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Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual

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Office of Science & Technology
Office of Water
U.S. Environmental Protection Agency
Washington, DC 20460

Disclaimer

This technical manual provides a compilation of current information and recommendations for collecting, handling and manipulating sediment samples for physicochemical characterization and biological testing that are most likely to yield accurate, representative sediment quality data based on the experience of many monitoring programs and researchers. This manual has no immediate or direct regulatory consequence. It does not impose legally binding requirements on EPA, States, Tribes, other regulatory authorities, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA, State, Tribal, and other decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from those in this manual where appropriate. EPA may update this manual in the future as better information becomes available.

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Acknowledgments

This document is a general purpose manual intended to provide the user with sediment collection, storage, and manipulation methods that are most likely to yield accurate, representative sediment quality data for toxicity and chemical anlayses based on the experience of many monitoring programs and researchers. The approaches described in this manual represents a compilation of information presented in many publications, including Puget Sound Estuary Program (PSEP, 1997), Washington State Department of Ecology (1995), Environment Canada (1994), US Environmental Protection Agency - US Army Corps of Engineers (USEPA-USACE, 1998), American Society for Testing and Materials (ASTM, 2000), and USEPA (2000).

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Acronym List

ACOE	Army Corps of Engineers
ARCS	Assessment and Remediation of Contaminated Sediments
ASTM	American Society for Testing and Materials
AVS	Acid Volatile Sulfides
BMPs	Best Management Practices
BOD	Biochemical Oxygen Demand
CEC	Cation Exchange Capacity
COD	Chemical Oxygen Demand
CV	Coefficient of Variation
DOC	Dissolved Organic Carbon
DQO	Data Quality Objectives
EDMI	Electronic Distance Measurement Instrument
EMAP	Environmental Monitoring & Assessment Program
ERM	Effect Range Medium
GC/MS	Gas Chromatography/Mass Spectrophotometry
GC/FID	Gas Chromatography/Flame Ionization Detection
GC/ECD	Gas Chromatography/Electron Capture Detection
GLNPO	Great Lakes National Program Office
GPC	Gel Permeation Chromatography
GPS	Global Positioning System
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectoscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared Spectrophotometer
LORAN	LOng RAnge Navigation
NAWQA	National Water Quality Assessment

NDIR	Non-Dispersive Infrared Detector
NEP	National Estuary Program
NOAA	National Oceanic and Atmospheric Administration
NSI	National Sediment Inventory
NST	National Status & Trends
ORP	Oxidation Reduction Potential
OSHA	Occupational Safety & Health Administration
PCE	Power Cost Efficiency
POC	Particulate Organic Carbon
PSEP	Puget Sound Estuary Program
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RADAR	RAdio Detecting and Ranging
ROV	Remotely Operated Vehicle
RPD	Relative Percent Difference
SATNAV	SATellite NAVigation
SCV	Secondary Chronic Value
SEM	Simultaneously Extracted Metals
SIM	Selected Ion Monitoring
SOC	Suspended Organic Carbon
SOD	Sediment Oxygen Demand
SOPs	Standard Operating Procedures
SPMD	Semi-Permeable Membrane Device
SRM	Standard Reference Materials
TIC	Total Inorganic Carbon
TMDLs	Total Maximum Daily Loads
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
TVS	Total Volatile Solids

USEPA	United States Environmental Protection Agency
USGS	United States Geologic Survey
XRF	X-Ray Fluorescence

Foreword

Sediments provide essential habitat for many freshwater, estuarine, and marine organisms. In aquatic systems, most anthropogenic chemicals and waste materials, particularly persistent organic and inorganic chemicals, may accumulate in sediments. These sediments become repositories for many of the more toxic chemicals that are introduced into surface waters. United States Environmental Protection Agency's National Sediment Inventory (NSI) (USEPA 1998), a biennial report to Congress on sediment quality in the United States, demonstrates that sediment contamination exists in every state of the country. Contaminated sediments represent a hazard to aquatic life through direct toxicity as well as to aquatic life, wildlife and human health through bioaccumulation in the food chain. Assessments of sediment quality commonly include analyses of anthropogenic contaminants, benthic community structure, physicochemical characteristics, and direct measures of whole sediment and pore water toxicity. Accurate assessment of environmental hazards posed by sediment contamination depends in large part on the accuracy and representativeness of these analyses.

The methods described in this Manual are intended to provide the user with sediment collection, storage, and manipulation methods that are most likely to yield accurate, representative sediment quality data (e.g., toxicity, chemical) based on the experience of many monitoring programs and researchers.

This Manual represents a compilation of information presented in many publications, including:

- American Society for Testing and Materials (ASTM) 2000 document: *Standard Guide for Storage, Characterization, and Manipulation of Sediments for Toxicological Testing,* E-1391-94.

- Environment Canada 1994 manual: *Guidance Document on Collection and Preparation of Sediments for Physicochemical Characterization and Biological Testing*, EPS 1/RM/29.

- U.S. Environmental Protection Agency. 2000 manual: *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates. Second Edition*. EPA/600/R-99/064.

- U.S. Environmental Protection Agency / Army Corps of Engineers. 1998. *Inland Testing Manual: Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. - Testing Manual*. EPA-823-B-98-004.

- U.S. Environmental Protection Agency / Army Corps of Engineers. 1991. *Ocean Testing Manual: Evaluation of Dredged Material Proposed for Ocean Disposal: Testing Manual.* EPA-503/8-91/001.

In addition to many recent peer-reviewed technical journal papers, other publications that were relied on extensively include:

- Puget Sound Estuary Program (PSEP) 1997 manual: *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound*

- Washington Department of Ecology 1995 Document: *Guidance on the Development of Sediment Sampling and Analysis Plans Meeting the Requirements of the Sediment Management Standards*

- Great Lakes National Program Office (GLNPO) 1994 manual: *Assessment and Remediation of Contaminated sediments (ARCS) Program - Assessment Guidance* EPA-905-B94-002.

- U.S. Environmental Protection Agency. 2000 document: *Estuarine and Near Coastal Marine Waters: Bioassessment and Biocriteria Technical Guidance.* EPA-822-B-00-004.

This Manual addresses several needs identified in EPA's Contaminated Sediment Strategy (USEPA 1998) including: (1) an organized discussion of activities involved in sediment sampling and sample processing; (2) important issues that need to be considered within each activity; and (3) recommendations on how to best address issues such as sampling design, proper sampling procedures, and sample manipulations. Throughout this Manual, different considerations pertaining to sampling and sample processing are presented depending on the program need (e.g., dredge remediation versus status and trends monitoring).

EPA along with other agencies, assesses aquatic sediment quality under a variety of legislative requirements including:

- National Environmental Policy Act (NEPA)

- Clean Air Act; the Coastal Zone Management Act (CZMA)

- Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- Marine Protection, Research, and Sanctuaries Act (MPRSA)

- Resource Conservation and Recovery Act (RCRA)

- Toxic Substance Control Act (TSCA)

- Clean Water Act (CWA)

- Comprehensive, Environmental and Liability Act (CERCLA)

- Great Lakes Critical Programs Act of 1990.

In addition, many EPA offices coordinate sediment monitoring studies in specific geographic areas, such as through the Chesapeake Bay Program, the Great Lakes National Program, the Gulf of Mexico Program, the Washington State Sediment Management Standards Program, and in the States of Washington, Florida, California, New York, New Jersey, South Carolina, Texas, Massachusetts, and Wisconsin. To address its responsibilities within the above legislative acts, EPA has several ongoing programs that may involve sediment quality evaluation as summarized below.

Dredged Material Management

The U.S. Army Corps of Engineers (USACE), the Federal agency designated to maintain navigable waters, conducts a majority of the dredging projects and disposal under its Congressionally-authorized civil works program. The balance of dredging and disposal is conducted by a number of local public and private entities. In either case, the disposal is subjected to a regulatory program administered jointly by the USACE and EPA under Section 103 of the Marine Protection, Research, and Sanctuaries Act (MPRSA) for ocean disposal, and Section 404 of the Clean Water Act (CWA) for discharge at open water sites, confined disposal facilities with return flow to waters of the U.S., or for beneficial uses. EPA shares the responsibility of managing dredged material, principally in the development of the environmental criteria and guidelines by which proposed discharges are evaluated and disposal sites are selected, and in the exercise of its environmental oversight authority. Joint EPA/USACE guidance manuals detailing the testing and analysis protocols for dredged material disposal are well established.

National Estuary Program

EPA administers the National Estuary Program, established under the Clean Water Act to identify, restore, and protect nationally significant estuaries in the United States. Within the existing 28 programs, environmental monitoring is a key element of watershed protection strategies developed to maintain the chemical, physical, and biological properties of the estuarine ecosystems. The Puget Sound Estuary Program (PSEP), in particular, has been actively monitoring ecological health, including sediment quality, in Puget Sound, Washington for many years. PSEP, which includes EPA, the Puget Sound Water Quality Authority, and the Washington Department of Ecology, has developed sediment sampling and analysis procedures in collaboration with local governments and stakeholder groups (PSEP, 1997). The protocols are cited in and support the Washington Department of Ecology's (WDE) sediment management standards regulation, and have served as the foundation for many other guidance documents such as those produced by Environment Canada (1994) and American Society of Testing Materials (ASTM, 2000). This manual frequently refers to PSEP and WDE guidance.

Resource Conservation and Recovery Act (RCRA)

Under RCRA, EPA assesses whether releases from a hazardous waste treatment, storage, or disposal facility have contaminated sediments and requires corrective action, including possible remediation, if contamination is discovered. In many cases, sediment sampling and analyses, as discussed in this manual, are needed in RCRA facility assessments and RCRA facility investigations.

Office of Water

The Office of Water has been expanding provisions for sediment monitoring under the Clean Water Act, in the national monitoring framework developed by the Intergovernmental Task Force on Monitoring Water Quality (ITFM, 1995). Through this framework, agreements have been reached with other Federal, State, and local agencies concerning incorporation of sediment monitoring protocols, sediment monitoring QA/QC procedures, and appropriate information system linkages into monitoring programs. The Office of Water and the Office of Information Resources Management are also ensuring that the capability to store and use sediment data is enhanced as part of the ongoing modernization of the Agency's water quality data systems (STORET), and in coordination with the water quality data elements procedures being recommended by the National Methods and Data Comparability Board under the National Water Quality Monitoring Council. These data elements include information describing how samples were collected, stored, and processed prior to analysis.

Regional Environmental Monitoring and Assessment Program (REMAP)

REMAP, within the Office of Research and Development, gathers chemical and biological data describing sediment quality at many EMAP sampling stations. Data collected under REMAP are entered into the National Sediment Inventory (NSI). These data are used to assess status and trends on a regional scale, particularly for aquatic systems that may have water quality and/or sediment quality impairment.

Comprehensive, Environmental and Liability Act (CERCLA)

Under CERCLA, EPA carries out a detailed analysis at a site, evaluating the risks posed by contaminants to human health and the environment, and the feasibility of various response action alternatives to reduce risk. The *Risk Assessment Guidance for Superfund* (USEPA, 1997) provides a framework for the assessment of human health and environmental impacts. The CERCLA Program is using the EPA-wide sediment testing methods of the Tiered Testing Framework in the Remedial Investigation/Feasibility Study (CRI/FS) stage of analysis to help determine options for remedial actions. Much of the guidance presented in this manual supports the Tiered Testing Framework applicable to CERCLA sites.

Great Lakes Critical Programs Act of 1990

Annex 14 of the Great Lakes Water Quality Agreement between the United States and Canada (as amended by the 1987 Protocol) stipulates that the cooperating parties will identify the nature and extent of sediment contamination in the Great Lakes, develop methods to assess impacts, and evaluate the technological capability of programs to remedy such contamination. The 1987 amendments to the Clean Water Act authorized the Great Lakes National Program Office (GLNPO) to coordinate and conduct studies and demonstration projects relating to the appropriate treatment of toxic contaminants in bottom sediments. To fulfill the requirements of the Act, GLNPO initiated the Assessment and Remediation of Contaminated Sediments (ARCS) Program to help address contaminated sediment concerns in the development of Remedial Action Plans (RAPs) for all 43 Great Lakes Areas of Concern (AOCs, as identified by the United States and Canadian governments), as well as similar concerns in the development of Lakewide Management Plans. This manual frequently relies on information documented by the GLNPO and the ARCS program.

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Technical Terms

The following definitions were derived primarily from ASTM, USEPA, ACOE, and Environment Canada sources.

Acid Volatile Sulfide. The sulfides removed from sediment by cold acid extraction, consisting mainly of iron sulfide. AVS is the principal binding phase in sediment for divalent metals.

Artifact. An undesirable, detectable feature (e.g., chemical or physical change) in a sample, that has resulted from sampling, sample handling or storage, or from manipulations of the sample.

Benthic. Associated with the bottom of a waterbody.

Bioaccumulation. The net accumulation of a substance by an organism as a result of uptake from all environmental sources.

Bioavailability. The degree to which a chemical is taken up by aquatic organisms.

Chain-of-custody. The documentation that establishes the control of a sample between the time it is collected and the time it is analyzed. It usually applies to legal samples to demonstrate that there was no tampering with, or contamination of, the sample during this time.

Clean. Denotes a sediment or water test sample determined to not contain concentrations of contaminants which cause apparent and unacceptable harm (or effects) to the test organisms.

Composite sample. A sample that is formed by combining material from more than one sample or subsample.

Concentration. The ratio of weight or volume of test material(s) to the weight or volume of sediment or water.

Contaminated sediment. Sediment containing chemical substances at concentrations that pose a known or suspected threat to environmental or human health.

Control sediment. A sediment that is essentially free of contaminants and is used routinely to assess the acceptability of a test. Any contaminants in control sediment may originate from the global spread of pollutants and do not reflect any substantial input from local or non-point sources. Comparing test sediments to control sediments is a measure of the toxicity of a test sediment beyond inevitable background contamination.

Core sample. A sediment sample collected to obtain a vertical profile using a variety of instruments.

Data Quality Objectives (DQOs). Qualitative and quantitative statements that clarify the purpose of the monitoring study, define the most appropriate type of data to collect, and determine the most appropriate methods and conditions under which to collect them.

Decontamination. A process of washing or rinsing that removes chemicals adhering to equipment and supplies.

Ecotox Thresholds (ET). Benchmark values in ecological risk assessments defined as media-specific contaminant concentrations above which there is sufficient concern regarding adverse ecological effects to warrant further site investigation.

Elutriate. An aqueous solution obtained after adding water to a solid substance or loose material (e.g., sediment, tailings, drilling mud, dredge spoil), shaking the mixture, then centrifuging or filtering it or decanting the supernatant.

Equilibration. The condition in which a material or contaminant is at steady state between the solid or particulate sediment and the interstitial water.

Formulated Sediment. Mixtures of materials used to mimic a natural sediment.

Global Positioning system (GPS). A navigation system that relies on satellite information. It can give continuous position reports(i.e., latitude and longitude) that vary in accuracy depending on the sophistication of the receiving unit.

Grab. Any device designed to "bite" or "scoop" into the bottom sediment of a lake, stream, estuary, ocean, and similar habitats to sample the benthos. Grabs are samplers with jaws that are forced shut by weights, lever arms, springs or cables. Scoops are grab samplers that scoop sediment with a rotating container.

Head Space. The space in the storage container between the top of the sample and the lid of the container.

Holding time. The period of time during which a sediment or water sample can be stored after collection, and before analysis or use in a biological test. Changes that occur in sediments or water should be minimal during this period and the integrity of the sample should not be compromised to any substantial degree with respect to its physical, chemical, or biological characteristics.

Homogenization. The complete mixing of sediment, either by hand or mechanical means, until physical, chemical, and /or biological homogeneity of the sample is achieved.

Index Period. Specific time period in which sampling or *in-situ* analyses are conducted. Generally pertains to an ecologically important season and/or desired environmental conditions under which sampling is performed.

In Situ. Refers to the original (field) location from which test samples are collected, or at which organisms are exposed to undisturbed water or sediments for extended periods.

Interferences. Characteristics of sediments or sediment test systems that can potentially affect analytical results or test organism response aside from responses related to sediment contamination. Types of interferences include: non-contaminant characteristics (e.g., sediment texture or grain size, lighting); changes in chemical bioavailability due to sample handling or storage (e.g., ammonia generation); and the presence of indigenous organisms. Also referred to as confounding factors.

Interstitial water. Water occupying space between sediment or soil particles.

Measurement Quality Objectives (MQOs). Statements that describe the amount, type, and quality of data needed to address the overall project objectives.

Overlying water. The water placed over sediment in a test chamber during a test.

Peepers. Devices that collect interstitial water by diffusion through membranes attached to collection chambers. The chambers are typically placed in the sediment for extended periods of time to allow for equilibration between the internal water environment of the peeper and the surrounding ambient sediment/interstitial water matrix.

Pore water. See **interstitial water**.

Quality Assurance Project Plan. Project-specific document that specifies the data quality and quantity requirements needed for the study as well as all procedures that will be used to collect, analyze, and report those data.

Reference sediment. A whole sediment, collected near an area of concern, that is used as a point of comparison to assess sediment conditions exclusive of the material(s) or activities of interest. The reference sediment may be used as an indicator of localized sediment conditions exclusive of the specific pollutant input of concern. Such sediment would be collected near the site of concern and would represent the background conditions resulting from any localized pollutant inputs as well as global pollutant input. Program-specific guidance documents should be consulted, as some EPA programs have specific definitions and requirements for reference sediment.

Sampling Platform A working space, such as the deck of a boat, from which all sample collection activities are conducted.

Sediment. Particulate material that usually lies below water, or formulated particulate material that is intended to lie below water in a test.

Sediment Quality Triad. A weight-of-evidence sediment quality assessment approach which integrates data from sediment toxicity tests, chemical analyses, and benthic community assessments.

Sieving. Selectively removing certain size fractions of the sediment sample by processing sediment through selected mesh sizes.

Site. A study area that can be comprised of multiple sampling stations.

Spiking. Addition of a known amount of test material to a sediment often used as a quality control check for bias due to interference or matrix effects.

Station. A sampling location within a study area or site, where physical, chemical, or biological sampling and/or testing occurs.

Supernatant. The water separated from a sediment/water mixture following centrifugation or other separation techniques.

Toxicity. The property of a chemical, or combination of chemicals, to adversely affect organisms, tissues or cells.

Whole sediment. Sediment and associated interstitial water which have had minimal manipulation. Also referred to as **bulk sediment**.

Grammatical Terms

Consistent with guidance formulated by the American Society for Testing and Materials (ASTM), the following grammatical phrases, used in this manual, are defined as follows:

The words “must”, “should”, “may”, “can”, and “might” have specific meanings in this manual.

“Must” is used to express an absolute requirement, that is, to produce accurate results, a sample ought to be handled or manipulated in a specified manner, unless the purpose of the study requires a different procedure.

“Should” is used to state that the specified condition or procedure is recommended and ought to be met if possible. Although violation of one “should” is rarely a serious matter, violations of several will often render the results questionable.

“Desirable” is used in connection with less important factors.

“May” is used to mean “is allowed to.” “Can” is used to mean “is able to.” “Might” is used to mean “could possibly.” Thus, the classic distinction between “may” and “can” is preserved, and “might” is not used as a synonym for either “may” or “can.”

Using the Manual

Throughout this Manual, there are three categories of information that are organized into text boxes as part of the effort to make this methods document more useful and accessible to users. Each box always appears with the same icon throughout the Manual:

Recommendations for procedures and equipment.

Consideration, or issues, that should be addressed

Checklists of information

The full list of Recommendation Boxes are identified on page xix as part of the Table of Contents.

CHAPTER 1 Introduction

1.1 Background

Protecting sediment quality is an important part of restoring and maintaining the biological integrity of our Nation's waters as well as protecting aquatic life, wildlife and human health. Sediment is an integral component of aquatic ecosystems, providing habitat, feeding, spawning, and rearing areas for many aquatic organisms. Sediment also serves as a reservoir for pollutants and therefore a potential source of pollutants to the water column, organisms, and ultimately human consumers of those organisms. These pollutants can arise from a number of sources, including municipal and industrial discharges, urban and agricultural runoff, atmospheric deposition, and port operations.

Contaminated sediment can cause lethal and sublethal effects in benthic (sediment-dwelling) and other sediment-associated organisms. In addition, natural and human disturbances can release pollutants to the overlying water, where pelagic (water column) organisms can be exposed. Sediment pollutants can reduce or eliminate species of recreational, commercial, or ecological importance, either through direct effects or by affecting the food supply that sustainable populations require. Furthermore, some sediment pollutants can bioaccumulate through the food chain and pose health risks to wildlife and human consumers even when sediment-dwelling organisms are not themselves impacted.

The extent and severity of sediment contamination in the U.S. has been documented in the National Sediment Inventory (NSI)[1] and through other historical information. The NSI screening evaluation of sediment contamination data indicates that associated adverse effects are probable in thousands of locations throughout the country. The results emphasize the widespread need to address sediment contamination in the U.S.

1.2 Significance and Use of this Manual

Sediment quality assessment is an important component of water quality protection programs. Sediment assessments commonly include physicochemical characterization, toxicity tests, and/or bioaccumulation tests, as well as benthic community analyses. USEPA's NSI, for example, collates this information to develop a biennial report to Congress on sediment quality in the United States, required under the Water Resources Development Act of 1992. The use of consistent sediment collection, manipulation, and storage methods will help provide high quality samples with which accurate data can be obtained for the national inventory and for other programs to prevent, remediate, and manage contaminated sediment.

