachment 2. In some cases, it may be necessary to check both, as not all requirements may be fulfilled. All points are then totaled and the percentage of the maximum possible points is then calculated. Questions which are not applicable to a particular facility are not scored, and are not counted toward the maximum possible points, thereby neither rewarding or penalizing the laboratory. Responses to questions which have no point value will be used to determine marginal cases of pass or fail. The following criteria are given for acceptability or nonacceptability:

86–100% of maximum possible points	=	acceptable audit
76–85% of maximum possible points	=	provisionally acceptable audit (based on responses to nonpoint questions)
below 76% of maximum possible points	=	unacceptable audit

10. AUDIT REPORT

An internal memo summarizing the results should be provided to the EZ staff who requested the audit be performed. In many cases, the third party may wish to receive copies of the completed audit report for their records. An example memo is provided as Attachment 3 of this procedure. If it has been requested, a copy should also be provided to the audited laboratory.

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Attachment 1

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ANALYTICAL CHEMISTRY LABORATORY AUDIT GUIDELINES

Laboratory: _____ Date: _____

Address: _____ Telephone: _____

_____

Auditor(s): _____

_____

Laboratory Personnel Interviewed:

Name	Title

Laboratory Accreditation/Certification:

		Expiration	

Comments:

_____

_____

_____

Score:

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	Yes	No	Points	Comments
A. Organization and Personnel				
1. Is there an organizational chart available?	___	___	___	
2. Is everyone in the organization familiar with it?	___	___	___	
3. Is an up-to-date file maintained in the laboratory describing the educational background and/or related work experience of all laboratory personnel?	___	___	___	
4. Is there a formal training program for personnel?	___	___	___	
5. Are employees required to demonstrate proficiency with analytical instrument operation, methods, or techniques prior to working on client samples?	___	___	___	
6. Is this proficiency testing documented?	___	___	___	
7. Is the organization adequately staffed to meet commitments in a timely manner?	___	___	___	
8. Is there a designated QA/QC Officer?	___	___	___	
9. To whom does the lab QA/QC Officer report? _____				
10. Was the lab QA/QC Officer available during the audit?	___	___	___	
11. Was a program manager or laboratory manager available during the evaluation?	___	___	___	

Comments: _____

B. Sample Receipt and Storage Area				
1. Is a sample custodian designated?	___	___	___	
2. Are the responsibilities clearly defined?	___	___	___	
In writing?	___	___	___	
3. Is there a standard sample login procedure followed?	___	___	___	
4. Does the procedure include adequate inspection of samples and accompanying documents to verify that they are intact, complete, and consistent?	___	___	___	
5. Is there an inspection checklist?	___	___	___	
6. Does it document adequately the nature and condition of samples and documentation?	___	___	___	
7. Is the integrity of samples and shipping containers being documented?	___	___	___	

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	Yes	No	Points	Comments
8. Are samples logged into a bound notebook?	___	___	___	
a. Computerized lab management system?	___	___	___	
b. Other? (describe: _____)	___	___	___	
9. Does the login record document:				
a. Field and laboratory ID	___	___	___	
b. Analyses requested	___	___	___	
c. Storage location	___	___	___	
d. Signature of custodian	___	___	___	
e. Collection date	___	___	___	
f. Receipt date	___	___	___	
g. Analysis due date	___	___	___	
h. Sample holding time	___	___	___	
i. Special instructions	___	___	___	
10. Is there a daily summary of information such as samples received, analyses requested, date sampled, or date received?	___	___	___	
11. To whom is this summary distributed? _____				
12. Are login records filed and readily retrievable?	___	___	___	
13. How far back in time can records be retrieved? _____				
14. Are written SOPs developed for receipt and storage of samples?	___	___	___	
15. Are they available to and understood by laboratory personnel?	___	___	___	
16. Is a clean area available for receiving and opening sample shipments?	___	___	___	
17. Is this area separated from other lab operations (consider not only spatial separations, but air flow, personnel, traffic, etc.)?	___	___	___	
18. Does the custodian understand the importance of preventing lab contamination?	___	___	___	
19. If appropriate, are the pHs of samples measured and recorded to verify that they are preserved?	___	___	___	
20. What percentage of samples is checked? _____				
21. Are records of these checks retained?	___	___	___	
22. Are facilities adequate for the storage of samples?	___	___	___	
23. Are samples stored so as to maintain their preservation?	___	___	___	

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	Yes	No	Points	Comments
24. Are volatile samples stored separately from semivolatile samples?	___	___	___	
25. Is the temperature of the cold storage area recorded daily?	___	___	___	
a. Are excursions noted, along with descriptions of corrective action taken?	___	___	___	
b. Is this being reviewed periodically by a supervisor or the QC unit?	___	___	___	
26. Is the sample storage area secure?	___	___	___	
27. How is sample identification maintained? _____ _____ _____				
28. Is positive sample chain-of-custody maintained within the lab?	___	___	___	
29. How are samples tracked through the lab? _____ _____ _____				
30. How long are samples retained? _____ Sample extracts? _____				
31. How are special instructions regarding preparation, analysis, or turnaround times transmitted within the laboratory? _____ _____				

Comments: _____
_____
_____

C. Sample Preparation Area/Facilities

1. Is the laboratory maintained in a clean and organized manner?	___	___	___	
2. Does the lab appear to have adequate work space (120 ft^2 per analyst)?	___	___	___	
3. Are the toxic chemical handling areas either stainless steel benches or an impervious material covered with absorbent paper?	___	___	___	
4. Are contamination-free work areas provided for the handling of toxic materials?	___	___	___	

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	Yes	No	Points	Comments
5. Are adequate exhaust hoods available to prevent contamination of personnel and the laboratory facility?	___	___	___	
6. Are the flow rates and/or face velocities of these hoods periodically checked and recorded?	___	___	___	
7. How frequently are they checked? _____				
8. Are the procedures and records adequate to demonstrate the proper face velocity profile for each hood over the period of record?	___	___	___	
9. Is the near-face interior of each hood clear of objects that might interfere with the proper face velocity profile and thereby reduce hood efficiency?	___	___	___	
10. Are chemical waste disposal policies/procedures well-defined and followed by the laboratory?	___	___	___	
11. Are records of waste containerization and disposal (lab logs, manifest, etc.) filed and retrievable?	___	___	___	
12. Are voltage control devices installed on major instrumentation?	___	___	___	
13. What is the laboratory's source of distilled/deionized water? _____				
14. Is the conductivity of this water checked daily and data recorded (acceptable conductivity is 2.0–5.0 μmhos/cm at 25°C)?	___	___	___	
15. Is the analytical balance located away from draft and areas subject to rapid temperature fluctuations?	___	___	___	
16. Is it protected from vibration associated with activities in the facility (i.e., it should be on a heavy table, on a floor that does not bounce when walked on, etc.)?	___	___	___	
17. Is the balance maintained by a certified technician?	___	___	___	
18. Is the balance routinely calibrated with Class S weights and are the calibration data recorded?	___	___	___	
19. Are the Class S weights handled properly to prevent contamination/damage?	___	___	___	
20. How often are the Class S weights certified? _____				
21. Are pH and ion selective meters properly calibrated and maintained; and are these activities recorded?	___	___	___	
22. Are laboratory thermometers (including mercury-in-glass) calibrated at least yearly against an NIST traceable thermometer and documented?	___	___	___	

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	Yes	No	Points	Comments
23. Are reagents dated upon receipt by labeling each container with the date received?	___	___	___	
24. Is there a complete log of reagent and solvent supply giving the quantity, batch number, receipt date, percent activity, or purity?	___	___	___	
25. Are reagents and standards checked prior to use?	___	___	___	
26. Are solvent lots checked and documented prior to use?	___	___	___	
27. Are reference materials properly labeled?	___	___	___	
28. Is each spiking/calibration standard completely traceable to documented neat material or a documented purchased standard?	___	___	___	
29. Is each logbook entry signed and dated by the individual who prepared the solution?	___	___	___	
30. Are logbooks periodically reviewed and signed by a manager/supervisor?	___	___	___	
31. Are logbooks maintained in a manner which allows complete traceability?	___	___	___	
32. Are standards stored separately from samples and sample extracts?	___	___	___	
33. Are volatile and semivolatile standard compounds properly segregated?	___	___	___	
34. Are SOPs readily available to laboratory personnel?	___	___	___	
35. Are glassware cleaning procedures documented?	___	___	___	
36. Are the cleaning procedures consistent with EPA recommended procedures?	___	___	___	
37. Is the temperature of the drying ovens recorded daily?	___	___	___	
38. Is cleaned glassware properly handled and stored to prevent contamination?	___	___	___	
39. How do lab personnel recognize glassware that has been prepared for specific function (e.g., organic vs. inorganic)? _____				
40. Is the laboratory secured?	___	___	___	