It is now widely known that the methods used in sample collection, transport, handling, storage, and manipulation of sediments and interstitial waters can influence the physicochemical properties and

[1]The National Sediment Inventory, or NSI, is the database of sediment quality information used to develop EPA's 1997 Report to Congress, *The Incidence and Severity of Sediment Contamination in Surface Waters of the United States*, *Volume 1: National Sediment Quality Survey* (U.S. EPA, 1997a). The database is updated periodically with new available information on sediment quality at sites throughout the U.S. **http://www.epa.gov/OST/cs/report.html**

the results of chemical, toxicity, and bioaccumulation analyses. Addressing these variables in an appropriate and systematic manner will help assure more accurate sediment quality data and facilitate comparisons among sediment studies.

This Technical Manual provides current information and recommendations for collecting and handling sediments for physicochemical characterization and biological testing, using procedures that are most likely to maintain *in situ* conditions, most accurately represent the sediment in question, or satisfy particular program needs, to help ensure consistent, high quality data collection.

1.3 Applicability and Scope of this Manual

This manual is intended to provide technical support to those who design or perform sediment quality studies under a variety of regulatory and non-regulatory programs. Information is provided concerning general sampling design considerations, field and laboratory facilities needed, safety, sampling equipment, sample storage and transport procedures, and sample manipulation issues common to chemical or toxicological analyses. Information contained in this manual reflects the knowledge and experience of several internationally-known sources including American Society for Testing and Materials (ASTM), Puget Sound Estuary Program (PSEP), Washington State Department of Ecology (WDE), United States Environmental Protection Agency (USEPA), US Army Corps of Engineers (ACOE), National Oceanic and Atmospheric Administration (NOAA), and Environment Canada. This manual attempts to present a coherent set of recommendations on field sampling techniques and sediment/interstitial water sample processing based on the above sources, as well as extensive information in the current peer-reviewed literature.

As the scope of this manual is broad, it is impossible to adequately present detailed information on every aspect of sediment sampling and processing for all situations or all programs. Nor is such detailed guidance warranted because much of this information (e.g., how to operate a particular sampling device or how to use a Geographical Positioning System (GPS) device) already exists in other published materials referenced in this manual. Furthermore, many programs have specific sampling and sample processing procedures. While an attempt is made to give examples from different programs, the manual repeatedly instructs the reader to check their own specific program requirements.

Given the above constraints, this manual: (1) presents an organized discussion of activities involved in sediment sampling and sample processing; (2) alerts the user to important issues that need to be considered within each activity; and (3) gives recommendations on how to best address the issues raised such that appropriate samples are collected and analyzed. An attempt is made to alert the user to different considerations pertaining to sampling and sample processing depending on the program need (e.g., dredge remediation versus status and trends monitoring).

Figure 1-1 presents a flow chart of the general activities discussed in this manual. The organization of these activities reflects the desire to give field personnel and managers a useful tool for choosing appropriate sampling locations, characterize those locations, collect and store samples, and manipulate those samples for analyses. Chapters are written so that the reader could obtain information on only one activity or set of activities (e.g., subsampling or sample processing), if desired, without necessarily reading the entire manual. Many sections are cross-referenced so that the reader is alerted to relevant issues that might be covered elsewhere in the manual. This is particularly important for certain chemical or toxicological applications in which appropriate sample processing or laboratory procedures are associated with specific field sampling procedures.

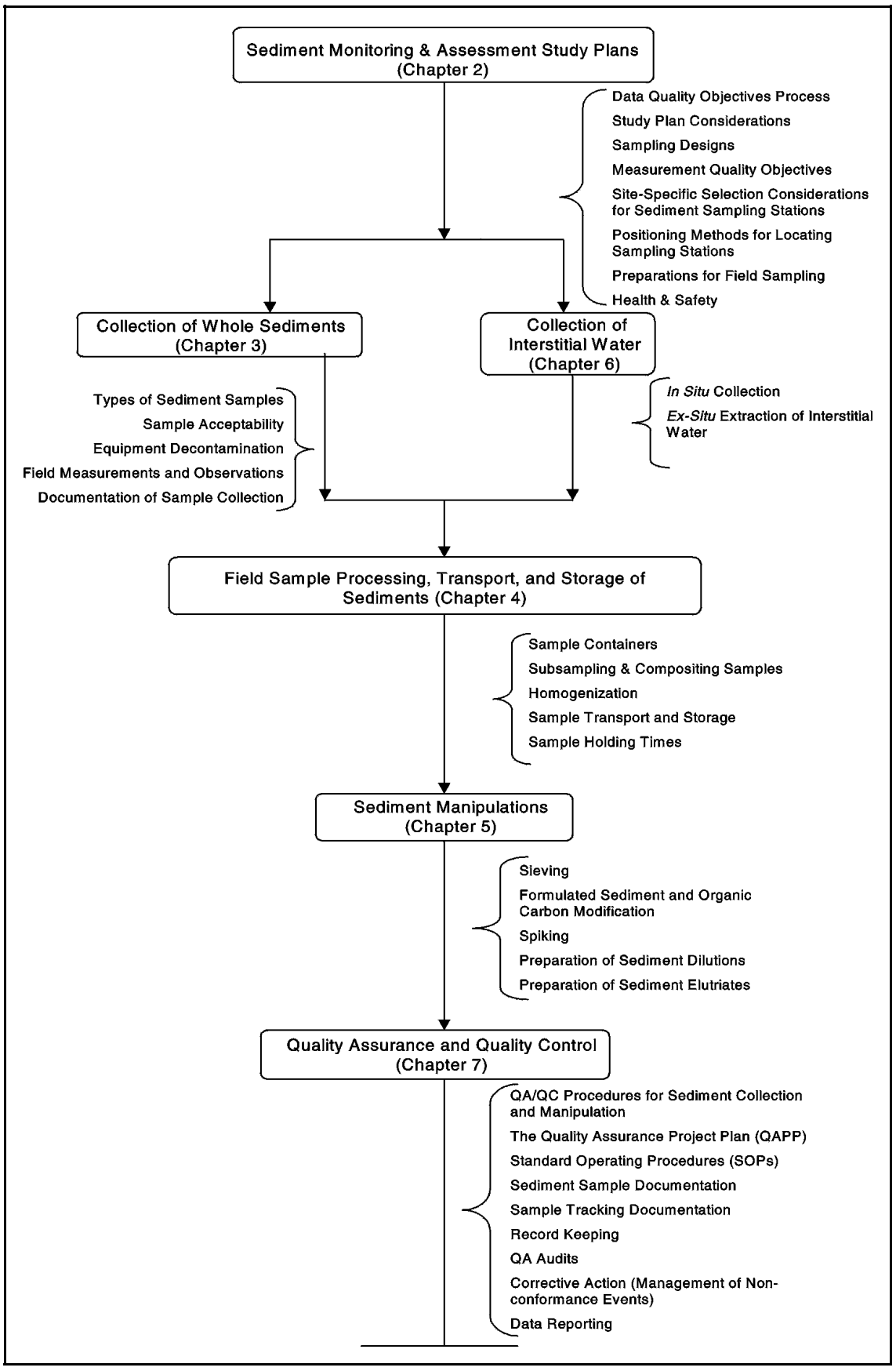


Figure 1-1. Flow chart summarizing activities for collection, storage, and manipulation of sediments and interstitial water.

The methods contained in this manual are widely applicable to any entity wishing to collect consistent, high quality sediment data. This manual **does not** provide guidance on how to implement any specific regulatory requirement, or design a particular sediment quality assessment, but rather it is a compilation of technical methods on how to best collect environmental samples that most appropriately address common sampling objectives.

Although the data from these samples might be used in environmental decision-making at a variety of levels, this manual does not address how data are to be used. The Foreword section summarizes a variety of EPA programs that assess sediment quality and may benefit from the methods described in this manual. Other Agencies and programs are also encouraged to consider these methods in order to generate consistent and high quality sediment data.

The information presented in this manual should not be viewed as the final statement on all the recommended procedures. Some of the areas covered in this document (e.g., sediment holding time, formulated sediment composition, interstitial water collection and processing) are being actively researched and debated. As data from sediment monitoring and research becomes more available in the future, EPA may update this manual as necessary.

CHAPTER 2 Sediment Monitoring and Assessment Study Plans

Every study site and project are unique; therefore, sediment monitoring and assessment study plans should be carefully prepared to best meet the project objectives (MacDonald et al., 1991; see Figure 2-1).

Considerations

The initial issues that need to be considered prior to preparing study plans are...

- define the potential problem or general project objective
- determine what resources (e.g., time, money, personnel) are available for the project
- review existing information and identify specific objectives of the study
- determine what data are likely to be needed to answer project objectives, including the role of site-specific conditions and/or issues that might influence the process of data collection and analyses

Before collecting any environmental data, it is important to determine the type, quantity, and quality of data needed to meet the project objectives (e.g., specific parameters to be measured) and support a decision based on the results of data collection and observation. Not doing so creates the risk of expending too much effort on data collection (i.e., more data are collected than necessary), not expending enough effort on data collection (i.e., more data are necessary than were collected), or expending the wrong effort (i.e., the wrong data are collected).

2.1 Data Quality Objectives Process

The **Data Quality Objectives (DQO) Process** developed by EPA (GLNPO, 1994; USEPA, 2000a) is a flexible planning tool that systematically addresses the above issues in a coherent manner. The purpose of this process is to improve the effectiveness, efficiency, and defensibility of decisions made based on the data collected, and to do so in an effective manner (USEPA, 2000a). The information compiled in the DQO process is used to develop a project-specific **Quality Assurance Project Plan (QAPP)** (see Chapter 7 and USEPA, 2000a) which should be used to plan the majority of sediment quality monitoring or assessment studies. In some instances, a programmatic QAPP may be prepared, as necessary, on a project-by-project basis.

The Data Quality Objectives (DQO) process addresses the uses of the data (most importantly, the decision(s) to be made) and other factors that will influence the type and amount of data to be collected (e.g., the problem being addressed, existing information, information needed before a decision can be made, and available resources). From these factors the qualitative and quantitative data needs are determined (see Figure 2-2). DQOs are qualitative and quantitative statements that clarify the purpose of the monitoring study, define the most appropriate type of data to collect, and determine the most appropriate methods and conditions under which to collect them. The products of the DQO process are criteria for data quality and a data collection design that ensures that data will meet the criteria.

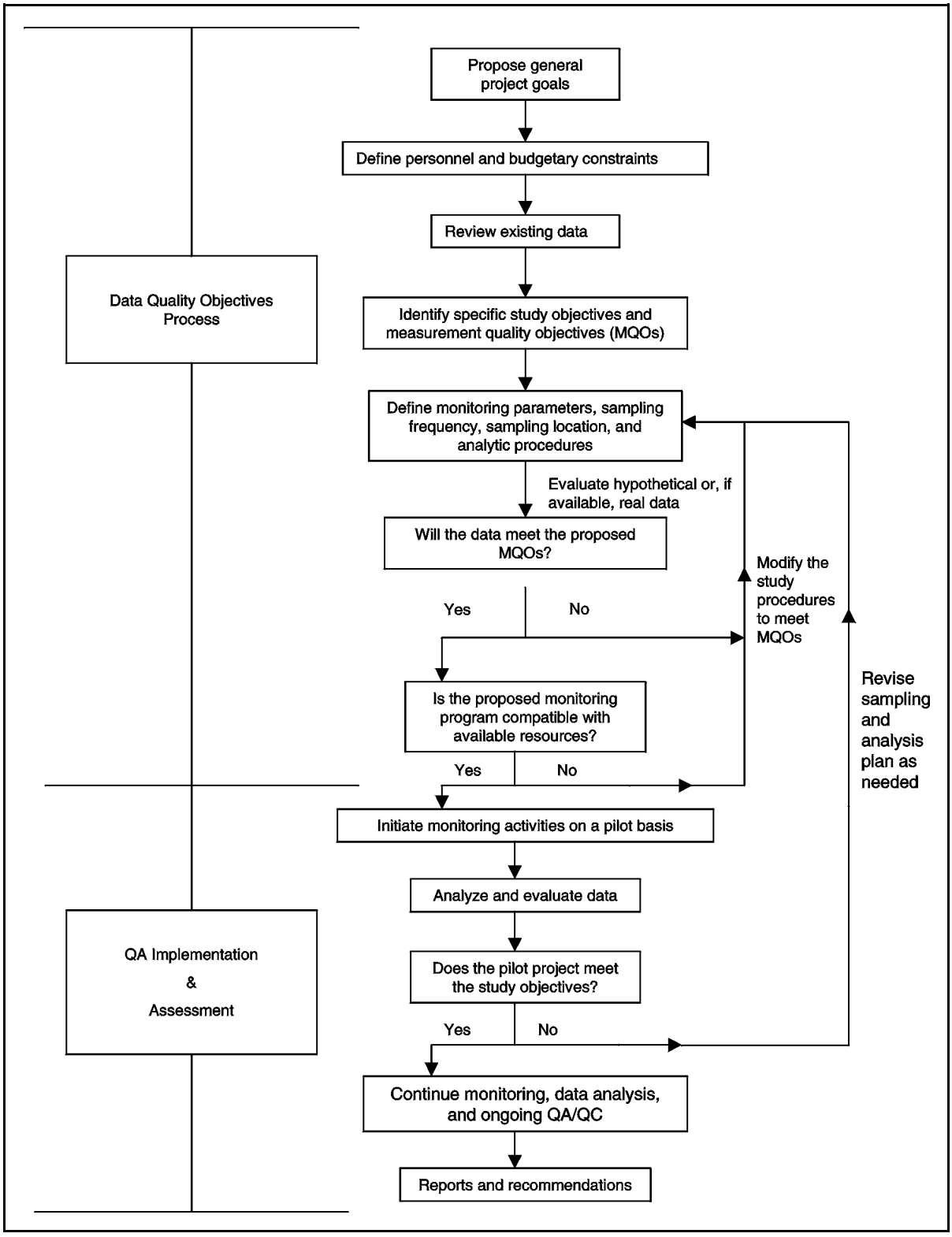


Figure 2-1. Flow chart summarizing the process that should be implemented in designing and performing a monitoring study (modified from MacDonald et al. (1991)).

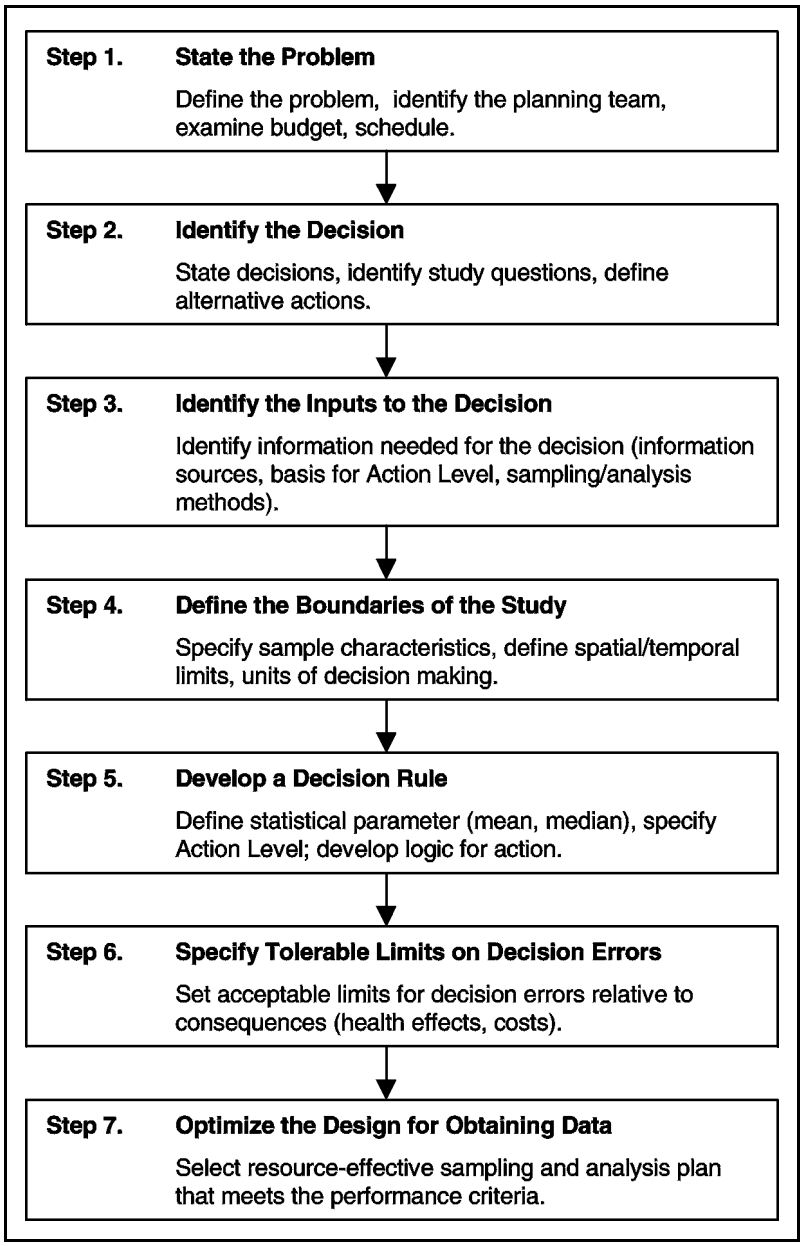


Figure 2-2. Flow chart summarizing the Data Quality Objectives Process (after USEPA, 2000a).

Checklist

In the DQO process, the following steps should be addressed:

✓ **Clearly state the problem: purpose and objectives, available resources, members of the project team:** e.g., The purpose might be to evaluate current sediment quality conditions, historical conditions, evaluate remediation effects, or validate a sediment model. It is important to review and evaluate available historical data relevant to the study at this point in the process.

✓ **Identify the decision; the questions(s) the study attempts to address**: e.g., Is site A more toxic than site B?; Are sediments in Lake Y less toxic now than they used to be?; Does the sediment at site D need to be remediated? What point or nonpoint sources are contributing to sediment contamination?

✓ **Identify inputs to the decision: information and measurements that need to be obtained**; e.g., analyses of specific contaminants, toxicity test results, biological assessments, bioaccumulation data, habitat assessments, hydrology, and water quality characterization.

✓ **Define the study boundaries (spatial and temporal).** Identify potential sources of contamination; determine the location of sediment deposition zones; determine the frequency of sampling and need for a seasonal sampling and/or sampling during a specific index period; consider areas of previous dredged or fill material discharges/disposal. Consideration of hydraulic patterns, flow event frequency, and/or sedimentation rates could be critical for determining sampling frequency and locations.

✓ **Develop a decision rule: define parameters of interest and determine the value of a parameter that would cause follow-up action of some kind**; e.g., exceedance of Sediment Quality Guideline value, NOAA Effect Range Median (ERM) value, or toxicity effect (e.g., 50% mortality), results in some action (Long et al., 1995). For example, in the Great Lakes Assessment and Remediation of Contaminated Sediments (ARCS) Program, one decision rule was: if total PCB concentration exceeds a particular action level, then the sediments will be classified as toxic and considered for remediation (GLNPO, 1994). Specifying decision rules or criteria is especially critical in sediment remediation programs and any study in which the results could be subject to legal scrutiny (e.g., superfund).

✓ **Specify limits on decision errors:** establish the measurement quality objectives (MQOs) which include determining the level of confidence required from the data; precision, bids, representativeness, and completeness of data; the sample size (weight or volume) required to satisfy the analytical methods and QA/QC program for all analytical tests; the number of samples required, to be within limits on decision errors, and compositing needed, if any.

✓ **Optimize the design:** choose appropriate sampling and processing methods; select appropriate method for determining the location of sampling stations; select an appropriate positioning method for the site and study. Consult historical data and a statistician before the study begins regarding the sampling design (i.e., the frequency, number, and location of field-collected samples) that will best satisfy study objectives.

For most programs, a Sampling and Analysis Plan (SAP) is developed prior to sampling which should describe the study objectives, sampling design and procedures, and other aspects of the DQO process outlined above (see Appendix B for an example of SAP requirements recommended by Washington State Department of Ecology). The following sections provide guidance on many of the primary issues that should be addressed in the study plan.

2.2 Study Plan Considerations

Monitoring and assessment studies are performed for a variety of reasons (ITFM, 1995) and sediment assessment studies can serve many different purposes. Developing an appropriate sampling plan is one of the most critical steps in monitoring and assessment studies. The sampling plan, including definition of the site and sampling design, will be a product of the general study objectives (Figure 2-1). Station location, selection, and sampling methods will necessarily follow from the study design. Ultimately, the study plan should control extraneous sources of variability or error to the extent possible so that data are appropriately representative of the sediment and fulfill the study objectives.

2.2.1 Definition of the Study Area and Study Site

The study area refers to the body of water that contains the study site(s) to be monitored and/or assessed, as well as adjacent areas (land or water) that might affect or influence the conditions of the study site. The study site refers to the body of water and associated sediments to be monitored and/or assessed. EMAP, for example, often defines a site as an area of concern (AOC) which might extend several miles in length, or may encompass large geographical or coastal areas. CERCLA defines a site in terms of a specific source of contamination such as a waste disposal area.

The size of the study area will greatly influence the type of sampling design (see Section 2.3) and site positioning methods that are appropriate (see Section 2.6). The boundaries of the study area need to be clearly defined at the outset and should be outlined on a hydrographic chart or topographic map.