Comments: _____

D. Instrumentation

1. Are instrument operating manuals available?	___	___	___	

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	Yes	No	Points	Comments
2. Do the operators demonstrate a good familiarity with the manuals?	___	___	___	
3. Are there service contracts on the instrumentation (and is a record maintained of the service)?	___	___	___	
4. Are in-house replacement parts available?	___	___	___	
5. Have the instruments been modified in any way?	___	___	___	
Describe the modifications and discuss ramifications: _____ _____				
6. Are instruments properly vented or are appropriate traps in place?	___	___	___	
7. Is a logbook maintained for each instrument?	___	___	___	
8. Is a complete list of laboratory instrumentation available?	___	___	___	
9. Are all calibration data hard-copied and retained?	___	___	___	
10. When calibrating an AA:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a new curve generated for each run?	___	___	___	
c. Is a standard blank always run?	___	___	___	
d. Is calibration checked immediately after completing as well as periodically throughout the run?	___	___	___	
11. When calibrating an ICP:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a new curve generated for each run?	___	___	___	
c. Is a standard blank always run?	___	___	___	
d. Is calibration checked immediately after completing as well as periodically throughout the run?	___	___	___	
12. When calibrating a GC:				
a. How many standards are run to generate the calibration curve?_____				
b. Is a calibration check standard run daily?	___	___	___	
c. What are the performance criteria for this standard?_____				
d. Is the instrument typically calibrated for every compound of interest?	___	___	___	

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	Yes	No	Points	Comments
e. How are retention times monitored for each compound of interest, and when is corrective action taken? _____				
13. When calibrating a GC/MS:				
a. How many standards are run to generate the calibration curve? _____				
b. Is a calibration check standard run daily?	___	___	___	
c. What are the performance criteria for this standard? _____				
d. Is the instrument typically calibrated for every compound of interest?	___	___	___	
e. Is the instrument tuned at least daily?	___	___	___	
f. Do the tuning procedures conform to the methods for which the instrument is being used?	___	___	___	
g. What compound and performance criteria are used? _____				
h. Are surrogates and internal standards used?	___	___	___	
i. Are surrogate and internal standard recoveries monitored?	___	___	___	
j. What are the action limits? _____				

Comments: _____

E. Quality Control

1. Are method blanks prepared and analyzed with each batch of samples, for each analytical procedure, or some percentage?	___	___	___	
What percentage:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
2. At what frequency are lab duplicates prepared and analyzed:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				

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	Yes	No	Points	Comments
d. For wet chemistry? _____				
3. How are duplicate sample results tracked and used:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
4. At what frequency are lab spikes (e.g., spiked deionized water or clean soil) prepared and analyzed:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
5. At what stage of processing are samples spiked:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
6. Are matrix spiked samples employed:				
a. For GC/MS analyses?	___	___	___	
b. For GC analyses?	___	___	___	
c. For AA/ICP analyses?	___	___	___	
d. For wet chemistry?	___	___	___	
7. What action is taken when results exceed control limits:				
a. For GC/MS analyses? _____				
b. For GC analyses? _____				
c. For AA/ICP analyses? _____				
d. For wet chemistry? _____				
8. Are surrogate compounds utilized for GC/MS analyses?	___	___	___	
9. When are the surrogates added to the samples? _____				
10. How many surrogate compounds are introduced? _____				
11. Is the percent recovery for each surrogate calculated?	___	___	___	
12. Are those data reported?	___	___	___	
13. Are performance criteria established for surrogates?	___	___	___	
14. Are percent recoveries plotted on control charts?	___	___	___	

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	Yes	No	Points	Comments
15. What action is taken when results exceed limits? _____				
16. Are surrogate compounds utilized for GC analyses?	___	___	___	
17. When are the surrogates added to the samples? _____				
18. How many surrogate compounds are introduced? _____				
19. Is the percent recovery for each surrogate calculated?	___	___	___	
20. Are those data reported?	___	___	___	
21. Are performance criteria established for surrogates?	___	___	___	
22. Are percent recoveries plotted on control charts?	___	___	___	
23. What action is taken when results exceed limits? _____				
F. Data Handling and Review				
1. Are computer programs validated prior to use?	___	___	___	
2. Are records of the validation maintained?	___	___	___	
3. Are user instructions complete and available to all users?	___	___	___	
4. Do analysts/technicians record data in a neat and accurate manner?	___	___	___	
5. Are all handwritten data recorded in nonerasable ink?	___	___	___	
6. Have entries been obliterated (e.g., through cross-outs or "whiteout")?	___	___	___	
7. Are data calculations spot-checked by a second person?	___	___	___	
What percentage? _____				
8. Are these checks documented on the hard-copy data record, and dated and initialed by the reviewer?	___	___	___	
9. Are raw data being identified with client name, project number, date, and other pertinent tracking information?	___	___	___	
10. Are raw data (notebooks, data sheets, computer files, strip chart recordings) being retained for 5 years?	___	___	___	
11. Is there a system for report, record, or data retrieval?	___	___	___	
12. Do supervisory personnel review the data or QC results?	___	___	___	
What percentage? _____				