Common purposes of sediment quality studies:

- Status and trends
- Evaluating program or BMP (best management practice) effectiveness
- Validating sediment quality models
- Designing regulatory programs
- Identifying whether significant contamination exists and extent of contamination
- Identifying sources of contamination
- Ranking existing and identifying emerging problems
- Establishing goals for sediment remediation
- Evaluating dredged or fill material discharges/disposal

2.2.2 Controlling Sources of Variability

A key factor in effectively designing a sediment quality study is controlling those sources of variability in which one is not interested (USEPA 2000a,b). There are two major sources of variability that, with proper planning, can be minimized, or at least accounted for, in the design process, thereby ensuring a successful study. In statistical terms, the two sources of variability are sampling error and measurement error (USEPA 2000b; Solomon et al., 1997).

Sampling error is the error attributable to selecting a certain sampling station that might not be representative of the site or population of sample units (e.g., an estuary or a CERCLA site). Sampling error is controlled by either: (1) using unbiased methods to select stations if one is performing general monitoring of a given site (USEPA, 2000b); or (2) several stations along a spatial gradient if a specific location is being targeted (see Section 2.3).

Measurement error is the degree to which the investigator accurately characterizes the sampling unit or station. Thus, measurement error includes components of natural spatial and temporal variability within the sample unit as well as actual errors of omission or commission by the investigator. Measurement error is controlled by using standardized and comparable methods: standardized methods include proper training of personnel and quality assurance procedures. To help minimize measurement error, each station should be sampled in the same way, within a site or study, using a standardized set of procedures and in the same time frame to minimize confounding sources of variability (see Section 2.2.3). In analytical laboratory or toxicity procedures, measurement error is estimated by duplicate determinations on some subset of samples (but not necessarily all). Similarly, in field investigations, some subset of sample units (e.g., 10% of the sites) should be measured more than once to estimate measurement error (see Replicate and Composite Samples, Section 2.4.3).

Measurement error can be reduced by analyzing multiple observations at each station (e.g., multiple grab samples at each sampling station, multiple observations during a season), or by collecting depth-integrated, or spatially integrated (composite) samples (see Section 2.4.3).

Checklist
To minimize measurement error:

- ✓ Sample all stations similarly within a study
- ✓ Use standardized procedures
- ✓ Sample during the same time period
- ✓ Collect and analyze multiple samples at a station
- ✓ Collect and analyze composited samples

Optimizing sampling design requires consideration of tradeoffs among the measures used, the effect that is considered meaningful, desired power, desired confidence, and resources available for the sampling program. Statistical power is the ability of a given sampling design to detect an effect that actually exists, and will be a product of the collection methods, analytical procedures, and quality control processes used. Power is typically expressed as the probability of correctly finding a difference among sites or between reference and test sites (e.g., toxicity or biological impairment) when one exists. For a fixed confidence level (e.g., 90%), power can be increased by increasing the sample size or the number of replicates (see Section 2.4.3 for more information). Most programs do not estimate power of their sampling design because this generally requires prior information such as pilot sampling, which entails further resources. One study (Gilfillan et al., 1995) reported power estimates for a shoreline monitoring program following the Valdez oil spill in Prince William Sound, Alaska. However, these estimates were computed after the sampling took place. It is desirable to estimate power before sampling is performed to ensure credibility of non-significant results (see Appendix C).

2.2.3 Sampling Using an Index Period

Most monitoring programs do not have the resources to characterize variability or to assess sediment quality for all seasons. Sampling can be restricted to an **index period** when biological and/or toxicological measures are expected to show the greatest response to pollution stress and within-season variability is small (Holland, 1985; Barbour et al., 1999). This type of sampling might be especially advantageous for characterizing sediment toxicity, sediment chemistry, and benthic macroinvertebrate and other biological assemblages (USEPA, 2000c). In addition, this approach is useful if sediment contamination is related to, or being separated from, high flow events. By sampling overlying waters during both low and high flow conditions, the relative contribution of

each to pollutant loads or sediment contamination can be better assessed, thereby better directing remedial activities, or other watershed improvements.

Those programs that sample the same site over multiple years (e.g., many EMAP and superfund studies), are interested in obtaining comparable data with which they can assess changes over time, or following remediation (GLNPO, 1994). In these cases, index period sampling is especially useful because hydrological regime (and therefore biological processes) is likely to be more similar between similar seasons than among different seasons.

2.3 Sampling Designs

As mentioned in earlier sections of this chapter, the type of sampling design used is a function of the study Data Quality Objectives and more specifically, the types of questions to be answered by the study. A summary of various sampling designs is presented in Figure 2-3 along with recommendations concerning the conditions under which a given design is appropriate. Generally, sampling designs fall into two major categories: random or probabilistic, and targeted (USEPA, 2000b). USEPA (2000b;c) present a thorough discussion of sampling design issues and detailed information on different sampling designs. Some program-specific guidance documents (e.g., USEPA/ACOE 1991, 1998 for dredged material disposal issues) also discuss relevant sampling designs. Table 2-1 presents suggested sampling designs given different overall objectives and constraints. Appendix A presents hypothetical examples of sediment quality monitoring designs given different objectives or regulatory applications.

> ***Sampling Design*** refers to the array, or network, of sampling sites selected for a monitoring program; usually taking one of two forms:
>
> - *Probabilistic Design* — Network that includes sampling sites selected randomly in order to provide an unbiased assessment of the condition of the waterbody at a scale above the individual site or stream; can address questions at multiple scales.
> - *Targeted Design* — Network that includes sampling sites selected based on known existing problems, knowledge of upcoming events in the watershed, or a surrounding area that will adversely affect the waterbody such as development or deforestation; or installation of BMPs or habitat restoration that are intended to improve waterbody quality; provides assessments of individual sites or reaches.

2.3.1 Probabilistic and Random Sampling

Probability-based or random sampling designs avoid bias in the results of sampling by randomly assigning and selecting sampling locations. A probability design requires that all sampling units have a known probability of being selected. Both EPA's Environmental Monitoring Assessment Program and NOAA's National Status and Trends Program use a probabilistic sampling design to infer regional and national patterns with respect to contamination or biological effects.

Sites can be selected on the basis of a truly random scheme or in a systematic way (e.g., sample every 10 meters along a randomly chosen transect). In ***simple random sampling***, all sampling units have an equal probability of selection. This design is appropriate for estimating means and totals of environmental variables if the population is homogeneous. To apply simple random sampling, it is necessary to identify all potential sampling times or locations, then randomly select individual times or locations for sampling.

In ***grid or systematic*** sampling, the first sampling location is chosen randomly and all subsequent stations are placed at regular intervals (e.g. 50m apart) throughout the study area. Clearly, the number of sampling locations could be large if the study area is large and one desires "fine-grained" contaminant or toxicological information. Thus, depending on the types of analyses desired, such sampling might become expensive unless the study area is relatively small and/or the density of stations (that is how closely spaced are the stations) is relatively low. Grid sampling might be effective for detecting previously unknown "hot spots" in a limited study area.

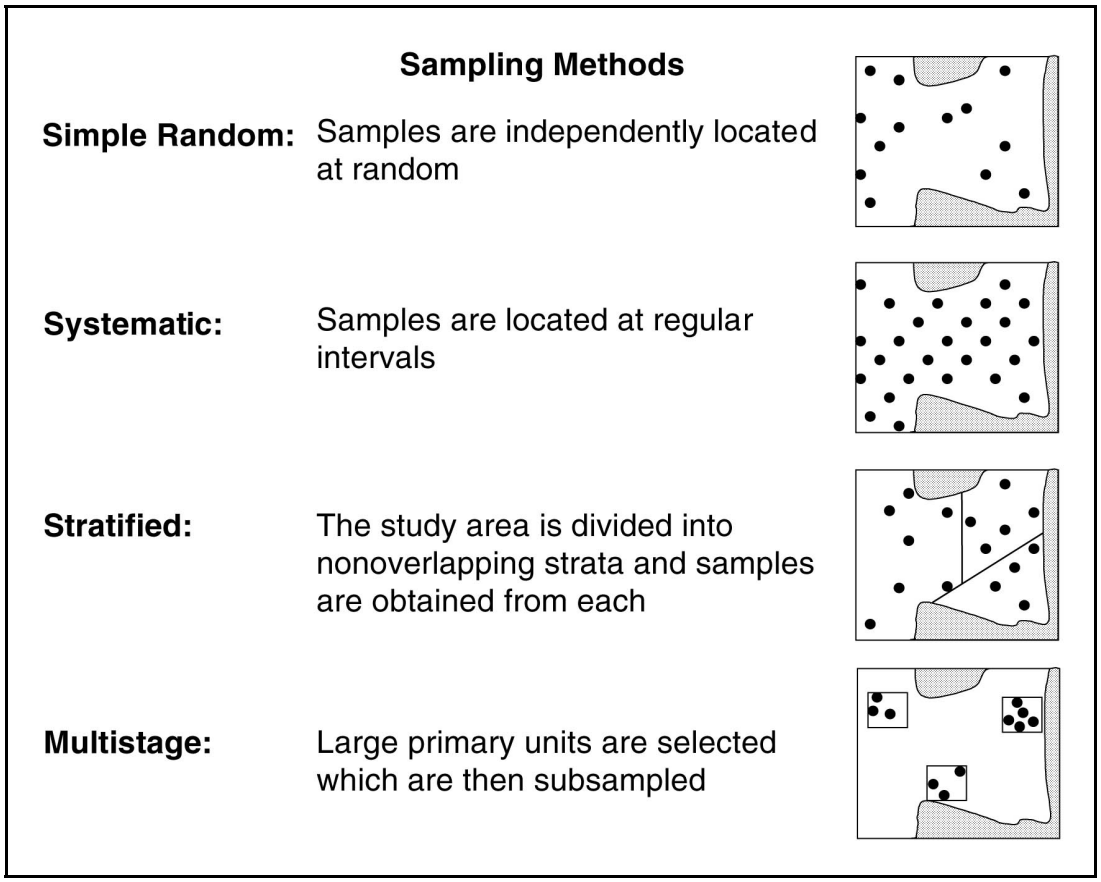


Figure 2-3. Description of various sampling methods. Adapted from USEPA, 2000c.

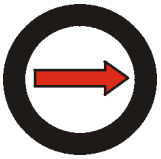
In ***stratified designs***, the selection probabilities might differ among strata. Stratified random sampling consists of dividing the target population into non-overlapping parts or subregions (e.g., ecoregions, watersheds, or specific dredging or remediation sites) termed strata to obtain a better estimate of the mean or total for the entire population. The information required to delineate the strata and estimate sampling frequency must either be known prior to sampling using historic data, available information and knowledge of ecological function, or obtained in a pilot study. Sampling locations are randomly selected from within each of the strata. Stratified random sampling is often used in sediment quality monitoring because certain environmental variables can vary by time of day, season, hydrodynamics, or other factors. Major environmental monitoring programs that incorporate a stratified random design include EPA's Mid-Atlantic Integrated Assessment (MAIA). One disadvantage of using random designs is the possibility of encountering unsampleable sites that were randomly selected by the computer. Such problems result in the need to reposition the vessel to an alternate location. Furthermore, if one is sampling to determine the percent spatial extent of

degradation, it might be important to sample beyond the boundaries of the study area to better evaluate the limits of the impacted area.

A related design is ***multistage*** sampling in which large subareas within the study area are first selected (usually on the basis of professional knowledge or previously collected information). Stations are then randomly located within each subarea to yield average or pooled estimates of the variables of interest (e.g., concentration of a particular contaminant or acute toxicity to *Hyalella*) for each subarea. This type of sampling is especially useful for statistically comparing variables among specific parts of a study area.

Table 2-1. Suggestions for selecting an appropriate sampling design (from USEPA 2000b).

If you are...	**and you have...**	**consider using...**	**in order to...**
performing a screening phase of an investigation and with an understanding of a relatively small-scale problem	a limited budget and/or a limited schedule	judgmental or targeted sampling	assess whether further investigation is warranted that should include a statistical probabilistic sampling design.
developing an understanding of when contamination is present	adequate budget for the number of samples needed	systematic sampling	have coverage of the time periods of interest.
developing an understanding of where contamination is present	adequate budget for the number of samples needed	grid sampling	have coverage of the area of concern and have a given level of confidence that you would have detected a hot spot of a given size.
estimating a population mean	adequate budget	systematic or grid sampling	also produce information on spatial or temporal patterns.
	budget constraints and analytical costs that are high compared to sampling costs	compositing	produce an equally precise or a more precise estimate of the mean with fewer analyses and lower cost.
	budget constraints and professional knowledge or inexpensive screening measurement that can assess the relative amounts of the contaminant at specific field sample locations	ranked set sampling	reduce the number of analyses needed for a given level of precision.
estimating a population mean or proportion	spatial or temporal information on contaminant patterns	stratified sampling	increase the precision of the estimate with the same number of samples, or achieve the same precision with fewer samples and lower cost.
delineating the boundaries of an area of contamination	a field screening method	stratified sampling	simultaneously uses all observations in estimating the mean.
estimating the prevalence of a rare trait	analytical costs that are high compared to sampling costs	random and composite sampling	produce an equally precise or more precise estimate of the prevalence with fewer analyses and lower cost.
assessing whether a population contains a rare trait	the ability to physically mix aliquots from the samples and then retest additional aliquots	composite sampling and retesting	classify all samples at reduced cost by not analyzing every sample.



Recommendation Box #1

What type of sampling strategy should be used?

- ➡ Historical data, if available, should be considered when selecting sampling stations.
- ➡ Location of sediment depositional zones can be important in defining subareas for sampling or for stratifying sampling in some programs.
- ➡ If the objective of the survey is to identify areas of toxic and/or contaminated sediments on a quantitative spatial and/or temporal basis (e.g., superfund site), a systematic or regular grid-sampling strategy might be most appropriate (USEPA, 2000b).
- ➡ If the monitoring objective is to determine sediment contamination originating from a specific source or tributary, a targeted site location design might be most appropriate. Factors affecting dispersion of substances or materials from the point source (e.g., currents) should be considered.
- ➡ Stratified random sampling should be used where historical, sediment-mapping data are available and there are well-defined zones of different sediment types or adjacent land uses (Burton, 1991). This design is commonly used in NOAA National Status and Trends (NS&T) monitoring of sediment quality to ensure that the data can be attributed to the strata in which they were collected (Long et al., 1996).
- ➡ For dredge management programs, multi-stage, stratified-random, or even targeted sampling is often appropriate, since the need is to represent specific areas to be dredged and disposed.
- ➡ For watershed or regional assessment programs, a probabilistic sampling design might be most appropriate.
- ➡ Small-scale, targeted study designs might require many samples within a small area if fine spatial resolution is needed (e.g., Superfund).

Use of random sampling designs might also miss relationships among variables, especially if there is a relationship between an explanatory and a response variable. As an example, estimation of benthic response or contaminant concentration, in relation to a discharge or landfill leachate stream, requires sampling targeted around the potential contaminant source, including stations presumably unaffected by the source (e.g., Warwick and Clarke, 1991). A simple random selection of stations is not likely to capture the entire range needed because most stations would likely be relatively removed from the location of interest.

2.3.2 Targeted Sampling Designs

In ***targeted*** (also referred to as ***judgmental*****,** or ***model-based***) designs, stations are selected based on prior knowledge of other factors, such as contaminant loading, depth, salinity, and substrate type. The sediment studies conducted in the Clark Fork River (Pascoe and DalSoglio, 1994; Brumbaugh et al., 1994), in which contaminated areas were a focus, used a targeted sampling design.

Targeted designs are useful if the objective of the investigation is to screen an area(s) for the presence or absence of contamination at levels of concern, such as risk-based screening levels or toxicity, or to compare specific sediments against reference conditions or biological guidelines. In general, targeted sampling is appropriate for situations in which any of the following apply (USEPA, 2000b):

- The site boundaries are well defined or the site physically distinct (e.g., superfund or CERCLA site, proposed dredging unit).

- Small numbers of samples will be selected for analysis/characterization.

- Information is desired for a particular condition (e.g., "worst case") or location.

- There is reliable historical and physical knowledge about the feature or condition under investigation.

- The objective of the investigation is to screen an area(s) for the presence or absence of contamination at levels of concern, such as risk-based screening levels. (Note that if such contamination is found, follow-up sampling is likely to involve one or more statistical designs to compare specific sediments against reference conditions, chemical or biological guidelines, or applicable sediment quality values).

- Schedule or budget limitations preclude the possibility of implementing a statistical design.

- Experimental testing of a known pollution gradient to develop or verify testing methods or models (i.e., as in evaluations of toxicity tests, Long et al., 1990).

Because targeted sampling designs often can be quickly implemented at a relatively low cost, this type of sampling can often meet schedule and budgetary constraints that cannot be met by implementing a statistical design. In many situations, targeted sampling offers an additional important benefit of providing an appropriate level-of-effort for meeting investigation objectives without excessive consumption of project resources.

Targeted sampling, however, limits the inferences made to the stations actually sampled and analyzed. Extrapolation from those stations to the overall population from which the stations were sampled is subject to unknown selection bias. This bias might be unimportant for those regulatory programs in which information is needed for a particular condition or location (e.g., Dredged Management Materials Program or Superfund).

2.4 Measurement Quality Objectives

As noted in Section 2.1, a key aspect of the DQO process is specifying measurement quality objectives (MQOs): statements that describe the amount, type, and quality of data needed to address the overall project objectives.

Appendix B presents examples of MQOs and sampling designs that have been used in several different programs. Also included in Appendix B is excerpted information from Washington Department of Ecology's Sampling and Analysis Plan Guidance (WDE, 1995). Similar to Quality Assurance Project Plans (QAPP) mentioned earlier in Section 2.1, a Sampling and Analysis Plan includes, among other things, many of the elements of the Data Quality Objectives Process, including MQOs.

A key factor determining the types of MQOs needed in a given project or study is the types of analyses required because these will determine the amount of sample required (see Section 2.4.1) and how samples are processed (see Chapter 4). The case examples presented in Appendix B illustrate a variety of chemical, biological, and toxicological analyses that are often included in sediment quality monitoring projects. Metals, organic chemicals (including pesticides, PAHs, and PCBs), whole

sediment toxicity, and organism bioaccumulation of specific target chemicals, are frequently analyzed in many sediment monitoring programs.

A number of other, more "conventional" parameters, are also often analyzed as well to help interpret chemical, biological, and toxicological data collected in a project. Table 2-2 summarizes many of the commonly measured conventional parameters and their uses in sediment quality studies (WDE, 1995). It is important that conventional parameters receive as much careful attention, in terms of sampling and sample processing procedures, as do the contaminants or parameters of direct interest. The guidance presented in Chapters 3 and 4 provides information on proper sampling and sample processing procedures, respectively, to ensure that one has appropriate samples for these analyses.

This section concentrates on three aspects of MQO development that are generally applicable to all sediment quality studies, regardless of the particular program or objectives: sample volume, number of samples, and replication vs. composite sampling.

Checklist

MQOs are defined in terms of the following attributes:

- ✓ **Detection Limit** – The lowest concentration of an analyte that a specified analytical procedure can reliably detect.
- ✓ **Bias** – The difference between an observed value and the "true" value (or known concentration) of the parameter being measured; bias is the first component of accuracy, which is the ability to obtain precisely a nonbiased (true) value.
- ✓ **Precision** – The level of agreement among multiple measurements of the same characteristic; precision is the second component of accuracy.
- ✓ **Representativeness** – The degree to which the data collected accurately represent the population of interest (e.g., contaminant concentrations).
- ✓ **Comparability** – The similarity of data from different sources included within individual or multiple data sets; the similarity of analytical methods and data from related projects across areas of concern.
- ✓ **Completeness** – The quantity of data that is successfully collected with respect to the amount intended in the experimental design.

2.4.1 Sample Volume

Before commencing a sampling program, the type and number of analyses and tests should be determined, and the required volume of sediment per sample calculated. Each physicochemical and biological test requires a specific amount of sediment which, for chemical analyses, depends on the detection limits attainable and extraction efficiency by the procedure and, for biological testing, depends on the test organisms and test method. Typical sediment volume requirements for each end use are summarized in Table 2-3. Specific program guidance should be consulted regarding sample volumes that might be required.

Table 2-2. Conventional sediment variables and their use in sediment investigations (Adapted from WDE, 1995).

Conventional Sediment Variable	Use
Total organic carbon (TOC)	• Normalization of the concentrations of nonionizable organic compounds • Identification of appropriate reference sediments for biological tests
Acid Volatile Sulfide (AVS)	• Normalization of the concentrations of divalent metals in anoxic sediments
Sediment grain size	• Identification of appropriate reference sediments for biological tests • Interpretation of sediment toxicity test data and benthic macroinvertebrate abundance data • Evaluation of sediment transport and deposition • Evaluation of remedial alternatives
Total solids	• Expression of chemical concentrations on a dry-weight basis
Ammonia	• Interpretation of sediment toxicity test data
Total sulfides	• Interpretation of sediment toxicity test data

When determining the sample volumes necessary, one must know what is required for all of the sample analyses (considering adequate replication) and it is also helpful to know the general characteristics of the sediments being sampled. For example, if interstitial water analyses or elutriate tests are to be conducted, the percent water (or percent dry weight) of the sediment will greatly affect the amount of water extracted. Many non-compacted, depositional sediments have interstitial water contents ranging from 30 to 70%. However, interstitial waters are very difficult to remove from sandy or gravel-rich sediments.