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	Yes	No	Points	Comments
13. Are these reviews documented?	___	___	_____	
14. Are in-house QC charts maintained and available for onsite inspection for:				
a. Matrix spikes?	___	___	_____	
b. Laboratory duplicates?	___	___	_____	
c. Surrogate recoveries?	___	___	_____	
d. Calibration check standards?	___	___	_____	
15. Have method detection limit studies been performed for each method in use?	___	___	_____	
a. How recently? _____				
b. Any procedural or configurational changes since then?	___	___	_____	
16. Do records indicate that appropriate corrective action has been taken when analytical results fail to meet the QC criteria?	___	___	_____	

Comments: _____

G. QC Manual Checklist

1. Does the laboratory have a QC manual?	___	___	_____	
2. Does the manual address the following:				
a. Personnel?	___	___	_____	
b. Facilities or equipment?	___	___	_____	
c. Operation of instruments?	___	___	_____	
d. Method validation	___	___	_____	
e. Calibration frequency	___	___	_____	
f. Standards preparation	___	___	_____	
g. Documentation of procedures	___	___	_____	
h. Preventive maintenance	___	___	_____	
i. Reliability of data	___	___	_____	
j. Data validation	___	___	_____	
k. Feedback and corrective action	___	___	_____	
l. Record-keeping	___	___	_____	
m. Internal audits	___	___	_____	

Comments: _____

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	Yes	No	Points	Comments
H. Summary				
1. Do responses to the evaluation indicate that laboratory personnel are aware of QA/QC and its potential impact on the data?	___	___	_____	
2. Is a positive emphasis placed on QA/QC by laboratory management?	___	___	_____	
3. Have the responses been open and direct?	___	___	_____	
4. Has the attitude been cooperative?	___	___	_____	
5. Is the proper emphasis placed on quality assurance?	___	___	_____	

Comments: _____

_____

_____

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Attachment 2

[redacted]

ANALYTICAL AUDIT SCORING GUIDELINES

Point distributions for each response that can be answered "yes" or "no" are given in the following guideline. In cases of incomplete fulfillment of requirements, both responses may be checked. All points are then totaled and the percentage of the maximum possible points is then calculated. Questions that are not applicable to a particular facility are not scored, and are not counted toward the maximum possible points, thereby neither rewarding nor penalizing the laboratory. Responses to questions which have no point value will be used to determine marginal cases of pass or fail. The following criteria are given for acceptability or nonacceptability:

86–100% of maximum possible points	=	acceptable audit
76–85% of maximum possible points	=	provisionally acceptable audit (based on responses to nonpoint questions)
below 76% of maximum possible points	=	unacceptable audit

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		Yes	No	Comments
A.	**Organization and Personnel**			
1.	Is there an organizational chart available?	1	–1	
2.	Is everyone in the organization familiar with it?	1	–1	
3.	Is an up-to-date file maintained in the laboratory describing the educational background and/or related work experience of all laboratory personnel?	1	–1	
4.	Is there a formal training program for personnel?	1	–2	
5.	Are employees required to demonstrate proficiency with analytical instrument operation, methods, or techniques prior to working on client samples?	2	–2	
6.	Is this proficiency testing documented?	2	–1	
7.	Is the organization adequately staffed to meet commitments in a timely manner?	5	–1	
8.	Is there a designated QA/QC Officer?	2	–1	
9.	To whom does the lab QA/QC Officer report? _____			
10.	Was the lab QA/QC Officer available during the audit?	1	–1	
11.	Was a program manager or laboratory manager available during the evaluation?	1	–1	

Comments: _____

B.	**Sample Receipt and Storage Area**			
1.	Is a sample custodian designated?	2	–1	
2.	Are the responsibilities clearly defined?	1	–1	
	In writing?	1	–1	
3.	Is there a standard sample login procedure followed?	1	–1	
4.	Does the procedure include adequate inspection of samples and accompanying documents to verify that they are intact, complete, and consistent?	2	–1	
5.	Is there an inspection checklist?	1	–1	
6.	Does it document adequately the nature and condition of samples and documentation?	1	–1	
7.	Is the integrity of samples and shipping containers being documented?	1	–1	
8.	Are samples logged into a bound notebook?	5	–2	
	a. Computerized lab management system?	5	–2	
	b. Other? (describe: _____)	5	–2	

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		Yes	No	Comments
9.	Does the login record document:			
	a. Field and laboratory ID	2	–2	
	b. Analyses requested	2	–2	
	c. Storage location	2	–2	
	d. Signature of custodian	2	–2	
	e. Collection date	2	–2	
	f. Receipt date	2	–2	
	g. Analysis due date	2	–2	
	h. Sample holding time	2	–2	
	i. Special instructions	2	–2	
10.	Is there a daily summary of information such as samples received, analyses requested, date sampled, or date received?	2	–2	
11.	To whom is this summary distributed? _____			
12.	Are login records filed and readily retrievable?	2	–2	
13.	How far back in time can records be retrieved? _____			
14.	Are written SOPs developed for receipt and storage of samples?	2	–1	
15.	Are they available to and understood by laboratory personnel?	1	–1	
16.	Is a clean area available for receiving and opening sample shipments?	1	–1	
17.	Is this area separated from other lab operations (consider not only spatial separations, but air flow, personnel, traffic, etc.)?	1	–1	
18.	Does the custodian understand the importance of preventing lab contamination?	1	–1	
19.	If appropriate, are the pHs of samples measured and recorded to verify that they are preserved?	1	–1	
20.	What percentage of samples is checked? _____			
21.	Are records of these checks retained?	1	–1	
22.	Are facilities adequate for the storage of samples?	1	–1	
23.	Are samples stored so as to maintain their preservation?	2	–1	
24.	Are volatile samples stored separately from semivolatile samples?	5	–2	
25.	Is the temperature of the cold storage area recorded daily?	2	–1	

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	Yes	No	Comments
a. Are excursions noted, along with descriptions of corrective action taken?	2	–1	
b. Is this being reviewed periodically by a supervisor or the QC unit?	2	–1	
26. Is the sample storage area secure?	1	–1	
27. How is sample identification maintained? _____ _____ _____	1	–1	
28. Is positive sample chain-of-custody maintained within the lab?	1	–1	
29. How are samples tracked through the lab? _____ _____ _____			
30. How long are samples retained? _____ Sample extracts? _____			
31. How are special instructions regarding preparation, analysis, or turnaround times transmitted within the laboratory? _____ _____			

Comments: _____
_____
_____

C. Sample Preparation Area/Facilities

1. Is the laboratory maintained in a clean and organized manner?	2	–2	
2. Does the lab appear to have adequate work space (120 ft^2 per analyst)?	1	–1	
3. Are the toxic chemical handling areas either stainless steel benches or an impervious material covered with absorbent paper?	1	–1	
4. Are contamination-free work areas provided for the handling of toxic materials?	1	–1	
5. Are adequate exhaust hoods available to prevent contamination of personnel and the laboratory facility?	2	–1	
6. Are the flow rates and/or face velocities of these hoods periodically checked and recorded?	1	–1	

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		Yes	No	Comments
7.	How frequently are they checked? _____			
8.	Are the procedures and records adequate to demonstrate the proper face velocity profile for each hood over the period of record?	1	–1	
9.	Is the near-face interior of each hood clear of objects that might interfere with the proper face velocity profile and thereby reduce hood efficiency?	1	–1	
10.	Are chemical waste disposal policies/procedures well-defined and followed by the laboratory?	1	–1	
11.	Are records of waste containerization and disposal (lab logs, manifest, etc.) filed and retrievable?	1	–1	
12.	Are voltage control devices installed on major instrumentation?	1	–1	
13.	What is the laboratory's source of distilled/deionized water? _____			
14.	Is the conductivity of this water checked daily and data recorded (acceptable conductivity is 2.0–5.0 µmhos/cm at 25°C)?	2	–2	
15.	Is the analytical balance located away from draft and areas subject to rapid temperature fluctuations?	1	–1	
16.	Is it protected from vibration associated with activities in the facility (i.e., it should be on a heavy table, on a floor that does not bounce when walked on, etc.)?	1	–1	
17.	Is the balance maintained by a certified technician?	2	–2	
18.	Is the balance routinely calibrated with Class S weights and are the calibration data recorded?	2	–2	
19.	Are the Class S weights handled properly to prevent contamination/damage?	2	–2	
20.	How often are the Class S weights certified? _____			
21.	Are pH and ion selective meters properly calibrated and maintained; and are these activities recorded?	1	–1	
22.	Are laboratory thermometers (including mercury-in-glass) calibrated at least yearly against an NIST traceable thermometer and documented?	1	–1	
23.	Are reagents dated upon receipt by labeling each container with the date received?	1	–1	