For benthic macroinvertebrate bioassessment analyses, sampling a prescribed area of benthic substrate is at least as important as sampling a given volume of sediment. In many programs, macroinvertebrates are sampled using multiple grab samples within a given station location, typically to a standard sediment depth (e.g., per 10-20 cm of sediment; Klemm et al., 1990; GLNPO, 1994; Long et al., 1996; USEPA 2000c). More than 6 liters of sediment from each station might be necessary in order to have adequate numbers of organisms for analyses, especially in many lakes, estuaries, and large rivers (Barbour et al., 1999). However, this is very site specific and should be determined by the field sampling crew. This only applies to whole sediment sampling methods and not to surficial stream methods using methods such as kick-nets and Surber samplers. If the sediment quality triad approach is used (i.e., biological, toxicological, and physicochemical analyses performed on samples from the same sites), more than 10 liters of sediment from each site might be required depending on the specific analyses conducted. NOAA routinely collects 7-8 liters of sediment at each station for multiple toxicity tests and chemical analyses (Long et al., 1996).

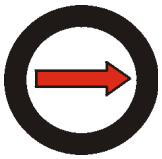
Table 2-3. Typical sediment volume requirements for various analyses per sample

Sediment Analysis	Minimum Sample Volume
Inorganic chemicals	90 mL
Non-petroleum organic chemicals	230 mL
Other chemical parameters (e.g., total organic carbon, moisture content)	300 mL
Particle size	230 mL
Petroleum hydrocarbons[1]	250-1000 mL
Acute and chronic whole sediment toxicity tests[2]	1-2 L
Bioaccumulation tests[3]	15 L
Benthic macroinvertebrate assessments	8-16 L
Pore water extraction	2 L
Elutriate preparation	1 L

[1] The maximum volume (1000 mL) is required only for oil and grease analysis; otherwise, 250 mL is sufficient.

[2] Amount needed per whole sediment test (i.e., one species) assuming 8 replicates per sample and test volumes specified in USEPA, 2000d

[3] Based on an average of 3 L of sediment per test chamber and 5 replicates (USEPA, 2000d).



Recommendation Box #2

How many samples and how much sample volume should be collected?

- The testing laboratory should be consulted to confirm the amount of sediment required for all desired analyses.
- The amount of sediment needed from a given site will depend on the number and types of analyses to be performed. If biological, toxicological, and chemical analyses are required (sediment triad approach), then at least 10 liters of sediment might be required from each station.
- Since sampling events might be expensive and/or difficult to replicate, it is useful to collect extra samples if possible, in the event of problems encountered by the analytical laboratories, failure of performance criteria in assays, or need to verify/validate results.
- Consider compositing samples from a given station or across similar station types to reduce the number of samples needed.

2.4.2 Number of Samples

Considerations
The appropriate number of samples is usually determined by...

- size of the study site
- type and distribution of the contaminants being measured
- characteristics and homogeneity of the sediment
- concentrations of contaminants likely to be found in the sediments
- sample volume requirements
- desired level of statistical resolution or precision

The number of samples collected directly affects the representativeness and completeness of the data for purposes of addressing project goals. As a general rule, a greater number of samples will yield better definition of the areal extent of contamination or toxicity. Many programs specify a certain number of samples per location (e.g., CERCLA site or dredging unit).

Accordingly, sample requirements should be determined on a case-by-case basis. The number of samples to be collected will ultimately be an outcome of the questions asked. For example, if one is interested in characterizing effects of a point source or a gradient (e.g., effects of certain tributaries or land uses on a lake or estuary), then many samples in a relatively small area might need to be collected and analyzed. If, however, one is interested in screening "hot spots" or locations of high contamination within a watershed or water body, relatively few samples at regularly-spaced locations might be appropriate. In most monitoring and assessment studies, the number of samples to be collected usually results from a compromise between the ideal and the practical. The major practical constraints are the costs of analyses and logistics of sample collection.

The major costs associated with the collection of sediment samples are those for travel to the site and for sample analysis. The costs of actual on-site sampling are minimal by comparison. Consequently, it is good practice to collect an excess number of samples, and a subset equal to the minimum number required is selected for analysis. The archived replicate samples can be used to replace lost samples, for data verification, to rerun analyses yielding questionable results, or for the independent testing of *a posteriori* hypotheses that might arise from screening the initial data. However, storage of sediments might result in changes in bioavailability of chemical contaminants (see Section 4.5). Therefore, follow-up testing of archived samples should be done cautiously.

2.4.3 Replicate and Composite Samples

Replicate Samples

As mentioned in the previous section, the number of samples collected and analyzed will always be a compromise between the desire of obtaining high quality data that fully addresses the overall project objectives (MQOs) and the constraints imposed by analytical costs, sampling effort, and study logistics. Therefore, every sampling program needs to find a balance between obtaining information to satisfy the stated DQOs or study goals in a cost-effective manner, and yet have enough confidence in the data to make appropriate decisions (e.g., remediation, dredging; Step 3 in the DQO process, Figure 2-2). Two different concepts are used to satisfy this challenge: replication and sample compositing.

Replication is used to assess precision of a particular measure and can take many forms depending on the type of precision desired. For most programs, analytical replicates are the most frequently used form of replication because most MQOs are concerned with analytical data quality (see examples in

Appendix B). The extent of analytical replication (duplicates) varies with the program or study DQOs. Performing duplicate analyses on at least 10% of the samples collected is considered satisfactory for most programs (GLNPO, 1994; USEPA/ACOE, 1991; PSEP, 1997a; USEPA/ACOE, 1998). An MQO of ≤ 20 - 30% relative percent difference (RPD) is commonly used for analytical replicates depending on the analyte.

Field replicates can provide useful information on the spatial distribution of contaminants at a station and the heterogeneity of sediment quality within a site. Furthermore, field replicates provide true replication at a station (analytical replicates and split samples at a station provide a measure of precision for a given sample, not the station) and therefore can be used to statistically compare analyses (e.g., toxicity, tissue concentration, whole sediment concentration) across stations.

Checklist

Replication can take several forms and satisfy different purposes:

- ✓ Collect field replicate samples at a station if there is a need to statistically compare results among stations within a site.
- ✓ Analytical replicates: separate laboratory analyses on subsamples from the same field sample.
- ✓ Field replicates: separate samples collected at a station each of which is analyzed individually.
- ✓ Field-split replicates: a single field sample is split into subsamples, each of which is then analyzed individually.
- ✓ Compositing samples is one way to reduce the number of replicates needed for analysis.

Results of field replicate analysis yield the overall variability or precision of both the field and laboratory operations (as well as the variability between the replicate samples themselves, apart from any procedural error). Because field replicate analyses integrate a number of different sources of variability, they might be difficult to interpret. As a result, failure to meet a precision MQO for field replicates might or might not be a cause of concern in terms of the overall study objectives but would suggest some uncertainty in the data. Many monitoring programs perform field replicates at 10% of the stations sampled in the study as a quality control procedure. An MQO of ≤ 30 - 50% relative percent difference (RPD) is typically used for field replicates depending on the analyte (see examples in Appendix B). Many regulatory programs (e.g., Dredged Disposal Management within the Puget Sound Estuary Program) routinely use 3-5 field replicates per station. Appendix C summarizes statistical considerations in determining the appropriate number of replicate samples given different sampling objectives.

Split sample replication is less commonly performed in the field because many programs find it more useful to quantify data precision through the use of analytical and field replicates described above. However, split sample replication is frequently used in the laboratory in toxicity and bioaccumulation analyses (USEPA, 2000d) and to verify homogeneity of test material in spiked sediment tests (see Section 5.3). In the field, samples are commonly split for different types of analyses (e.g., toxicity, chemistry, benthos) rather than to replicate a given sample. This type of sample splitting or subsampling is further discussed in Section 4.2.

Composite Samples

A composite sample is one that is formed by combining material from more than one sample or subsample. Because a composite sample is a combination of individual aliquots, it represents an

"average" of the characteristics making up the sample. Compositing, therefore, results in a less detailed description of the variability within the site as compared to taking field replicates at each station. However, for characterizing a single station, compositing is generally considered an excellent way to provide quality data with relatively low uncertainty. Furthermore, many programs find it useful to average the naturally heterogeneous physicochemical conditions that often exist within a station (or dredging unit, for example), even within a relatively small area (GLNPO, 1994; PSEP, 1997a; ASTM, 2000a). Many programs find it useful to composite 3-5 samples from a given location or depth strata (PSEP, 1997a; GLNPO, 1994).

Considerations
Composite samples are collected because they...

- ! Yield a single "average estimate for a given station with less cost than using replicates.
- ! Can obtain useful information over many stations at reduced analytical costs.
- ! Are an efficient way to provide sufficient sample volume for multiple types of analyses, particularly biological/toxicity analyses.

Compositing is also a practical way to control analytical costs while providing information from a large number of stations. For example, with relatively little more sampling effort, five analyses can be performed to characterize a project segment or site by collecting 15 samples and combining sets of three into five composite samples. The increased coverage afforded by taking composite samples might justify the increased time and cost of collecting the extra 10 samples in this case (USEPA/ACOE, 1998). Compositing is also an important way to provide the large sample volumes required for some biological tests (see Table 2-1) and for multiple types of analyses (e.g., physical, chemical, toxicity, and benthos). However, compositing is not recommended where combining samples could serve to "dilute" a highly toxic but localized sediment "hot spot" (WDE, 1995; USEPA/ACOE, 1998). Also, samples from stations with very different grain size characteristics or different stratigraphic layers of core samples should not be composited (see Section 4.3).

Checklist
Before sampling:

- ✓ Review available information about the site including physical conditions and potential contaminant sources.
- ✓ Inspect the site to confirm that the sampling design and procedure chosen are feasible.
- ✓ Perform a pilot or screening sampling, if possible, to ensure that sampling equipment and procedures are adequate for the types of stations selected.

2.5 Site-Specific Considerations for Selecting Sediment Sampling Stations

Several site-specific factors might ultimately influence the appropriate location of sampling stations, both for large-scale monitoring studies, in which general sediment quality status is desired, and for

smaller, targeted studies, in determining the need for sediment remediation. If a targeted or stratified random sampling design is chosen, it might be important to locate sediment depositional and erosional areas to properly identify contaminant regimes. Table 2-4 presents a summary of site-specific factors that should be considered when developing a sampling plan. A comprehensive review of such considerations is provided by Mudroch and MacKnight (1994).

Table 2-4. Practical considerations for site-specific selection of sampling stations in developing a sampling plan.

Activity	Consideration
Determination of areas where sediment contamination might occur	Hydrologic information • quality and quantity of runoff • potential depositional inputs of total suspended solids • up-wellings • seepage patterns
Determination of depositional and erosional areas	Bathymetric maps and hydrographic charts • water depth • zones of erosion, transport, and deposition • bathymetry • distribution, thickness, and type of sediment • velocity and direction of currents • sedimentation rates Climatic conditions • prevailing winds • seasonal changes in temperature, precipitation, solar radiation, etc. • tides, seiches • seasonal changes in anthropogenic and natural loadings
Determination of potential sources of contamination	Anthropogenic considerations location of urban centers • historical changes in land use • types, densities, and size of industries • location of waste disposal sites • location of sewage treatment facilities • location of stormwater outfalls and combined sewer overflows • location, quantity, and quality of effluents • previous monitoring and assessment or geochemical surveys • location of dredging and open-water dredged material disposal sites • location of historical waste spills
Factors affecting contaminant bioavailability	Geochemical considerations • type of bedrock and soil/sediment chemistry • physical and chemical properties of overlying water
Determination of representativeness of samples	• area to be characterized • volume to be characterized • depth to be characterized • possible stratification of the deposit to be characterized

2.5.1 Review Available Data

Review of available historical and physical data is critical in the sample selection process and subsequent data interpretation. Local experts should be consulted to obtain information on site conditions and the origin, nature, and degree of contamination. Other potential sources of information include government agency records, municipal archives, harbor commission records, past geochemical analyses, hydrographic surveys, bathymetric maps, and dredging/disposal history. Potential sources of contamination should be identified and their locations noted on a map or chart of the proposed study area. It is important that recent hydrographic or bathymetric data be used in identifying representative sampling locations, especially for dredging or other sediment removal projects. The map or chart should also note adjacent land and water uses (e.g., fuel docks, storm drains, etc.). The quality and age of the available data should be critically weighed.

2.5.2 Site Inspection

A physical inspection of the site is strongly recommended when developing a study plan, in order to assess the completeness and validity of the collected historical data, and to identify any significant changes that might have occurred at the site or study area (Mudroch and MacKnight, 1994). A site inspection of the immediate drainage area and upstream watershed might also identify potential stressors (such as erosion), and help determine appropriate sampling gear (such as corer vs. grab samplers and boat type) and sampling logistics.

If resources allow, it is useful to perform some screening or pilot sampling and analyses at this stage to further refine the actual sampling design needed. Pilot sampling is particularly helpful in defining appropriate station locations for targeted sampling or to identify appropriate strata or subareas in stratified or multistage sampling, respectively.

2.5.3 Identify Sediment Deposition and Erosional Zones

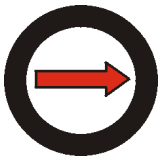
When study DQOs direct sampling to the highest contamination levels or specific subareas of a site, it might be important to consider sediment deposition and sediment erosional zones, since grain size and related physicochemical characteristics (including conventional parameters such as total organic carbon and acid volatile sulfide, as well as contaminants), are likely to vary between these two types of zones. Depositional zones typically contain fine-grained sediment deposits which are targeted in some sampling programs because fine-grained sediments tend to have higher organic carbon content (and are therefore a more likely repository for pollutants) relative to larger sediment particle size fractions (e.g., sand and gravel) (ASTM, 2000a; Environment Canada, 1994). However, for some programs such as remediation dredging evaluations or superfund, eroding sediment beds and non-depositional zones might be of most concern as these could be a major source of pollutants in the water column and in organisms (USEPA/ACOE, 1991,1998).

Various non-disruptive technologies are available to assist in the location of fine-grained sediments ranging from simplistic to more advanced. For example, use of a steel rod or PVC pipe can be used in many shallow areas to quickly and easily probe the sediment surface to find coarse (sand, gravel) vs. fine sediments (silt, clay). This technique can not, however, determine sediment grain size at depth. Other more advance methods, including acoustic survey techniques (e.g., low frequency echo sounding, seismic reflections, etc.) and side-scan sonar used with a sub-bottom profiler (Wright et al., 1987), can provide useful information on surficial as well as deeper sediment profiles. However, these techniques are often limited in their accuracy and have high equipment costs (Guignè et al., 1991).

Aerial reconnaissance, with or without satellite imagery, might assist in visually identifying depositional zones where clear water conditions exist. These methods are not reliable, however, if waters are turbid. Other methods that can be used to locate sediment deposition zones include grab sampling, inspection by divers, or photography using an underwater television camera or remotely operated vehicle (Burton, 1992; ASTM, 2000a).

2.6 Positioning Methods for Locating Sampling Stations

The most important function of positioning technology is to determine the location of the sampling station (e.g., latitude and longitude), so that the user can later re-sample to the same position (USEPA, 1987). Knowing the precise location of sampling stations is also important so that regulators can determine if the area(s) of interest have been sampled. There are a variety of navigation and/or position-fixing systems available, including optical or line-of-site techniques, electronic positioning systems, and satellite positioning systems. Global Positioning System (GPS) is generally regarded as the positioning technique of choice as it is accurate, readily available, and often less expensive than many other comparably sophisticated systems. Given the removal of selective availability of satellite data by the U.S. military, GPS is now capable of high accuracy positioning (1-10 m). The characteristics, advantages, and disadvantages of a variety of positioning systems are summarized in Appendix D.



Recommendation Box #3

How should station positioning be performed?

- Depending on level of accuracy needed, regular calibration of the positioning system by at least two methods might be required to ensure accuracy.
- For monitoring and assessment studies of large areas (e.g., large lakes or offshore marine environments), where an accuracy of ± 100 m typically is sufficient, either the Long Range Navigation (LORAN) or Global Positioning System (GPS) system is recommended.
- For near-shore areas, or areas where the sampling stations are numerous or located relatively close together, GPS or a microwave system should be used if the required position accuracy is less than 10 m. Where visible or suitable and permanent targets are available, RADAR can be used if the required position accuracy is between 10 and 100 m.
- For small water bodies and urban waterfronts, GPS is often capable of giving precise location information. Alternatively, visual angular measurements (e.g., sextant) by an experienced operator, a distance line, or taut wire could also provide accurate and precise positioning data.

Regardless of the type of system selected, calibration of the system is recommended by using at least two of these methods to ensure accuracy particularly for stations that will be reoccupied. At each sampling station, a fathometer or meter wheel can be used to determine the sampling depth. This will ensure that the water is the desired depth and the bottom is sufficiently horizontal for proper operation of sampling equipment. Ideally, it is best to print out a copy of the ship's location from the GPS monitor navigation chart, as well as the latitude / longitude, so the sampling station can be placed in a spatial context.

2.7 Preparations for Field Sampling

Proper preparation for any field sampling study is an essential part of Quality Assurance that ensures a successful project outcome and adherence to the objectives specified in the Quality Assurance Project Plan (QAPP). Chapter 7 further discusses related Quality Assurance/Quality Control procedures that should be used in sediment quality studies.

Prior to performing field work, characteristics of the site and accessibility of the individual sampling stations should be ascertained. Pictures of sampling stations both before as well as during sampling are often useful to ensure that the correct stations were sampled and to document weather and water conditions during sampling. Adequate reconnaissance of stations prior to sampling is also valuable for preparing against potential sampling hazards or unforeseen difficulties. Such a reconnaissance can also help determine the necessary time needed to perform the desired sampling (i.e., time to get from one station to the next).

Checklist
Logistical Considerations:

- ✓ site description
- ✓ study site accessibility
- ✓ adequate sampling platform
- ✓ qualified personnel
- ✓ specific responsibilities of field crew
- ✓ locating and maintaining stations
- ✓ adequate time for sampling
- ✓ adequate space and equipment
- ✓ communication system
- ✓ access to temporary field storage
- ✓ health, safety, and waste management
- ✓ emergency plans and equipment
- ✓ number of samples to be collected
- ✓ sample holding times

The appropriate vessel or sampling platform is one of the most important considerations in preparing for field sampling. The vessel must be appropriate for the water body type, and should provide sufficient space and facilities to allow collection, any on-board manipulation, and storage of samples. Ice chests or refrigeration might be required for sample storage, depending on the time course of the operation. The vessel should provide space for storage of decontamination materials, as well as clean sampling gear and containers to avoid contamination risks associated with normal vessel operations. Space for personal safety equipment is also required.

Additionally, the vessel should be equipped with sufficient winch power and cable strength to handle the weight of the sampling equipment, taking into account the additional suction pressure associated with extraction of the sediments. Large sampling devices typically weigh between 50 and 400 kg empty, and when filled with wet sediment might weigh from 125 to over 500 kg.

Care should be taken in operating the vessel to minimize disturbances of the sediment to be sampled as well as sampling equipment. This would include physical disturbance through propellar action and chemical contamination from engines or stack emissions. For example, Page et al. (1995) reported that they positioned the ships' stern into the wind to prevent stack gases from blowing onto sampling equipment during deployment, recovery, and subsampling of sediments in Prince William Sound, Alaska.

The sampling plan and projected time schedule should be posted for view by all personnel. The names, addresses, and telephone numbers of all participants involved with the preparation and execution of the sampling program should be available to all participants, and the duties and responsibilities of each participant clearly documented. The study supervisor should ensure that the appropriate personnel clearly understand their role and are capable of carrying out their assigned responsibilities and duties. Contingency planning should address the need for backup personnel in the event of accident or illness.

A variety of sampling and sample handling equipment and supplies are often needed in sediment monitoring studies. Besides the actual samplers themselves (e.g., grab or core device to be used), equipment is needed to remove and process the samples such as spatulas, scoops, pans or buckets, and gloves. If it is important to maintain anoxic conditions of the sample, a glovebox and inert gas source (e.g., nitrogen) is needed. Sample storage and transport equipment and supplies need to be available as well. These include refrigeration, ice chests, dry ice or ice, insulation material to stabilize samples in transport, custody seals, and shipping airbills.

The reagents for cleaning, operating or calibrating equipment, and/or for collecting, preserving or processing samples should be handled by appropriately qualified personnel and the appropriate data for health and safety (e.g., Material Safety Data Sheets) should be available. Written approved protocols and standard operating procedures (including QA/QC requirements) should be readily accessible at all times, to ensure proper and safe operation of equipment. Data forms and log books should be prepared in advance so that field notes and data can be quickly and efficiently recorded. Extra forms should be available in the event of a mishap or loss. These forms and books should be waterproof and tear resistant. Under certain circumstances audio or audio/video recordings might prove valuable.

All equipment used to collect and handle samples must be cleaned and all parts examined to ensure proper functioning before going into the field. A repair kit should accompany each major piece of equipment in case of equipment failure or loss of removable parts. Backup equipment and sampling gear should be available.