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		Yes	No	Comments
24.	Is there a complete log of reagent and solvent supply giving the quantity, batch number, receipt date, percent activity, or purity?	1	–1	
25.	Are reagents and standards checked prior to use?	1	–1	
26.	Are solvent lots checked and documented prior to use?	1	–1	
27.	Are reference materials properly labeled?	1	–1	
28.	Is each spiking/calibration standard completely traceable to documented neat material or a documented purchased standard?	2	–1	
29.	Is each logbook entry signed and dated by the individual who prepared the solution?	1	–1	
30.	Are logbooks periodically reviewed and signed by a manager/supervisor?	1	–1	
31.	Are logbooks maintained in a manner which allows complete traceability?	2	–2	
32.	Are standards stored separately from samples and sample extracts?	1	–1	
33.	Are volatile and semivolatile standard compounds properly segregated?	1	–1	
34.	Are SOPs readily available to laboratory personnel?	1	–1	
35.	Are glassware cleaning procedures documented?	2	–2	
36.	Are the cleaning procedures consistent with EPA recommended procedures?	5	–2	
37.	Is the temperature of the drying ovens recorded daily?	1	–1	
38.	Is cleaned glassware properly handled and stored to prevent contamination?	2	–2	
39.	How do lab personnel recognize glassware that has been prepared for specific function (e.g., organic vs. inorganic)? _____			
40.	Is the laboratory secured?	1	–1	

Comments: _____

D. Instrumentation

1.	Are instrument operating manuals available?	1	–1	
2.	Do the operators demonstrate a good familiarity with the manuals?	1	–1	

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		Yes	No	Comments
3.	Are there service contracts on the instrumentation (and is a record maintained of the service)?	1	–1	
4.	Are in-house replacement parts available?	1	–1	
5.	Have the instruments been modified in any way?	–1	1	
	Describe the modifications and discuss ramifications: _____			
6.	Are instruments properly vented or are appropriate traps in place?	1	–1	
7.	Is a logbook maintained for each instrument?	1	–1	
8.	Is a complete list of laboratory instrumentation available?	1	–1	
9.	Are all calibration data hard-copied and retained?	5	–2	
10.	When calibrating an AA:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a new curve generated for each run?	5	–2	
	c. Is a standard blank always run?	5	–2	
	d. Is calibration checked immediately after completing as well as periodically throughout the run?	5	–2	
11.	When calibrating an ICP:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a new curve generated for each run?	5	–2	
	c. Is a standard blank always run?	5	–2	
	d. Is calibration checked immediately after completing as well as periodically throughout the run?	5	–2	
12.	When calibrating a GC:			
	a. How many standards are run to generate the calibration curve? _____			
	b. Is a calibration check standard run daily?	5	–2	
	c. What are the performance criteria for this standard? _____			
	d. Is the instrument typically calibrated for every compound of interest?	5	–2	

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	Yes	No	Comments
e. How are retention times monitored for each compound of interest, and when is corrective action taken? _____			
13. When calibrating a GC/MS:			
a. How many standards are run to generate the calibration curve? _____			
b. Is a calibration check standard run daily?	5	–2	
c. What are the performance criteria for this standard? _____			
d. Is the instrument typically calibrated for every compound of interest?	5	–2	
e. Is the instrument tuned at least daily?	5	–2	
f. Do the tuning procedures conform to the methods for which the instrument is being used?	5	–2	
g. What compound and performance criteria are used? _____			
h. Are surrogates and internal standards used?	5	–2	
i. Are surrogate and internal standard recoveries monitored?	5	–2	
j. What are the action limits? _____			

Comments: _____

E. Quality Control

1. Are method blanks prepared and analyzed with each batch of samples, for each analytical procedure, or some percentage?	5	–2	
What percentage:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
2. At what frequency are lab duplicates prepared and analyzed:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			

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	Yes	No	Comments
d. For wet chemistry? _____			
3. How are duplicate sample results tracked and used:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
4. At what frequency are lab spikes (e.g., spiked deionized water or clean soil) prepared and analyzed:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
5. At what stage of processing are samples spiked:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
6. Are matrix spiked samples employed:			
a. For GC/MS analyses?	1	–1	
b. For GC analyses?	1	–1	
c. For AA/ICP analyses?	1	–1	
d. For wet chemistry?	1	–1	
7. What action is taken when results exceed control limits:			
a. For GC/MS analyses? _____			
b. For GC analyses? _____			
c. For AA/ICP analyses? _____			
d. For wet chemistry? _____			
8. Are surrogate compounds utilized for GC/MS analyses?	5	–2	
9. When are the surrogates added to the samples? _____			
10. How many surrogate compounds are introduced? _____			
11. Is the percent recovery for each surrogate calculated?	5	–2	
12. Are those data reported?	2	–2	
13. Are performance criteria established for surrogates?	2	–2	
14. Are percent recoveries plotted on control charts?	2	–2	