Checklist

Equipment and/or reagents needed:

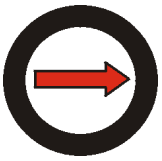
- ✓ sampling equipment and spare parts
- ✓ sample handling equipment
- ✓ special sample handling equipment (e.g., glovebox or shielded compartment).
- ✓ decontamination and cleaning equipment
- ✓ field measurement equipment and supplies
- ✓ sample storage supplies/equipment
- ✓ sample transport supplies
- ✓ personnel supplies
- ✓ maps, navigation, and communication equipment

Storage, transport, and sample containers, including extra containers should be available in the event of loss or breakage (see Section 4.2 for more information on appropriate containers). These containers should be pre-cleaned and labeled appropriately (i.e., with a waterproof adhesive label to which the appropriate data can be added, using an indelible ink pen capable of writing on wet surfaces). The containers must have lids that are fastened securely, and if the samples are collected for legal purposes, they should be transported to and from the field in a locked container with custody seals secured on the lids. Samples to be frozen before analyses must not be filled to the lids. Leave a 10% headspace to accommodate expansion during freezing. Whether for legal purposes or not, all samples should be accompanied by a chain-of-custody form that documents field samples to be submitted for analyses (see Chapter 7). Transport supplies also include shipping airbills and addresses.

A sample-inventory log and a sample-tracking log should be prepared in advance of sampling. A single person should be responsible for these logs who will track the samples from the time they are collected until they are analyzed and disposed of or archived.

2.8 Health and Safety

Collection and processing of sediments for analyses and testing might involve substantial risks to personal safety and health; particularly in situations involving potentially hazardous materials or challenging sampling conditions. If a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP) is prepared prior to sampling, it should include or reference health and safety procedures. A health and safety field officer should be appointed to ensure that personnel use safety precautions and equipment applicable to the operation of the vessel, the sampling equipment, and sample handling. Personnel collecting or handling sediment samples should not work alone, and they should take all safety precautions necessary for the prevention of bodily injury and illness which might result from sampling activities (e.g., boat safety), ingestion or invasion of infectious agents, inhalation or absorption of corrosive or toxic substances through skin contact, or asphyxiation. Because sediment collection often occurs without complete knowledge of the source or degree of hazard, contact with sediment should to be minimized by: (1) using gloves, laboratory coats, safety glasses, face shields and respirators, as appropriate, and (2) manipulating sediments in open air, under a ventilated hood, or in an enclosed glove box. USEPA (1986a), Walters and Jameson (1984), and the Occupational Health and Safety Administration (OSHA) standards provide guidance on safe sediment handling. Program specific guidance should be consulted first when available (e.g., Washington Department of Ecology's Sampling and Analysis Plan Guidance [WDE, 1995] or Puget Sound Estuaries Program [PSEP, 1997a]). Other references (e.g., ASTM, 2000b; Waters, 1980) should also be consulted concerning special safety procedures for sampling and handling samples from hazardous waste sites. The NOAA Diving Manual (NOAA, 1991) or the EPA Diving Safety Manual (USEPA, 1997b) should be consulted for information regarding diving safety plans and protocols.



Recommendation Box #4

What health and safety precautions should be followed?

- Follow Coast Guard approved safety procedures, including use of life vests.
- All samples must be handled in a manner that satisfies the Quality Assurance Project Plan, Standard Operating Procedures, and DQOs.
- Skin contact with sediment should be minimized to avoid potential contact with hazardous substances. Protective clothing and equipment (e.g., gloves, boots, lab coats or aprons, safety glasses, and respirator) are recommended during sampling, sample handling, and preparation of test substances or sediments.
- Handling of samples should be performed in a well-ventilated area (e.g., outside, in a fume hood, or in an enclosed glove box) to minimize the inhalation of sediment gases such as hydrogen sulfide if present.
- A spill control protocol should be in place in the sampling vessel and laboratory.
- Disposal of all hazardous waste should be in accordance with applicable laws, guidelines, and regulations.
- Provide procedures regarding hazard assessment (chemical and physical hazards).
- Provide procedures regarding decontamination.
- Meet the training and medical monitoring requirements.
- Provide emergency planning and emergency contacts.

CHAPTER 3 Collection of Whole Sediments

Most sediment collection devices are designed to isolate and consistently retrieve a specified volume and surface area of sediment, from a required depth below the sediment surface, with minimal disruption of the integrity of the sample and no contamination of the sample. ***Maintaining the integrity*** of the collected sediment, for the purposes of the measurements intended, is a primary concern in most studies because disruption of the sediment's structure could change its physicochemical and biological characteristics, thereby influencing the bioavailability of contaminants and the potential toxicity of the sediment. This chapter discusses the factors to be considered in selecting a sediment collection device. A variety of samplers are described (and pictured in Appendix E), and recommendations are made regarding their use in different situations.

The flowchart in Figure 3-1 shows recommended sampling gear based on monitoring objective or site-specific issues of concern. Figures 3-2 and 3-3 provide recommended grab and core samplers, respectively, based on site factors (such as depth and particle size), and sampling requirements (such as sample depth and volume of sample needed).

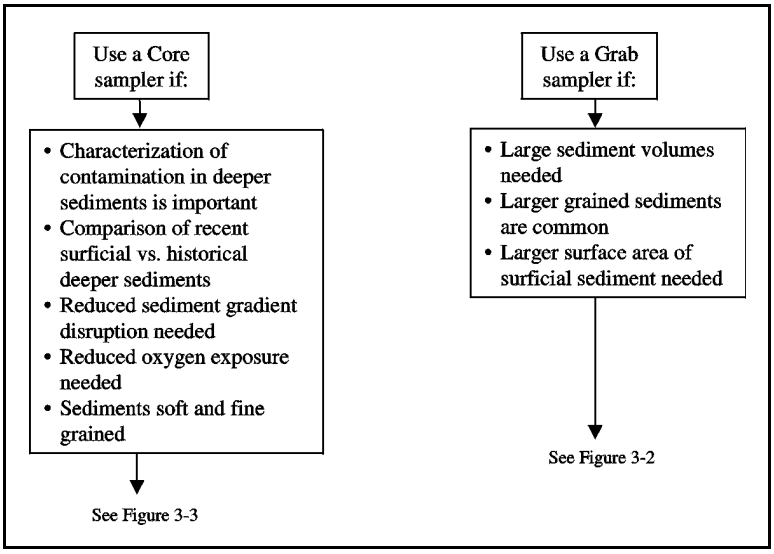


Figure 3-1. General types of considerations or objectives that are appropriate for grab or core sampling devices.

3.1 General Procedures

The planned mode of access to the sampling area (e.g., by water, over land or ice, or from the air) plays an important role in the selection of sampling gear. If the sampling gear needs to be transported to a remote area or shipped by air, its weight and volume might need to be taken into account. It is often the case that a specific vessel, having a fixed lifting capacity based on the configuration of its winch, crane, boom, A-frame, or other support equipment, is the only one available for use. This will affect the type of sampling equipment that can be safely operated from that vessel.

Many samplers are capable of recovering a relatively undisturbed sample in soft, fine-grained sediments, but fewer are suitable for sampling harder sediments containing significant quantities of sand, gravel, firm clay, or till (Mudroch and Azcue, 1995). One of the most important factors in determining the appropriate sampling device for the study are **Data Quality Objectives**. Many monitoring programs, such as EPA's Environmental Monitoring and Assessment Program (EMAP) and the NOAA National Status and Trends program, are primarily interested in characterizing recent environmental impacts in lakes, estuaries and coastal waters and therefore sample surface sediments

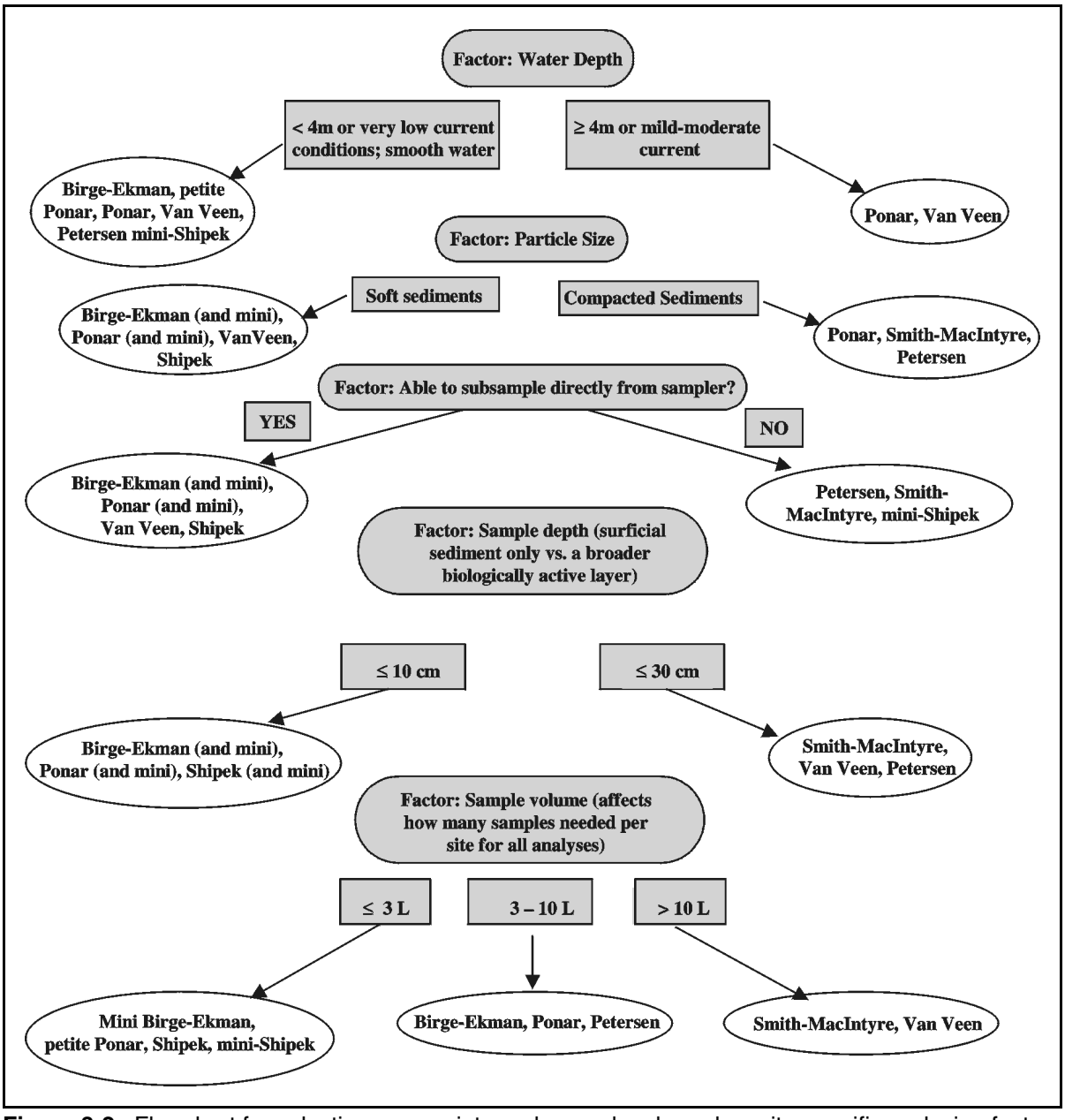


Figure 3-2. Flowchart for selecting appropriate grab samplers based on site-specific or design factors

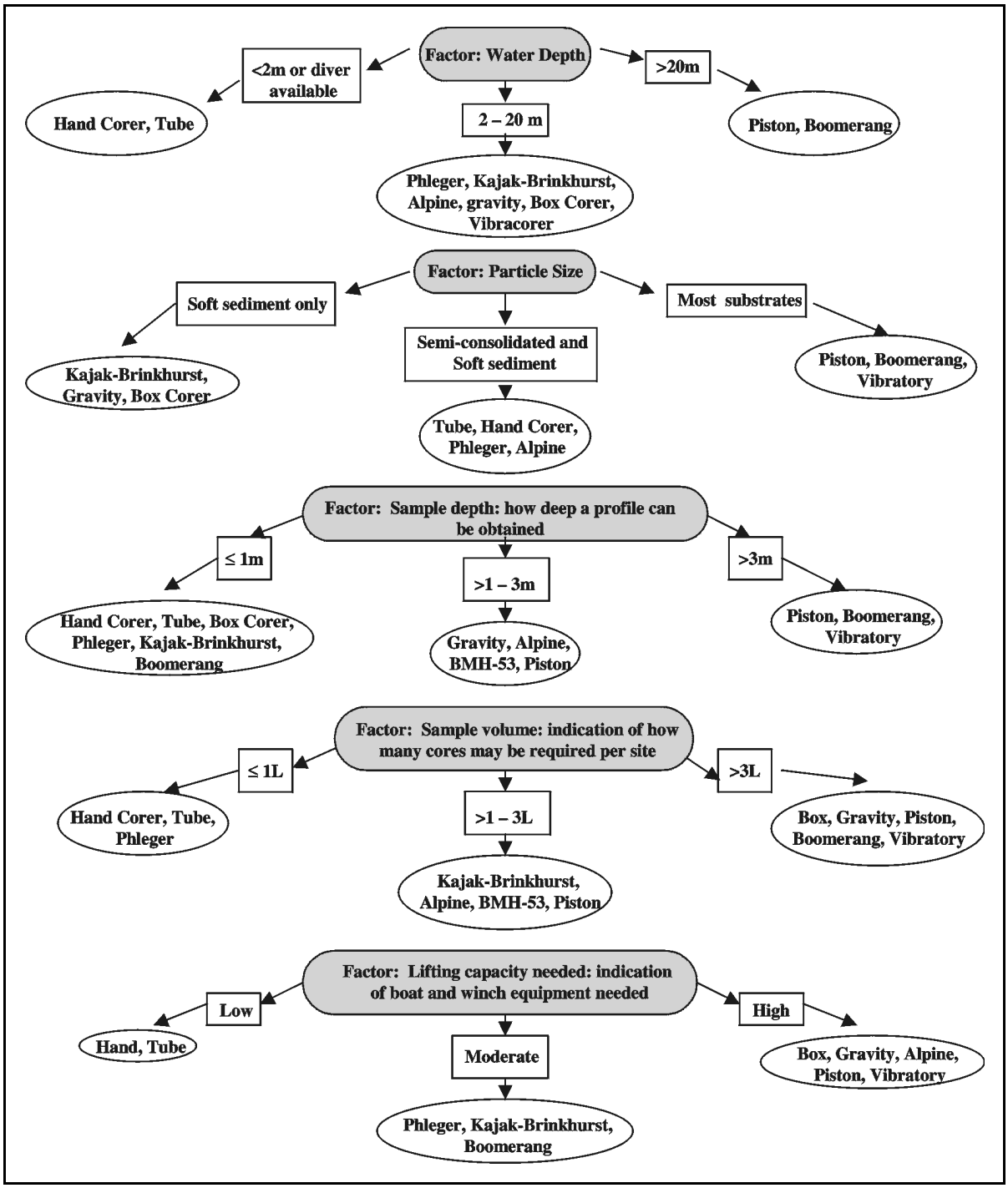


Figure 3-3. Flowchart for selecting appropriate core samplers based on site-specific factors

Considerations

Although there is no one sampler that satisfies all possible considerations, the ideal sampler...

- avoids a pressure wave
- penetrates cleanly to minimize disturbance
- closes tightly
- allows for subsampling
- can accommodate weighting
- collects sufficient sediment volume
- retrieves sediment from a wide range of water and sediment depths
- does not contaminate the sample
- is easy and safe to operate
- is easily transported/assembled at the site

(e.g., Long et al., 1996). Other programs (e.g., dredged material characterization studies conducted for EPA and the US Army Corps of Engineers), are concerned with the vertical distribution of contaminants in sediment to be dredged and therefore seek to characterize a sediment column (USEPA/ACOE, 1991,1998). Each program would employ different sampling devices.

Related to study objectives, another important factor in selecting a sampler is desired depth of sediment penetration. For monitoring and assessment studies where historical contamination is not the focus, the upper 10 to 15 cm is typically the horizon of interest. Generally, the most recently deposited sediments and most epifaunal and infaunal organisms are found in this horizon. To ensure minimum disturbance of the upper layer during sampling, a minimum penetration depth of 6 to 8 cm is recommended, with a penetration depth of 10 to 15 cm being preferred. However, if sediment contamination is being related to organism exposures (e.g., benthic macroinvertebrates and/or fish) then more precise sampling of sediment depths might be needed, such as with a core sampler. The life history and feeding habits of the organisms (receptors) of concern should be considered. For example, some organisms (e.g., shrimp, rotifers) might be epibenthic and are only exposed to surficial sediments (e.g., 0 to 1 cm) while others (e.g., amphipods, polychaetes) that are infaunal irrigators might receive their primary exposure from sediments that are several centimeters in depth. Relating contaminant levels that occur in sediment layers other than where resident organisms are exposed, might produce incorrect conclusions.

Sampling of the surface layer provides information on the horizontal distribution of parameters or properties of interest for the most recently deposited material. Information obtained from analysis of surface sediments can be used, for example, to map the distribution of a chemical contaminant in sediments across a specific body of water (e.g., lake, embayment, estuary). A sediment column, including both the surface sediment layer and the sediment underneath this layer, is collected to study historical changes in parameters of interest (as revealed through changes in their vertical distribution) and to characterize sediment quality with depth.

Once study objectives and the general type of sampler have been identified, a specific sampler is selected based on knowledge of the bathymetry and areal distribution of physically different sediment types at the sampling site. Therefore, it is strongly recommended that this information be gathered during the initial planning stage of all sample collection efforts (see Section 2.5.1).

The quantity of sediment to be collected at each sampling site may also be an important consideration in the selection of a sampling device (see also Section 2.4.1). The required quantity of sediment typically depends on the number and type of physicochemical and biological tests to be carried out (See Table 2-3 for typical sediment volumes needed for different analyses).

Regardless of the type of sampler used, it is important to follow the standard operating procedures specific to each device. Before retrieving the sample, the outside of the sampling device should be carefully rinsed with water from the sampling station. Between each sampling event, the sampling device should be cleaned, inside and out, by dipping the sampler into and out of the water rapidly or by washing with water from the location being sampled. More rigorous between-sample cleaning of the sampler (e.g., chemical decontamination or washing with soap) might be required, depending on the nature of the investigation and specific program guidance (see Section 3.5).

To minimize cross-contamination of samples and to reduce the amount of equipment decontamination required, it might be prudent to sample **reference sites** (i.e., relatively clean sites) first, followed by test stations. If certain stations are known to be heavily contaminated, it might be prudent to sample those stations last when sampling many locations at one time.

3.2 Types of Sediment Samplers

There are three main types of sediment sampling devices: **grab samplers**, **core samplers**, and **dredge samplers**. Grab samplers (see Appendix E) are typically used to collect surficial sediments for the assessment of the horizontal distribution of sediment characteristics. Core samplers (see Appendix E) are typically used to sample thick sediment deposits, or to collect sediment profiles for the determination of the vertical distribution of sediment characteristics or to characterize the entire sediment column. Dredge samplers are used primarily to collect benthos. Dredges cause disruption of sediment and pore water integrity, as well as loss of fine-grained sediments. For these reasons, only grab and core samplers are recommended for sediment physicochemistry or toxicity evaluations. Since many grab samplers are appropriate for collecting benthos as well (Klemm et al., 1990; ASTM, 2000c), grab samplers are likely to be more useful than dredges in sediment quality assessments. Therefore, dredges are not considered further in this document.

Advantages and disadvantages of various grab and core samplers are summarized in Appendix Tables E-1 and E-2, respectively, and are discussed briefly in the following sections. Figure 3-1 provides recommendations regarding the type of sampler that would be appropriate given different study objectives. For many study objectives either cores or grab samplers can be used, however, in practice, one will often be preferred over the other depending on other constraints such as amount of sample required for analyses and equipment availability.

3.2.1 Grab Samplers

Grab samplers consist either of a set of jaws that shut when lowered into the surface of the bottom sediment or a bucket that rotates into the sediment when it reaches the bottom (see Appendix E). Grab samplers have the advantages of being relatively easy to handle and operate, readily available, moderately priced, and versatile in terms of the range of substrate types they can effectively sample.

Of the grab samplers, the **Van Veen**, **Ponar** (see photograph on page 3-6), and **Petersen** are the most commonly used. These samplers are effective in most types of surface sediments and in a variety of environments (e.g., lakes, rivers, estuaries, and marine waters). In shallow, quiescent water, the Birge-Ekman sampler also provides acceptable samples and allows for relatively nondisruptive sampling. However, this sampler is typically limited to soft sediments. The Van Veen sampler, or the modified Van-Veen (Ted Young), is used in several national and regional estuarine monitoring programs, including the NOAA National Status and Trends Program, the EPA Environmental Monitoring and Assessment Program (EMAP), and the EPA National Estuary Program because it can sample most types of sediment, is less subject to blockage and loss of sample than the Peterson or

Examples of grab samplers

Photo courtesy of Allen Burton

Ponar

Photo courtesy of Allen Burton

Eckman grab

Photo courtesy of Ed Long

Double VanVeen grab

Photo courtesy of Scott Carr

Birge-Eckman grab

Taking subsamples from a Ted Young modified VanVeen sampler

Photos on this page, courtesy of Ed Long

Sampling using a Ted-Young modified VanVeen. Large grab samplers such as these require winches and sufficient boat size for efficient operation.

Ted-Young VanVeen sampler in supporting frame. Illustrating movable cover flap to enable direct sampling from the grab sampler. Note the overlying water in the sampler and adequate volume, indicating an acceptable grab sample.

Ponar samplers, is less susceptible to forming a bow wave during descent, and provides generally high sample integrity (Klemm et al., 1990). The support frame further enhances the versatility of the VanVeen sampler by allowing the addition of either weights (to increase penetration in compact sediments) or pads (to provide added bearing support in extremely soft sediments). However, this sampler is relatively heavy and requires a power winch to operate safely (GLNPO, 1994).

As shown in Appendix Table E-1, grab sampler capacities range from approximately 0.5 L to 75 L. If a sampler does not have sufficient capacity to meet the study plan requirements, additional samples can be collected and composited to obtain the requisite sample size (see Section 5.3). Grab samplers penetrate to different depths depending on their size, weight, and the bottom substrate. Heavy, large volume samplers such as the Smith-McIntyre, large Birge-Ekman, Van Veen, and Petersen devices can effectively sample to a depth of 30 cm. These samplers might actually sample sediments that are too deep for certain study objectives (i.e., not reflective of recently deposited sediments). Smaller samplers such as the small Birge-Ekman, standard and petite Ponar, and standard Shipek devices can effectively collect sediments to a maximum depth of 10 cm. The mini-Shipek can sample to a depth of 3 cm.

Another consideration in choosing a grab sampler is how well it protects the sample from disturbance and washout. Grab samples are prone to washout which results in the loss of surficial, fine grained sediments that are often important from a biological and contaminant standpoint. The Ponar, Ted-Young modified grab, and Van Veen samplers are equipped with mesh screens and rubber flaps to cover the jaws. This design allows water to pass through the samplers during descent, reducing disturbance from bow waves at the sediment-water interface. The rubber flaps also serve to protect the sediment sample from washout during ascent.

The use of small or lightweight samplers, such as the small Birge-Ekman (see page 3-6), petite Ponar, and mini-Shipek, can be advantageous because of easy handling, particularly from a small vessel and/or using only a hand line. However, these samplers are not recommended for use in strong currents or high waves. This is particularly true for the Birge-Ekman sampler, which requires relatively calm conditions for proper performance. Lightweight samplers generally have the disadvantage of being less stable during sediment penetration. They tend to fall to one side due to inadequate or incomplete penetration, resulting in unacceptable samples.

In certain very shallow water applications, such as a stream assessment at a superfund site, it might be difficult to use even a lightweight sampler to collect a sample. In these cases, it might be acceptable to collect sediment from depositional areas, using a shovel or other hand implement. However, such sampling procedures are discouraged as a general rule and the use of a hand corer or similar device is preferred (see Section 3.2.2).

Figure 3-2 summarizes appropriate grab samplers based on two important site factors, depth and sediment particle size. This figure also indicates appropriate grab samplers depending on certain common study constraints such as sample depth and volume desired, and the ability to subsample directly from the sampler (see also Section 4.3; ASTM, 2000c). Based on all of these factors, the Ponar or Van Veen samplers are perhaps the most versatile of the grab samplers, hence their common usage in sediment studies.

Careful use of grab samplers is required to avoid problems such as loss of fine-grained surface sediments from the bow wave during descent, mixing of sediment layers upon impact, lack of sediment penetration, and loss of sediment from tilting or washout upon ascent (ASTM, 2000a; Environment Canada, 1994; Baudo, 1990; Golterman et al., 1983; Plumb,1981). When deploying a grab sampler, the speed of descent should be controlled, with no “free fall” allowed. In deep waters,

use of a winching system is recommended to control both the rate of descent and ascent. A ball-bearing swivel should be used to attach the grab sampler to the cable to minimize twisting during descent. After the sample is collected, the sampling device should be lifted slowly off the bottom, then steadily raised to the surface at a speed of about 30 cm/s (Environment Canada, 1994).

Recommendation Box #1

What are appropriate sampling devices given different study objectives?

- Grab or core samplers are preferred over dredges for collecting surficial sediments for physicochemical or toxicity analyses. Dredges might be acceptable for collecting macroinvertebrates.
- Grab samplers are recommended for surficial sediment analyses where accurate resolution of surficial sediment depths is not necessary. Core samplers are recommended for: (a) assessments requiring accurate surficial sediment depth resolution, (b) historical sediment analyses, (c) detailed sediment quality studies of vertical sediment profiles, to characterize sediment quality at depth, (d) when characterizing thick sediment deposits (such as shoals to be excavated), and/or (e) where it is important to maintain an oxygen-free environment.
- In sand, gravel, firm clay, or till sediments, grab samplers might be preferred over core samplers (when only surface material needs to be collected and samples at depth are not necessary) because the latter are often less efficient in these sediment types.
- Ponar, VanVeen, or Ekman samplers are commonly used and generally preferred for grab sampling. Ekman samplers, however, are less efficient in deep waters.
- The Kajak-Brinkhurst corer is a common core sampler for soft, fine grained sediments where large volumes or deep cores are not needed. The Phleger corer is commonly used for a variety of sediments including peat and plant roots but is not appropriate where large volumes or deep cores are needed.
- Box corers are especially recommended for: (a) studies of the sediment-water interface; (b) collecting larger volumes of sediment from a given depth (generally less than one meter depth, however); (c) for *in-situ* studies involving interstitial water characterization; and (d) collecting subsamples for different analyses from the same station.
- Vibracorers are recommended for studies requiring deep cores (> 1 m), or where sediment consists of very compacted or large grained material (e.g., gravel).

3.2.2 Core Samplers

Core samplers (corers) are used: (1) to obtain sediment samples for geological characterizations and dating, (2) to investigate the historical input of contaminants to aquatic systems and, (3) to characterize the depth of contamination at a site. Corers are an essential tool in sediments in which 3-dimensional maps of sediment contamination are necessary. Appendix Table E-2 discusses some of the advantages and disadvantages of common corers.

Vibracorer in use showing extrusion of the core sample for inspection and Subsampling.

Photos on this page, courtesy of Allen Burton

Core devices are recommended for projects in which it is critical to maintain the integrity of the sediment profile, because they are considered to be less disruptive than dredge or grab samplers. Core samplers should also be used where it is important to maintain an oxygen-free environment because they limit oxygen exchange with the air more effectively than grab samplers. Cores should also be used where thick sediment deposits must be representatively sampled (e.g., for dredging projects).

One limitation of core samplers is that the volume of any given depth horizon within the profile sample is relatively small. Thus, depending on the number and type of analyses needed, repetitive sampling at a site might be required to obtain the desired quantity of material from a given depth. Some core samplers are prone to "plugging" or "rodding" where the friction of the sediment within the core tube prevents it from passing freely and the core sample is compressed or does not sample to the depth required. This limitation is more likely with smaller diameter core tubes and heavy clay sediments. Except for piston corers and vibracorers, there are few core devices that function efficiently in substrates with significant proportions of sand, gravel, clay, or till.

Coring devices are available in various designs, lengths, and diameters (see Appendix E). With the obvious exception of hand corers, there are only a few corers that can be operated without a mechanical winch. The more common of these include the standard **Kajak-Brinkhurst corer**, suitable for sampling soft, fine-grained sediments, and the **Phleger corer**, suitable for a wider variety of sediment types ranging from soft to sandy, semi-compacted material, as well as peat and plant roots in shallow lakes or marshes (Mudroch and Azcue, 1995). The Kajak-Brinkhurst corer uses a larger core tube, and therefore recovers a greater quantity of sediment, than the Phleger corer. Both corers can be used with different liner materials including stainless steel and PVC. Stainless steel liners should not be used if trace metal contamination is an issue.

Gravity corers are appropriate for recovering up to 3 m long cores from soft, fine-grained sediments. Recent models include stabilizing fins on the upper part of the corer to promote vertical penetration into the sediment, and weights that can be mounted externally to enhance penetration (Mudroch and Azcue, 1995). A variety of liner materials are available including stainless steel; Lexan®, and PVC. For studies in which metals are a concern, stainless steel liners should not be used.

Vibracorers are perhaps the most commonly used coring device in sampling programs in the U.S. because they collect deep cores in most types of sediments, yielding excellent sample integrity. Vibracorers are one of the only sampling devices that can reliably collect

Checklist

Corers may consist of the following components (from Mudroch and Azcue, 1995)

- ✓ A hollow metal (or plastic) pipe that serves as the core barrel
- ✓ Easily removed plastic liners or core tubes that fit into the core barrel and retain the sediment sample
- ✓ A valve or piston mounted on top of the core barrel that is open and allows water to flow through the barrel during descent, but shuts upon penetration of the corer into the sediment to prevent the sediment from sliding through the corer during the ascent
- ✓ A core catcher to retain the sediment sample
- ✓ A core cutter for penetration of the sediment
- ✓ Removable metal weights (usually lead coated with plastic) or piston-driven impact or vibration to increase penetration of the corer into the sediment
- ✓ Stabilizing fins to ensure vertical descent of the corer

thick sediment samples (up to 10 meters or more). Some programs that rely on vibracorers include the Puget Sound Estuary Program, the Great Lakes ARCS Program, and the Dredged Materials Management Program.

Vibracorers have an electric-powered, mechanical vibrator located at the head end of the corer which applies thousands of vertical vibrations per minute to help penetrate the sediment. A core tube and rigid liner (preferably of relatively inert material such as cellulose acetate butyrate) of varying diameter depending on the specific vibrator head used, is inserted into the head and the entire assembly is lowered in the water. Depending on the horsepower of the vibrating head and its weight, a vibracorer can penetrate very compact sediments and collect cores up to 6 m long. For example, the ARCS program in the Great Lakes uses a Rossfelder® Model P-4 Vibracorer (Rossfelder Corporation, La Jolla, CA) that produces a force of 7,000 lbs and a mono-directional frequency of 3,400 vibrations per minute (GLNPO, 1994). Cores up to 6 m in length have been routinely collected using this vibracorer. However, this particular model is relatively heavy (113 kg as compared to 8.1 kg for the more portable Wacker® Model M3000 vibracorers [GLNPO, 1994]). Therefore, use of a heavy vibracorer requires a large vessel to maintain balance and provide adequate lift to break the corer out of the sediment and retrieve it (GLNPO, 1994; PSEP, 1997a).

When deployed properly, **box corers** can obtain undisturbed sediment samples of excellent quality. The basic box corer consists of a stainless steel box equipped with a frame to add stability and facilitate vertical penetration on low slopes. Box corers are recommended particularly for studies of the sediment-water interface or when there is a need to collect larger volumes of sediment from the depth profile. Because of the heavy weight and large size of almost all box corers, they can be operated only from a vessel with a large lifting capacity and sufficient deck space. Sediment inside a box corer can be subsampled by inserting narrow core tubes into the sediment. Thus, they are an ideal sampler for obtaining acceptable subsamples for different analyses at a given station. Carlton and Wetzel (1985) describe a box corer that permits the sediment and overlying water to be held intact as a laboratory microcosm under either the original *in situ* conditions or other laboratory controlled conditions. A box corer was developed that enables horizontal subsampling of the entire sediment volume recovered by the device (Mudroch and Azcue, 1995).

Figure 3-3 summarizes the core samplers that are appropriate given site factors such as depth and particle size and other study constraints such as sample depth and volume required, and lifting capacity needed to use the sampling device. Given the factors examined for general monitoring studies, the Phleger, Alpine, and Kajak-Brinkhurst corers might be most versatile. For dredged materials evaluations, and projects requiring sediment profile characterizations > 3 m in sediment depth, the vibracorer or piston corer are the samplers of choice.

Collection of core samples with hand-coring devices should be executed with care to minimize disturbance and/or compression of sediment during collection. To minimize disruption of the sediment, core samples should be kept as stationary and vibration-free as possible during transport. These cautions are particularly applicable to cores collected by divers.

The speed of descent of coring devices should be controlled, especially during the initial penetration of the sediment, to avoid disturbance of the surface and to minimize compression due to frictional drag from the sides of the core liner (ASTM, 2000d). In deep waters, winches should be used where necessary to minimize twisting and tilting and to control the rate of both descent and ascent. With the exception of piston corers or vibracorers, that are equipped with their own mechanical impact features, for other corers, only the weight or piston mechanism of the sampler should be used to force it into the sediment. The sampler should be raised to the surface at a steady rate, similar to that described for grab samplers. Where core caps are required, it is essential to quickly and securely cap

the core samples when the samples are retrieved. The liner from the core sampler should be carefully removed and kept in a stable position until the samples are processed (see Chapter 4). If there is little to no overlying water in the tube and the sediments are relatively consolidated, it is not necessary to keep the core sample tubes vertical. Core sample tubes should be quickly capped and taped to secure the sample. If sediment oxidation is a concern (e.g., due to potential changes in metal bioavailability or volatile substances), then the head space of the core tube should be purged with an inert gas such as nitrogen or argon.

Recommendation Box #2
How should sampling devices be used?

- The recommended depth of sediment sampling is dependent on the study objectives. Issues that determine the appropriate depth of sampling include: regulatory objectives (e.g., depth of dredging for sediment remediation), need to characterize sediments at depth (e.g., materials to be dredged versus shallow depositional areas in some superfund sites), historical comparisons, sediment deposition rates, and/or time period of contamination.
- Appropriate winching systems are required to control the rate of ascent and descent of the samplers.
- The sampler should be rinsed thoroughly with water at the sampling station between and within-station samples, and rinsed with water from the next sapling station before collecting a sample. Equipment used in the handling of sediment should also be washed thoroughly between samples.
- More rigorous equipment decontamination might be necessary if highly contaminated sites are sampled or if low level contaminants are a concern.
- To reduce the probability of cross-contamination of samples, it is useful to sample reference or relatively clean sites first and then suspected contaminated sites.

3.3 Sample Acceptability

Only sediments that are correctly collected with grab or core sampling devices should be used for subsequent physicochemical, biological or toxicity testing. Acceptability of grabs can be ascertained by noting that the samplers were closed when retrieved, are relatively full of sediment (but not over-filled), and do not appear to have lost surficial fines. Core samples are acceptable if the core was inserted vertically in the sediment and an adequate depth was sampled.

A sediment sample should be inspected as soon as it is secured. If a collected sample fails to meet any of the acceptability conditions listed below for the respective sampling device, then the sample might need to be rejected and another sample collected at the site. The location of consecutive attempts should be as close to the original attempt as possible and located in the “upstream” direction of any existing current. Rejected sediment samples should be discarded in a manner that will not affect subsequent samples at that station or other possible sampling stations. Illustrations of acceptable and unacceptable grab samples are provided in Figure 3-4.

Checklist
Sample acceptability for grab and core samples

Grab samples *should be visually inspected to ensure that the following acceptability conditions are satisfied (USEPA, 1986b; Environment Canada, 1994):*

- ✓ The sampler is not overfilled so that the sediment surface is touching the top of the sampler;
- ✓ Overlying water is present (indicates minimal leakage). This overlying water should be removed prior to processing and storage by siphoning, not decanting (see Chapter 6);
- ✓ The overlying water is clear or not excessively turbid;
- ✓ The sediment-water interface is intact and relatively flat, with no sign of channeling or sample washout;
- ✓ The desired depth of penetration has been achieved; and
- ✓ There is no evidence of sediment loss (incomplete closure of the sampler, penetration at an angle, or tilting upon retrieval).

Core samples *should meet the following acceptability conditions:*

- ✓ The core sampler was not inserted at an angle or tilted upon retrieval
- ✓ The core collected the required depth to meet the study objectives, with no loss of sediment.

3.4 Equipment Decontamination

For most sampling applications, site water rinse of equipment in between stations is normally sufficient (PSEP, 1997a). However, if one is sampling many stations, including some that could be heavily contaminated, a site water rinse might not be sufficient to minimize cross-contamination of samples among stations. In these cases, it might be necessary to decontaminate all sampling materials in between stations. This would include the sampling device, scoop, spatula, mixing bowls, and any other utensils that come in contact with sediment samples. An approach recommended by ASTM (2000a) for field samples of unknown composition includes: (1) soap and water wash, (2) distilled water rinse, (3) acetone or ethanol rinse, and (4) site water rinse. In general, organic solvents such as methylene chloride should not be used due to the associated health and safety risks. Waste solvents should be collected in labeled hazardous waste containers. If sediment can be collected from the interior of the sampling device, and away from potentially contaminated surfaces of the sampler, it might be adequate to rinse with site water between stations.

If metals or other inorganic compounds are specifically of concern, sampling and handling equipment should be suspended over a tub and rinsed from the top down with 10 percent nitric acid using a pump or squirt bottle (USEPA, 1993; ASTM, 2000a). If organic compounds are a specific concern, sampling equipment can be decontaminated using acetone followed by a site water rinse. Wash water from decontamination should be collected and disposed of properly.

Some specific programs (like Superfund) have their own decontamination procedures, which are legally required.

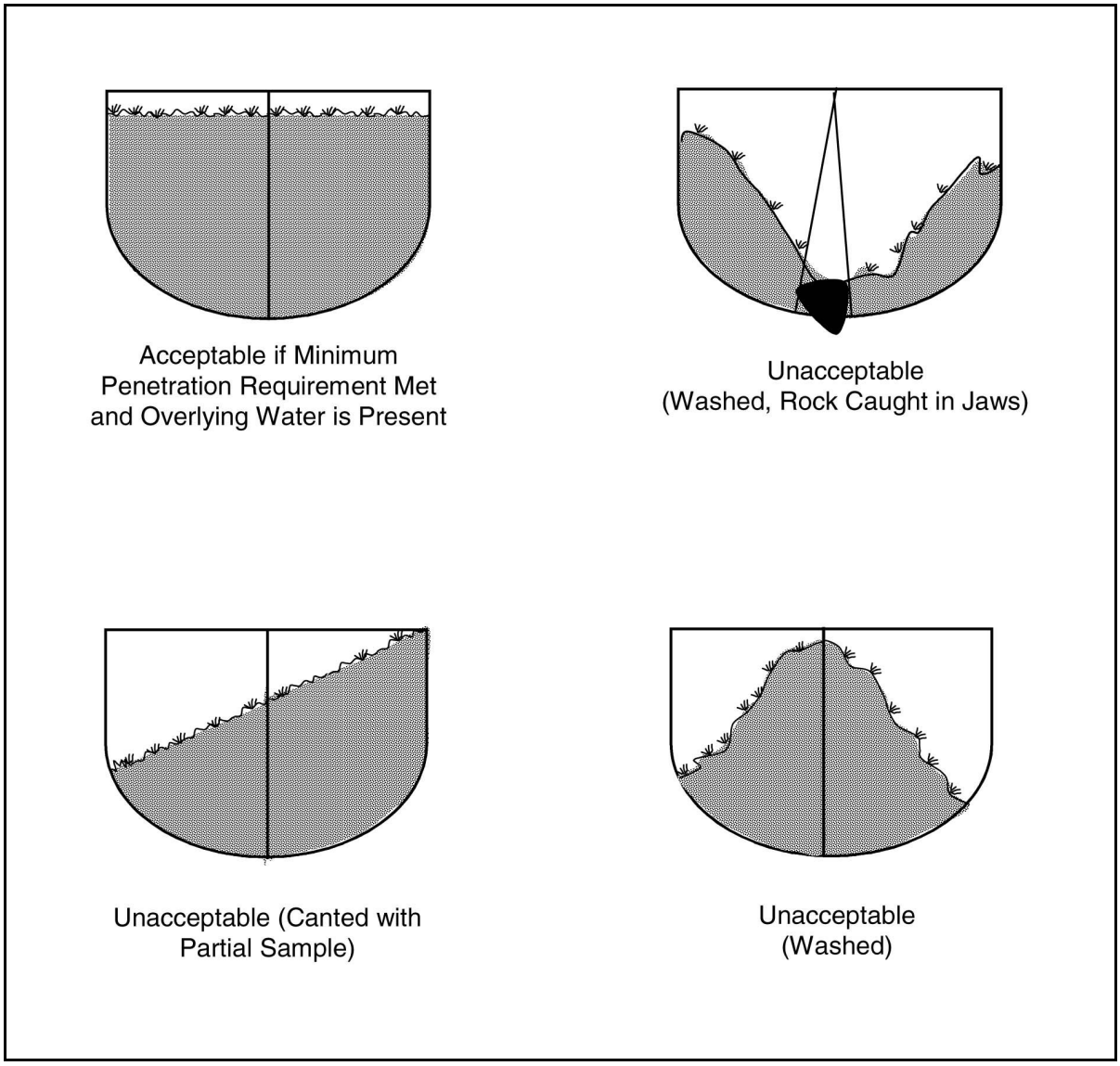


Figure 3-4. Illustrations of acceptable and unacceptable grab samples.

3.5 Field Measurements and Observations

Field measurements and observations are critical to any sediment collection study, and specific details concerning sample documentation should be included in the study plan. Section 2.7 summarizes the types of information commonly recorded in the field during sampling. Several programs, referenced in this Manual, provide specific guidance on field measurements and observations necessary (e.g., see the Sampling and Analyses Plan Guidance development by the Washington Department of Ecology in Appendix B [WDE, 1995 or PSEP, 1997a]). Measurements and observations should be documented clearly in a bound field logbook (or on pre-printed sample forms). Preferably, a logbook should be dedicated to an individual project. The investigator's name, project name, project number, and book number (if more than one is required) should be entered on

the inside of the front cover of the logbook. All entries should be written in indelible ink, and the date and time of entry recorded. Additionally, each page should be initialed and dated by the investigator. At the end of each day's activity, or entry of a particular event if appropriate, the investigator should enter his or her initials. All aspects of sample collection and handling as well as visual observations and field conditions should be documented in the field logbooks at the time of sample collection. Logbook entries should also include any circumstances that potentially affected sampling procedures and/or any field preparation of samples. Data entries should be thorough enough to allow station relocation and sample tracking. Since field records are the basis for later written reports, language should be objective, factual, and free of personal opinions or other terminology which might appear inappropriate. In describing characteristics of samples collected (see below), some cautions should be noted. First, polarized glasses are often worn in the field to reduce glare, however, they can also alter color vision. Therefore, visual examination or

Checklist

Depending on program objectives, field measurements might include the following:

- ✓ temperature and perhaps pH of the sediment at the sediment-water interface;
- ✓ concentration of dissolved oxygen in the water overlying the sediment in the system being sampled.
- ✓ salinity or conductivity of the overlying water.