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		Yes	No	Comments
15.	What action is taken when results exceed limits? _____			
16.	Are surrogate compounds utilized for GC analyses?	1	–1	
17.	When are the surrogates added to the samples? _____			
18.	How many surrogate compounds are introduced? _____			
19.	Is the percent recovery for each surrogate calculated?	1	–1	
20.	Are those data reported?	1	–1	
21.	Are performance criteria established for surrogates?	1	–1	
22.	Are percent recoveries plotted on control charts?	1	–1	
23.	What action is taken when results exceed limits? _____			
F.	**Data Handling and Review**			
1.	Are computer programs validated prior to use?	2	–1	
2.	Are records of the validation maintained?	2	–1	
3.	Are user instructions complete and available to all users?	2	–1	
4.	Do analysts/technicians record data in a neat and accurate manner?	2	–1	
5.	Are all handwritten data recorded in nonerasable ink?	2	–2	
6.	Have entries been obliterated (e.g., through cross-outs or "whiteout")?	–2	2	
7.	Are data calculations spot-checked by a second person?	2	–2	
	What percentage? _____			
8.	Are these checks documented on the hard-copy data record, and dated and initialed by the reviewer?	2	–2	
9.	Are raw data being identified with client name, project number, date, and other pertinent tracking information?	2	–2	
10.	Are raw data (notebooks, data sheets, computer files, strip chart recordings) being retained for 5 years?	2	–2	
11.	Is there a system for report, record, or data retrieval?	2	–1	
12.	Do supervisory personnel review the data or QC results?	2	–1	
	What percentage? _____			
13.	Are these reviews documented?	2	–1	

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	Yes	No	Comments
14. Are in-house QC charts maintained and available for onsite inspection for:			
a. Matrix spikes?	2	–2	
b. Laboratory duplicates?	2	–2	
c. Surrogate recoveries?	2	–2	
d. Calibration check standards?	2	–2	
15. Have method detection limit studies been performed for each method in use?	5	–2	
a. How recently? _____			
b. Any procedural or configurational changes since then?	–2	2	
16. Do records indicate that appropriate corrective action has been taken when analytical results fail to meet the QC criteria?	5	–2	

Comments: _____

G. QC Manual Checklist

1. Does the laboratory have a QC manual?	10	–10	
2. Does the manual address the following:			
a. Personnel?	1	–1	
b. Facilities or equipment?	1	–1	
c. Operation of instruments?	1	–1	
d. Method validation	1	–1	
e. Calibration frequency	1	–2	
f. Standards preparation	1	–1	
g. Documentation of procedures	1	–1	
h. Preventive maintenance	1	–1	
i. Reliability of data	1	–2	
j. Data validation	1	–2	
k. Feedback and corrective action	1	–2	
l. Record-keeping	1	–2	
m. Internal audits	1	–1	

Comments: _____

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	Yes	No	Comments
H. Summary			
1. Do responses to the evaluation indicate that laboratory personnel are aware of QA/QC and its potential impact on the data?	2	–2	
2. Is a positive emphasis placed on QA/QC by laboratory management?	2	–2	
3. Have the responses been open and direct?	2	–2	
4. Has the attitude been cooperative?	2	–2	
5. Is the proper emphasis placed on quality assurance?	2	–5	

Comments: _____

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Attachment 3

This is an example memorandum for a specific laboratory for which there were very few negative remarks. Naturally, not all laboratories will be of this quality.

EXAMPLE MEMORANDUM

(from an actual laboratory audit)

TO: [Audit Requestor]

FROM: [Auditor]

DATE: [Day/Month/Year]

SUBJECT: Laboratory Audit Visit to [Laboratory Name]
[Street Address]
[City, State, Zip Code]
[Phone Number]

An analytical chemistry laboratory observation visit was conducted on [date] at the [laboratory name and location]. The observation visit was performed by [auditor name] as part of the general QA/QC observations being conducted on behalf of [client name]. Samples were collected in the field by [source testing or field sampling company], and analyzed at the [laboratory name]. The following areas were included as a part of the observation process at [laboratory name]:

- Personnel and organization
- Sample receipt and storage
- Sample preparation facilities
- Instrumentation and equipment
- Quality control
- Data handling and review.

The attached Analytical Chemistry Laboratory Audit Guidelines were followed during the visit. Participating [laboratory name] staff included:

- [Names and titles].