Recommendation Box #3

What information should be documented for each sample collected? (PSEP, 1997a; ASTM, 2000a)

- ➡ project title, time and date of collection, sample number, replicate number, site identification (e.g., name); station number and location (e.g., positioning information);
- ➡ water depth and the sampling penetration depth;
- ➡ details pertaining to unusual events which might have occurred during the operation of the sampler (e.g., possible sample contamination, equipment failure, unusual appearance of sediment integrity, control of vertical descent of the sampler, etc.), preservation and storage method, analysis or test to be preformed;
- ➡ estimate of quantity of sediment recovered by a grab sampler, or length and appearance of recovered cores;
- ➡ description of the sediment including texture and consistency, color, presence of biota or debris, presence of oily sheen, changes in sediment characteristics with depth, and presence/location/thickness of the redox potential discontinuity (RPD) layer (a visual indication of black is often adequate for documenting anoxia);
- ➡ photograph of the sample is desirable, especially longitudinally-sectioned cores, to document stratification;
- ➡ deviations from approved work plans or SOPs.

NOTE: Some geological characterization methods might include an odor evaluation of the sediment as this can provide useful information on physicochemical conditions. However, sediment odor evaluation is potentially dangerous depending on the chemicals present in the sediment (ASTM 2000a) and should therefore be done cautiously, if at all.

characterization of samples should be performed without sunglasses (GLNPO, 1994). Second, descriptions of sediment texture and composition should rely on a texture-by-feel or "ribbon" test in addition to visual determinations (GLNPO, 1994). In this test, a small piece of suspected clay is rolled between the fingers while wearing protective gloves. If the piece easily rolls into a ribbon it is clay; if it breaks apart, it is silt (GLNPO, 1994).

3.6 Documentation of Sample Collection

Documentation of collection and analysis of sediment and porewater samples requires all the information necessary to: 1) trace a sample from the field to the final result of analysis; 2) describe the sampling and analytical methodology; and 3) describe the QA/QC program (Mudroch and Azcue 1995; Keith, 1993). Poor or incomplete documentation of sample collection can compromise the integrity of the sample(s) and thus, the study. In addition, stations that could not, or were not, sampled should be documented with an explanation. Samples should be accompanied by chain-of-custody forms that identify each sample collected and the analyses to be conducted on that sample. Specific guidance on quality assurance procedures regarding sample chain-of-custody is summarized in Chapter 7.

Checklist
Project documentation should include...

- ✓ type of vessel used (e.g., size, power, type of engine);
- ✓ notation of the system used to define the position of the sampling site;
- ✓ notation of the system used to identify and track samples;
- ✓ name of personnel collecting the samples;
- ✓ level of personal protective equipment worn;
- ✓ notation of any visitors to the site;
- ✓ sketch of sampling area with photographs, if possible;
- ✓ ambient weather conditions, including wind speed and direction, wave action, current, tide, vessel traffic, temperature of both the air and water, thickness of ice if present;
- ✓ type of sediment collection device and any modifications made during sampling;
- ✓ calibration data.

CHAPTER 4 *Field Sample Processing, Transport, and Storage of Sediments*

The way in which sediment samples are processed, transported, and stored might alter contaminant bioavailability and concentration by introducing contaminants to the sample or by changing the physical, chemical, or biological characteristics of the sample. Manipulation processes often change availability of organic compounds because of disruption of the equilibrium with organic carbon in the pore water/sediment system. Similarly, oxidation of anaerobic sediments increases the availability of certain metals (DiToro et al., 1990; Ankley et al., 1996). Materials and techniques should be selected to minimize sources of contamination and variation, and sample treatment prior to testing should be as consistent as possible.

A flowchart is presented in Figure 4-1 that summarizes common sediment processing procedures discussed in this section as well as issues and objectives relevant to each processing step.

4.1 Sample Containers

Any material that is in contact with a field sample has the potential to contaminate the sample or adsorb components from the sample. For example, samples can be contaminated by zinc from glassware, metals from metallic containers, and organic compounds from rubber or plastic materials. The use of appropriate materials, along with appropriate cleaning procedures, can minimize or mitigate interferences from sample containers.

Recommendation Box #1
Sample Containers

- ➡ High density polyethylene (HDPE) or polytetrafluoroethylene (PTFE) containers are suitable and preferred for most analytical measurements because they are made of relatively inert material and they are generally unbreakable.
- ➡ All containers should be pre-cleaned prior to filling with sample.
- ➡ Consider using certified, pre-cleaned containers, commercially available from many vendors.
- ➡ Purge containers with inert gas (e.g., nitrogen) prior to and after filling if anoxic conditions must be maintained.
- ➡ Fill containers completely if the sample will not be frozen prior to analysis.

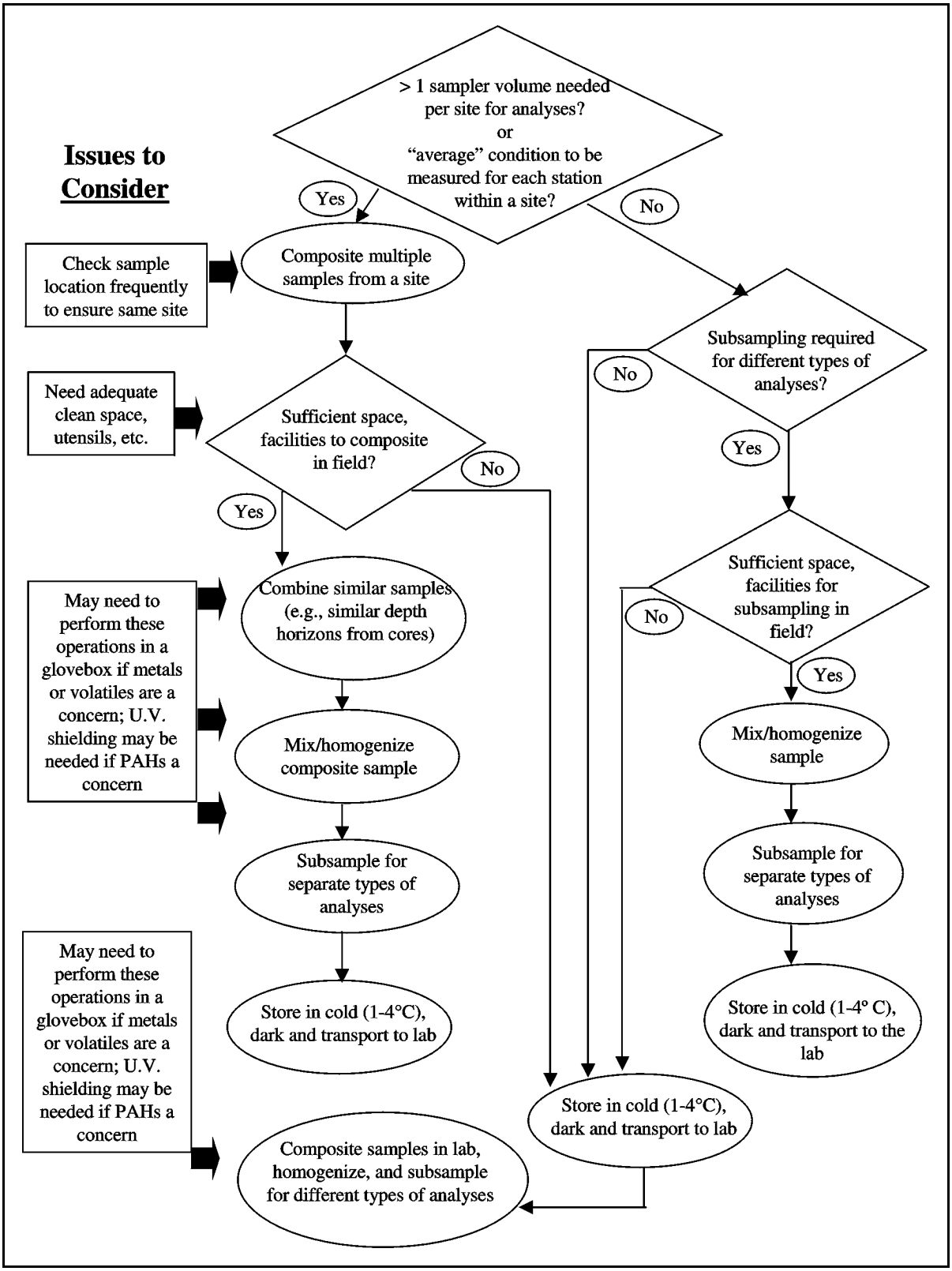


Figure 4-1. Flowchart of suggested sediment processing procedures

4.1.1 Container Material

Borosilicate Glass, and high-density polyethylene, polycarbonate and fluorocarbon plastics should be used whenever possible to minimize leaching, dissolution, and sorption (ASTM, 2000a; APHA, 1995). Direct contact between sediment samples and the following substances should be avoided: PVC, natural or neoprene rubber, nylon, talcum powder, polystyrene, galvanized metal, brass, copper, lead, other metal materials, soda glass, paper tissues, and painted surfaces. Table 4-1 summarizes the appropriate types of sampling containers and allowable holding times for various types of contaminants associated with sediments.

In general, sediments and pore waters with multiple or unknown chemical types should be stored in containers made from high density polyethylene plastic or polytetrafluoroethylene (PTFE or Teflon®) as these materials are least likely to add chemical artifacts or interferences and they are much less fragile than glass. Samples for organic contaminant analysis should be stored in brown borosilicate glass containers with PTFE lid liners. If volatile compounds will be analyzed, containers should have a septum to minimize escape of volatile gases during storage and analysis. Extra containers should be provided for these analyses in the event that re-analysis of the sample is required. If samples are contaminated with photoreactive compounds such as PAHs, exposure to light should be minimized by using brown glass containers or clear containers wrapped tightly with an opaque material (e.g., clean aluminum foil). Plastic or acid-rinsed glass containers are recommended when the chemicals of concern are heavy metals.

4.1.2 Container Preparation

Many vendors have commercially available pre-cleaned containers for a variety of applications. For chemical and toxicological analyses, certified pre-cleaned containers are often a cost-effective way to limit the potential for container contamination of samples. Thus, manufacturer-supplied pre-cleaned containers are often a prerequisite in QAPPs.

If new containers are used, Environment Canada (1994) recommends that new glassware and plasticware should be soaked in 1:1 concentrated acid prior to use. Soaking overnight is adequate for glassware. For plasticware, the recommended procedure involves soaking for seven days in hydrochloric acid (HCl), followed by seven days in nitric acid (HNO_3), followed by seven days in deionized water. Shorter soaking times might be satisfactory in most instances (ASTM, 2000a). Used sample containers should be washed following these steps: (1) non-phosphate detergent wash, (2) triple water rinse, (3) water-miscible organic solvent wash (acetone followed by pesticide-grade hexane), (4) water rinse, (5) acid wash (such as 5% concentrated HCl) and (6) triple rinse with deionized-distilled water. A dichromate-sulfuric acid cleaning solution can generally be used in place of both the organic solvent and the acid (Steps 3 through 5), but it might attack any silicone adhesive present in the container. See ASTM (2000a) and USEPA (2000d) for further information.

If a sample is to be refrigerated, the container should be filled to the brim to reduce oxygen exposure. This is particularly critical for volatile compounds (e.g., AVS). If a sample is to be frozen, the container should be filled to approximately 90% of its volume (i.e., 10% headspace) to allow for expansion of the sample during freezing. See Section 4.4 for preservation and storage conditions for various types of analyses. For studies in which it is critical to maintain the collected sediment under anoxic conditions (e.g., where metals are the pollutants of concern), the container should be purged with an inert gas (e.g., nitrogen) before filling and then again before capping tightly.

Table 4-1. Recommended sampling containers, holding times, and storage conditions for common types of sediment analyses (USEPA, 1983;1993; ASTM, 2000a). P=Plastic; G=Glass; PTFE=Polytetrafluoroethylene; R=refrigerate; F=freeze

Contaminant	Container	Holding Time	Storage Condition
Ammonia	P,G	28 days	R; F
Sulfate	P,G	28 days	R; F
Sulfide	P,G	28 days	R or NaOH; pH>9
Oil and Grease	G	28 days	HCl, pH<2
Mercury	P,G	6 weeks	H_2SO_4, pH<2; R
Metals (except Cr or Hg)	P,G	6 months	HNO_3, pH<2; F
Extractable organics (including phthalates, airosamines, organochlorine pesticides, PCBs aromatics, isophorone, PAHs, haloethers, chlorinated hydrocarbons, and TCDD)	G, PTFE-lined cap	7 days (until extraction) 30 days (after extraction)	R; F
Purgables (halocarbons and aromatics)	G, PTFE-lined septum	14 days	R; F
Pesticides	G, PTFE-lined cap	7 days (until extraction) 30 days (after extraction)	R; F
Sediment Toxicity (acute and chronic)	P, PTFE	2 weeks*	R, dark
Bioaccumulation testing	P, PTFE	2 weeks*	R, dark

*Holding time might be longer depending on the magnitude and type of contaminants present. See Section 4.5.

All sediment containers should be properly labeled with a waterproof marker prior to sampling. Containers should be labeled on their sides in addition to or instead of labeling the lids. Each label should include, at a minimum, the study title, station location and/or sample identification, date and time of collection, sample type, and name of collector. Blind sample labeling (i.e., a sample code) should be used, along with a sample log that identifies information about each sample (see Section 2.7) to minimize potential analytical bias. Additional information such as required analyses and any preservative used might also be included on the label although this information is typically recorded on the chain-of-custody form (see Section 2.7 and 7.6). Labeled containers should be stabilized in an upright position in the transport or storage container (see Section 4.4 Transport and Storage for further information). Extra containers should be carried on each sampling trip.

4.2 Subsampling and Compositing Samples

The decision to subsample and/or composite sediment samples within or among stations depends on the purpose and objectives of the study, the nature and heterogeneity of the sediments, the volume of sediment required for analytical and/or toxicity assessment, and the degree of statistical resolution that is acceptable. Subsampling and compositing might be accomplished in the field, if facilities, space, and equipment are available, or alternatively, in a laboratory setting following sample transport.

Recommendation Box #2

How should sediment samples be subsampled and composited?

- ➡ Overlying water should be siphoned off, not decanted, from grab samplers prior to subsampling.
- ➡ All utensils that are used to process samples should be made of inert materials such as Teflon®, high quality stainless steel, or HDPE.
- ➡ Subsamples should be collected away from the sides of the sampler to avoid potential contamination.
- ➡ Sediment samples should be processed prior to long-term storage, within 72 hours (and preferably within 24 hours) of collection.
- ➡ Sufficient sample homogenization, prior to placing in containers, is critical for accurate measurements and correct sediment quality determinations.
- ➡ If rigorous evaluation of metal contamination is a focus of the study, or if anaerobic conditions need to be maintained for other reasons, it might be necessary to homogenize, subsample, and composite samples in an oxygen-free glovebox or other suitable apparatus.
- ➡ Similar depth horizons or geologic strata should be subsampled when compositing core samples.

4.2.1 General Procedures

Subsampling is useful for collecting sediment from a specific depth of a core sample, for splitting samples among multiple laboratories, for obtaining replicates within a sample, or for forming a composite sample.

Compositing refers to combining aliquots from two or more samples and analyzing the resulting pooled sample (Keith, 1993). Compositing is often necessary when a relatively large amount of sediment must be obtained at each sampling site (for instance, to conduct several different physical, chemical or biological analyses). Compositing might be a practical, cost-effective way to obtain average sediment characteristics for a particular site (see Table 2-2), but not to dilute a polluted sample. Also, if an objective of the study is to define or model physicochemical characteristics of the sediment, it might be important not to composite samples because of model input requirements (EPRI, 1999).

All utensils (e.g., spoons, scoops, spatulas) which come in direct contact with sediment samples during handling and processing should be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon®).

Considerations

All handling procedures carry the risk of sample contamination. Therefore, sediment sample handling should be kept to a minimum. Potential sample contamination can be caused by the following common situations...

- making field measurements of sediments using contaminated probes, utensils, or other instruments.
- contaminated and uncontaminated stations are sampled without appropriate decontamination of equipment between stations.
- the parameter of interest is volatile (e.g., ammonia, acid volatile sulfides, or volatile organics) and samples are exposed to air.
- samples are exposed to vessel exhaust fumes, lubricants, or rust.

4.2.2 Grab Samples

If a sediment grab sample is to be subsampled in the laboratory, the sample should be released carefully and directly into a labeled container that is the same shape as the sampler and made of a chemically-inert material (see Section 4.1 for recommendations on containers). The container must be large enough to accommodate the sediment sample and should be tightly sealed with the air excluded.

If the grab sample is to be subsampled in the field, it is desirable to subsample from the sampler directly to minimize sediment handling and associated artifacts. Therefore, the sampler should allow access to the surface of the sample without loss of water or fine-grained sediment (see Section 3.1.1 for sampler descriptions). This typically dictates the use of a grab sampler with bucket covers that are either removable or hinged to allow access to the surface of the sediment sample (e.g., Ponar, VanVeen).

Prior to subsampling from the grab sampler, the overlying water should be removed by slow siphoning using a clean tube near one side of the sampler (WDE, 1995; PSEP, 1997a). If the overlying water in a sediment sampler is turbid, it should be allowed to settle if possible.

Considerations

When working with grab samples...

- decanting the water, or opening the jaws lightly to let the water run out is not recommended as these methods might result in unacceptable disturbance or loss of fine-grained sediment and organic matter.
- if metal contamination or sediment oxygen demand are of concern, oxidation of sediments could significantly alter their characteristics. Process the sample in a glovebox or similar apparatus under an oxygen-free environment.
- for samples that are suspected of heavily elevated polynuclear aromatic hydrocarbons (PAHs), process immediately under low light upon retrieval to minimize ultraviolet light-activated toxicity of PAHs (Ankley et al., 1994).

The general subsampling and compositing process for grab samples is illustrated in Figure 4-2. Subsampling can be performed using a spoon or scoop made of inert, non-contaminating material. *Sediment which is in direct contact with the sides of the grab sampler should be excluded* as a general precaution against potential contamination from the device. Subsamples may be combined or placed into separate clean, pre-labeled containers. If the sample is to be frozen, it is advisable to leave approximately 10% head space in the container to accommodate expansion and avoid breakage.

There are two alternatives for compositing sediment samples from grab samplers (see Figure 4-2): (1) compositing and homogenizing (mixing) in the field and (2) compositing in the field and homogenizing in the laboratory.

In some studies (e.g., where metals are the pollutants of concern), it might be necessary to subsample a grab sample under oxygen-free conditions to minimize oxidative changes. In these cases, it is recommended that a hand-coring device be used for subsampling. The core should be inserted immediately upon retrieval of the sampler, then removed and placed into a glove box or bag which is flushed with a constant, controlled volume of inert gas. The sediment within the core can then be extruded under oxygen-free conditions into deaerated containers. The presence of oxygen during handling and storage might be relatively unimportant (Brumbaugh et al., 1994) or very important (Besser et al., 1995), depending on the sediment characteristics, the contaminants of concern, and the study objectives.

Checklist
Compositing samples involves

In the field

- ✓ placing subsamples from individual grab samples in a clean container to form a composite sample
- ✓ transporting the composite to a laboratory
- ✓ homogenizing the sample at the laboratory to prepare it for testing (See Section 4.3 for further details)

In the lab

- ✓ placing subsamples from multiple grabs in a clean container
- ✓ mixing the subsamples to form a homogeneous composite sample
- ✓ placing the composite sample in one or more containers, depending on the number of analyses to be performed
- ✓ transporting the composite sample to a laboratory (or laboratories) for testing

4.2.3 Core Samples

Subsampling sediment core samples is usually done to focus the assessment on a particular sediment horizon or horizons and/or to evaluate historical changes or vertical extent in contamination or sedimentation rates. Whenever subsampling of retrieved sediment cores is required, particularly for analysis of contaminants, the sediment should be extruded from the core liners and subsampled as soon as possible after collection. This can be accomplished in the field if appropriate facilities and equipment are available, or in the laboratory after transport.

Systematic subsampling (see Figure 4-3) involves removing the sediment from the core in sections of uniform thickness. Each incremental core section corresponds to a particular sediment depth interval. In remedial dredging and geological applications, longer sections (e.g., 25-50 cm) are typically used to characterize a site.