The purpose of the observation visit was to determine whether [laboratory name] has the facilities, equipment, trained personnel, and QA/QC program in place to be capable of routinely producing data of known quality for site characterization programs. The completed checklist is appended.

AUDIT FINDINGS

Generally, the [laboratory name] was found to be capable of producing known quality, traceable data. There appeared to be an adequate understanding of QA/QC procedures within the laboratory. The employees interviewed displayed a positive attitude and an appreciation for the importance of quality assurance, and understood the potential impact of QA/QC upon data.

No major deficiencies were noted during the audit. The following recommendations are intended to improve a basically sound program:

- There should be more formal in-house QA/QC and training programs instituted for analysts and technicians; currently, training is dependent upon the more experienced analysts

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- An inspection checklist should be generated for incoming samples, which includes the nature and condition of samples and documentation
- Internal chain-of-custody procedures should be initiated
- As part of the SOPs, a specific policy should be instituted for the rejection of incoming compromised samples
- Control charts should be maintained for all types of QC samples that are run.

The [laboratory name] staff were very helpful and cooperative. There appears to be a positive emphasis placed on QA/QC by laboratory management, and the responses appeared to be open and direct.

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APPENDIX H

Format for the Sediment Testing Report

SEDIMENT TESTING REPORT FORMAT

The sediment testing report, including physical, chemical, bioassay, and bioaccumulation data, should be prepared using the format guidelines below.

A. INTRODUCTION

The project description should include the following information:

1. Location of the proposed dredging project and the disposal site.

2. A plan view map showing project design depth, side-slopes, allowable overdepth.

3. Proposed dredging and disposal quantities.

B. MATERIALS AND METHODS

1. Field sediment sampling and sediment sample handling procedures should be described or referenced.

2. References for laboratory protocols for physical, chemistry, bioassay, and bioaccumulation analyses should be included, such as:

   a. EPA method numbers and other EPA-approved methods that do not have a specific EPA number.

   b. Target detection limits and references used for physical, chemical and tissue analyses.

   c. Test species used in each test, the supplier or collection site for each test species, and QA/QC procedures for maintaining the test species.

   d. Locations of references and control sediment samples.

   e. Source of water used in all biological tests and documentation that the water is free of contaminants.

   f. Bioassay and bioaccumulation testing procedures and QA/QC information.

   g. Statistical analysis procedures.

C. LOCATION OF SAMPLING AREAS

1. The exact position of the dredging site sampling areas and each core taken within each sampling area should be mapped.

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2. A table should be prepared with the coordinates for each station in latitude and longitude (North America Datum 1983).

3. A table should be included showing the required sampling depth at each sampling location compared to the actual core depth achieved during field sampling. Any problems in collecting sediment from the required depth should be discussed.

4. The type of positioning equipment to be used for the sampling program should be specified.

5. Charts should be provided to show the location of the reference site, the control site(s) and the disposal site, including the coordinates of each site.

D. DESCRIPTION OF TESTING APPROACH

The rationale for performing specific types of tests (e.g. chemical analysis of elutiate for comparison to water quality standards, tissue analysis, etc.) should be presented in writing.

E. FINAL RESULTS

1. Summary data tables should be furnished. All data tables should be typed or produced as a computer printout.

2. Copies of the final raw data sheets should be included. These tables should be certified to be accurate by the analytical laboratory manager.

F. DISCUSSION AND ANALYSIS OF DATA

1. An evaluation of historical data from the proposed dredging site should be concisely discussed. References to previous sediment testing should also be included.

2. Statistical comparisons between the dredging site sediments and the reference sediment should be made.

G. REFERENCES

This list should include all references used in the field sampling program, laboratory and statistical data analyses, and historical data used to compare the dredging to the reference site.

H. DETAILED QA/QC PLANS AND INFORMATION

The following topics should be addressed in the QA Plan:

- Introductory material, including title and signature pages, table of contents, and project description.

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- QA organization and responsibilities (the QA organization should be designed to operate with a degree of independence from the technical project organization to ensure appropriate oversight)
- QA objectives
- Standard Operating Procedures
- Sampling strategy and procedures
- Sample custody
- Calibration procedures and frequency
- Analytical procedures
- Data validation, reduction, and reporting
- Internal QC checks
- Performance and system audits
- Facilities
- Preventive maintenance
- Calculation of data quality indicators
- Corrective actions
- QA reports to management
- References.

I. PERTINENT CORRESPONDENCE WITH SCOPING COMMENTS AND COORDINATION

The report should contain copies of the correspondence related to coordination on the testing activities for the proposed project.

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QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations

Chemical Evaluations

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