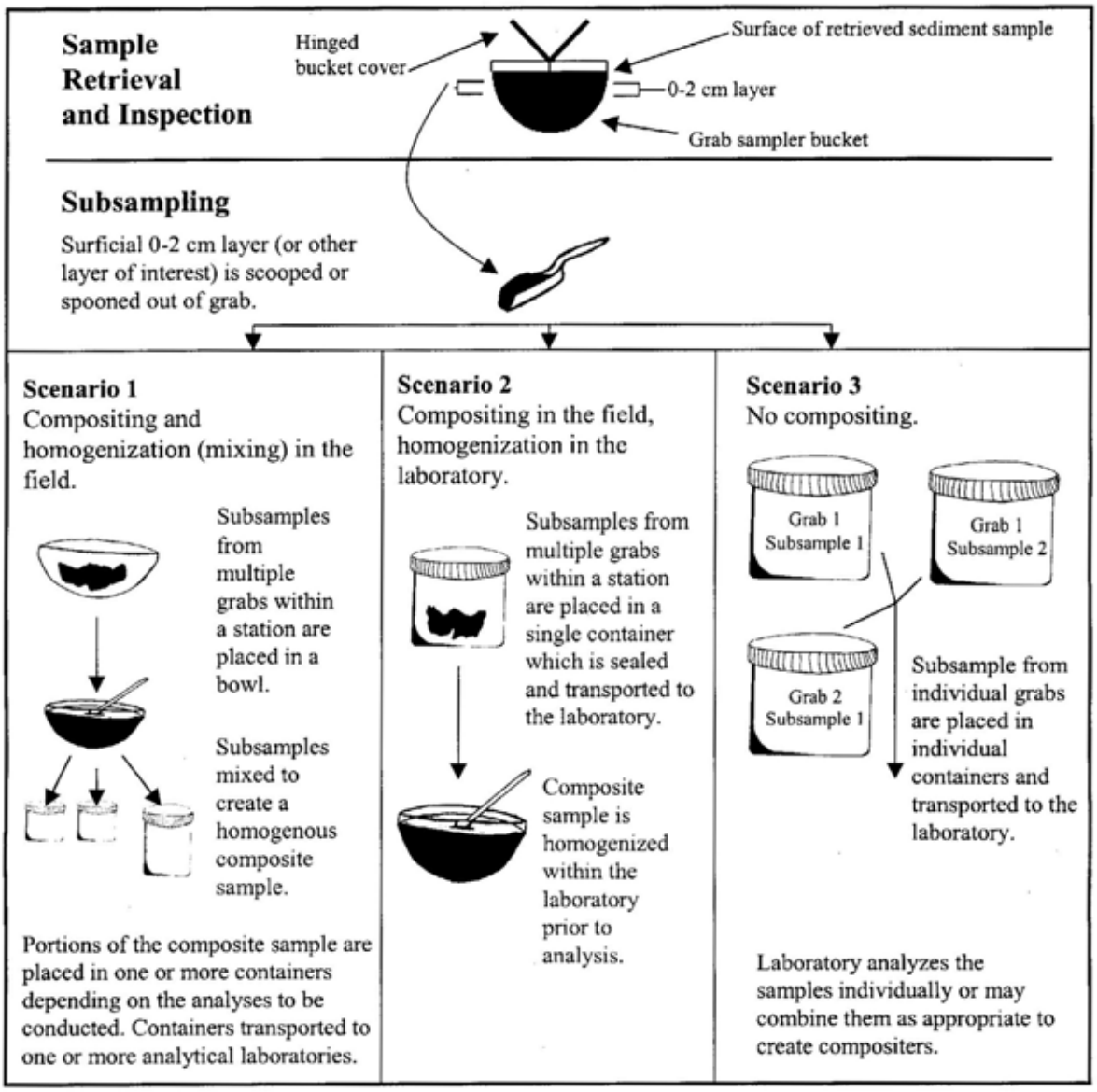


Figure 4-2. Alternatives for subsampling and compositing sediment grab samples.

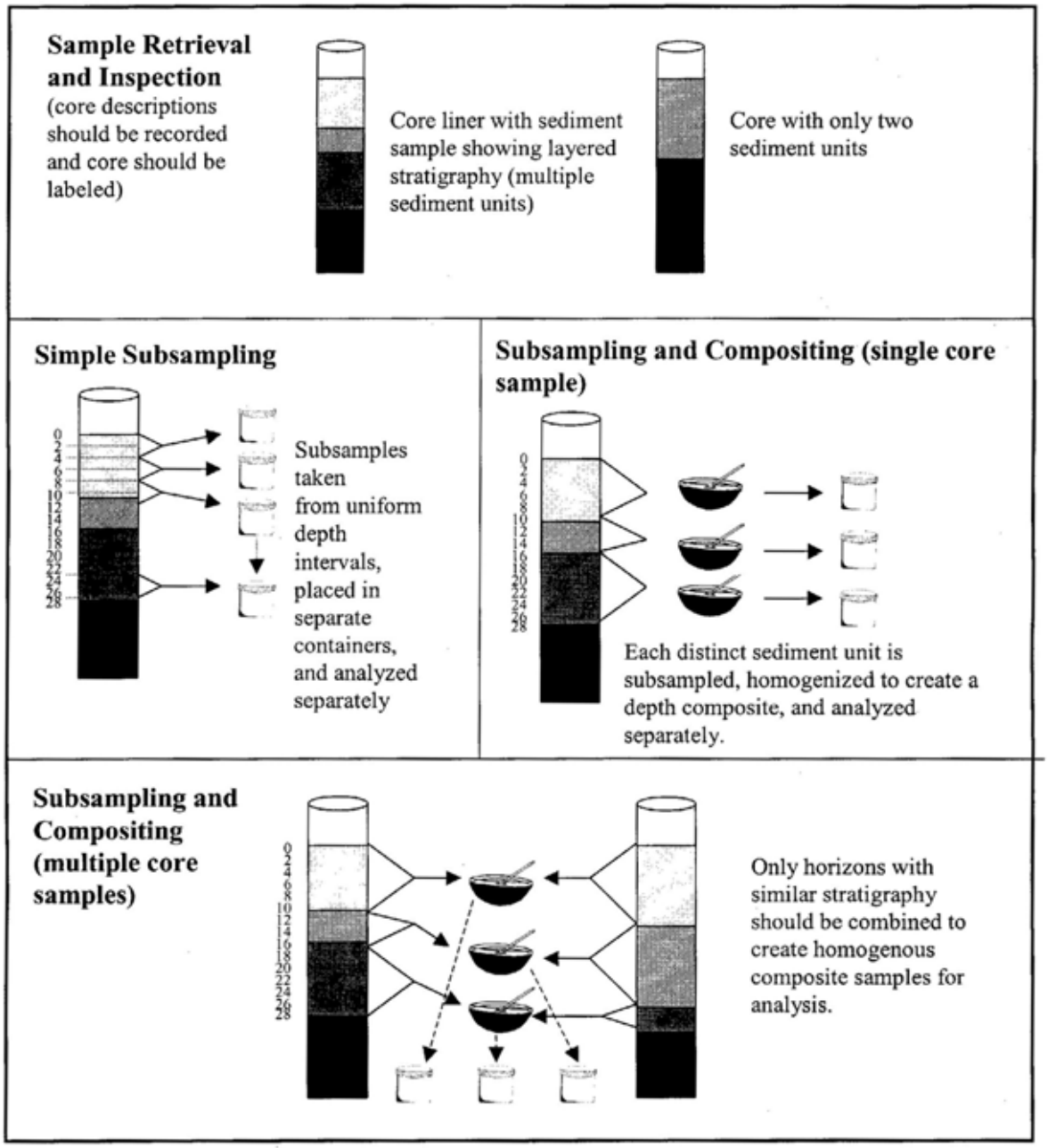


Figure 4-3. Alternatives for subsampling and compositing sediment core samples.

The depth horizon(s) sampled will depend on the study objectives as well as the nature of the substrate. For toxicological studies, the biologically active layer and sedimentation rates at the site might be important factors determining which core sections are sampled. In these studies, subsampling depth intervals include the 0 to 2 cm layer (for recent deposition) and the 0 to 5 cm or 0 to 15 cm layers (for biological activity, depending on resident organisms). Many programs have project-specific depths corresponding to study requirements, such as dredging depths for navigation or remediation dredging. In many regional or national environmental monitoring programs (e.g., EMAP), the uppermost surficial layer is sampled because information on the horizontal distribution of sediment contaminants is desired (USEPA, 2000d).

There are various methods for subsampling sediment cores including gradual extrusion, dissection of a core using a jig saw, reciprocating saws, use of a segmented gravity corer, a hand corer, or scoops and spoons. Cutting devices range from stainless steel knives to teflon or nylon string.

A piston-type extruder that applies upward pressure on the sediment is an instrument commonly used to gradually expose a core for sectioning in some monitoring programs where specific sediment depths have been defined a priori (Kemp et al., 1971). [Note: For dredged material studies and other types of remediation projects, where pre-determined depth strata are not necessarily defined, it is usually important to view the entire core prior to sectioning or compositing.] The capped core liner containing the sediment and overlying water is uncapped at the lower end and placed vertically on top of the piston. The top cap is removed and the water is siphoned off to avoid disturbance of the sediment-water interface. The core liner is then pushed slowly down until the surface of the sediment is at the upper end of the liner. Sediment sections are collected by pushing the liner down and cutting the exposed sediment into sections of the desired thickness using a stainless steel or Teflon® cutter (Environment Canada, 1994; Mudroch and Azcue, 1995). A 1- to 2-mm outer layer of sediment that has been in contact with the plastic or metal liner should be removed and discarded, if possible, to avoid contamination. Each sediment subsample should be placed into a labeled, clean and chemically-inert container, or, if subsamples are being composited, into an appropriately sized mixing bowl. The size of the container should be as close to the volume of the sediment as possible to minimize the head space in the container. If it is desirable to maintain an oxygen-free environment during subsampling, then all handling or manipulations should take place in a glove box or bag filled with an inert gas and modified to accommodate the core liner through an opening (Environment Canada, 1994; Mudroch and MacKnight, 1994).

Cores of more consolidated material can be mounted onto a horizontal U-shaped rail and the liner cut using a saw mounted on a depth-controlling jig. The final cut can then be made with a sharp knife to avoid contamination of the sediment by liner material, and the core itself can be sliced with Teflon® or nylon string. The core then becomes two D-shaped halves that can be easily inspected and subsampled (Mudroch and Azcue, 1995). Sediment in contact with the saw blade should not be used for toxicity tests or metals analyses due to potential contamination from the saw blade. Another alternative for sectioning and subsampling is a segmented gravity corer described by Aanderaa Instruments of Victoria, BC, Canada. The core tube of the sampler consists of a series of rings placed on top of one another. Subsampling is carried out by rotating the rings around its other axis so that it cuts sediment layers of similar thickness. This segmented core tube is suitable for sampling fine-grained sediments and allows one person in the field to subsample the core into 1-cm sections (Mudroch and Azcue, 1995).

Sediment from box-core samples can be effectively subsampled with a small hand corer after the overlying water has been carefully siphoned off and discarded. Hand corers with small inner diameters less than 3 cm tend to compact sediments, so they must be used with care. Spoons or

scoops have also been used to subsample surface sediments from a box corer (Environment Canada, 1994).

Like grab samples, core samples may be composited or subsampled in the field or laboratory after evaluating them for acceptability. Although there might be occasions when it is desirable to composite incremental core depths, it is recommended that only horizons of similar stratigraphy be composited. Depending on the study objectives and desired sampling resolution, individual horizons within a single core can be homogenized to create one or more "depth composites" for that core, or corresponding horizons from two or more cores might be composited (Figure 4-3). Composite samples must be homogenized prior to analysis or testing.

4.3 Homogenization

Homogenization refers to the complete mixing of sediment to obtain consistency of physicochemical properties throughout the sample prior to using in analyses. Homogenization is typically performed on individual samples, as well as on composited samples and can be done either in the field or the laboratory.

4.3.1 General Procedures

Prior to homogenization, unrepresentative materials (e.g., twigs, shells, leaves, stones, wood chips and seagrass) are often removed and documented in an appropriate field log (see Section 5.2 for techniques to remove unrepresentative material). The need for removal of larger matter depends on the analyses to be conducted.

Mixing should be performed as quickly and efficiently as possible, because prolonged mixing can alter the particle-size distribution in a sample and cause oxidation of the sediments (Ditsworth et al., 1990; Stemmer et al., 1990a;b). This can alter the bioavailability of contaminants, particularly metals, by increasing or decreasing their availability (Ankley et al., 1996). If metal contaminants or volatile chemicals are a concern, samples should be mixed in a glovebox under an inert atmosphere and quickly partitioned into sample containers for analysis.

Recommendation Box #3
How should samples be homogenized?

- Use a sufficiently large, precleaned glass or stainless steel mixing bowl to homogenize the sample.
- Use clean glass polyethylene, or stainless steel implements (e.g., spoon) to mix sediment.
- Mixing should be performed as quickly and efficiently as possible while attempting to reduce oxidation of the sample.
- Intensive manual mixing of wet sediment, in a suitably large container, is usually sufficient to homogenize the sample (Burton et al., 1989; Ingersoll and Nelson, 1990; Johns et al., 1991a; Carr and Chapman, 1992).
- Regardless of the mixing method selected, the effectiveness of the method should be demonstrated using a homogenate replicate.

Photo courtesy of Nile Kemble

Homogenizing a composited sediment sample using a mechanical mixer

Photo courtesy of Chris Ingersoll

Subsampling sediment for toxicity testing

Mixing should be performed in a large, precleaned glass or stainless steel bowl. The sediment should be thoroughly stirred with a clean glass, high density polyethylene, or stainless steel spoon until textural, color, and moisture homogeneity are achieved (Environment Canada, 1994; PSEP, 1995). Hand mixing has also been performed by rolling the sediment out flat on a sheet of plastic or pre-combusted foil and tumbling the sediment by alternately raising each corner of the sheet (Mudroch and Macknight, 1994). This procedure, however, is not recommended where the anaerobic integrity of the sediment must be maintained.

Considerations
Homogenization of anaerobic sediments...

! Beware of over-mixing and/or introducing air to the sample. Such mixing is likely to change the chemical characteristics of the sample and yield unrepresentative results. This is especially important if samples are initially anaerobic or if volatile or labile chemicals are of interest (e.g., AVS).

Mechanical mixers have also been used to homogenize samples (Ditsworth et al., 1990; Stemmer et al., 1990b; Kemble et al., 1993), including portable cement mixers (bare metal and Teflon-lined) and portable drills fitted with a variety of stainless steel paddles (Kemble et al., 1994b).

Homogenate replicates consist of two or more subsamples, taken from different locations within a mixed sample, and then comparing analytical results of the replicate samples. After the sediment has been homogenized, it is generally partitioned among sample containers. Partitioning sediments for chemical or toxicity analyses may be accomplished using various methods. In one method, a number of small portions are removed from random locations in the mixing container and distributed randomly in all sample jars until the appropriate volume of sediment is contained in each sample jar for each analysis. During distribution, the sediment is periodically mixed using a glass rod or porcelain spatula to minimize stratification effects due to differential settling, especially if the sediment is prone to rapid settling (ASTM, 2000a). An alternative is to use a splitter box designed to contain and then divide the homogenized sediment.

4.4 Sample Transport and Storage

Transport and storage methods should be designed to maintain structural and chemical qualities of sediment and pore water samples. Sediments collected using grab samplers are usually transferred from the sampler to containers that may or may not serve as the storage container. The containers might be stored temporarily in the field or they might be transported immediately to a laboratory for storage. If sediment core samples are not sectioned or subsampled in the field, they may be stored upright, in the core liner, for intact transportation to the laboratory. If sectioning or subsampling takes place in the field, then the subsamples may also be transferred to sample containers and stored temporarily. The sample containers with the field-collected sediments are then placed into a transport container and shipped to the laboratory.

4.4.1 General Procedures

Proper storage conditions (see Table 4-1) should be achieved as quickly as possible after sampling. For those parameters that are preserved via refrigeration (e.g., toxicity) samples should be stored in the field in refrigerated units on board the sampling vessel or in insulated containers containing ice or frozen ice packs. For samples that can be preserved via freezing (e.g., some metal and organic chemical analyses) dry ice can be used to freeze samples for temporary storage and transport (USEPA, 1983, 1993). Pelletized dry ice has been used effectively in the dredged materials management program to store core samples. It is important to know chilling capacities and

efficiencies to assure that temperature regulation is adequate. Care should be taken to prevent refrigerated samples from freezing and to keep frozen samples from thawing. Freezing changes the sediment volume depending on the water content, and it permanently changes the structure of the sediment and potentially alters the bioavailability of sediment associated contaminants.

Logistics for sample transport will be specifically tailored to each study. In some cases it is most efficient to transfer samples to a local storage facility where they can be either frozen or refrigerated. Depending on the logistics of the operation, field personnel may transport samples to the laboratory themselves or utilize an overnight courier service. If a freight carrier is employed, the user must be aware of any potentially limiting regulations (e.g. regarding the use of ice or dry ice). Samples that have a recommended storage temperature should be cooled to that temperature prior to placement in the transport container. Light should be excluded from the transport container.

Core samples should be transported as intact core liners (tubes). Prior to sample transport, the entire space over the sediment in the core liner should be filled with site water, and both ends of the core liner should be completely sealed to prevent mixing of the sediment inside. The cores should be maintained in an upright position particularly if the sample is not highly consolidated material, and secured in either a transport container (e.g., cooler or insulated box) with ice or ice packs, or in a refrigerated unit that can maintain a temperature near 4°C (Environment Canada, 1994). If the transport container cannot accommodate long core samples such as from vibracorers or piston corers (core liners > 1 m), then the core samples can be cut into 1-m lengths, and the ends securely capped such that no air is trapped inside the liners (see Section 4.3.3).

Impregnating unconsolidated sediment cores with epoxy or polyester resins will preserve sediment structure and texture (Ginsburg et al., 1966; Crevello et al., 1981) but not sediment chemical characteristics. Therefore, this procedure is not recommended for transporting or storing sediment samples for chemical characterization or biological testing (Environment Canada, 1994).

Recommendation Box #4
Sample Transport and Storage

- ➡ The volume of overlying water in sediment samples should be minimized to reduce the potential for resuspension of surface sediments during transport.
- ➡ Care should be taken to retain the surficial floc overlying a core sample.
- ➡ Cores should be secured in an upright position during transport to minimize disturbance of the sediment.
- ➡ Sediment samples collected in the field should be stored in containers without headspace at 4° C and in the dark to minimize changes in contaminant bioavailability.
- ➡ Prior to transport, headspace in the core liner should be filled with site water and both ends of the liner should be completely sealed.

4.5 Sample Holding Times

Limits for effective holding times are governed by sediment type and contaminant characteristics (ASTM, 2000a). Because these qualities are not always known, a general recommendation is to store sediments and interstitial water in the dark at 4 °C (SETAC, 2001). Preservation and recommended storage times for various types of analyses are summarized in Table 4-1.

Recommendation Box #5
How long should samples be stored before analysis?

- Unless site-specific information is available, sediment samples should be stored no longer than two weeks prior to using in toxicity testing.
- Preserved samples for chemical analyses should be stored no longer than the maximum holding times as defined by the particular program.

Samples collected for toxicity tests should be used as quickly as possible. Recommended maximum holding times range from 10 days (NOAA) to two weeks (ASTM, 2000a; USEPA, 2000d), to eight weeks (USEPA/ACOE, 1991, 1998). Preferred sample storage times reported for toxicity tests have varied substantially (Dillon et al., 1994; Becker and Ginn, 1990; Carr and Chapman, 1992; Moore et al., 1996; Sarda and Burton, 1995; Sijm et al., 1997; Defoe and Ankley, 1998), and differences appear to depend primarily upon the type or class of contaminant(s) present.

Extended storage of sediments that contain high concentrations of labile contaminants (e.g., ammonia, volatile organics) might lead to loss of these contaminants and a corresponding reduction in toxicity. Under these circumstances, the sediment should be tested as soon as possible after collection, but not later than two weeks (Sarda and Burton, 1995). Sediments that exhibit low to moderate toxicity might exhibit higher variability in toxicity when tested following storage of short duration (e.g. two weeks). Testing could actually be more reliable following longer storage for these types of samples if the longer storage reduces potential interference associated with indigenous predators (DeFoe and Ankley, 1998). Sediments contaminated with relatively stable compounds (e.g. high molecular weight compounds such as PCBs) or those that exhibit moderate-to-high toxicity, do not seem to vary appreciably in toxicity with increased storage time (Moore et al., 1996; DeFoe and Ankley, 1998). Longer term storage might be acceptable in such cases. Given our incomplete knowledge on the changes that occur, it is recommended that sediments should be stored no longer than two weeks for toxicity testing unless site-specific information indicates otherwise.

Periodic measurements of contaminants of concern provide a useful context for interpretation of toxicity test results when sediments or interstitial waters are stored for extended periods of time, but this is rarely cost-effective. It might be more efficient to conduct interstitial water toxicity tests within two weeks of sediment collection, corresponding with the start of sediment tests (Ingersoll et al., 1993). In general, though, interstitial water should be analyzed as quickly as possible following sampling to minimize possible changes in contaminant bioavailability.

Sediment cores collected for stratigraphical or geological studies can be stored at 4 °C in a humidity-controlled room for several months without any substantial changes in sediment properties (Mudroch and Azcue, 1995).

CHAPTER 5 Sediment Manipulations

Manipulation of sediments in the laboratory is often required to achieve certain desired characteristics or forms of material for toxicity testing and chemical analysis. As all manipulation procedures alter some qualities of field samples, it is critical to evaluate the effect that these changes might have on the study objective and on each critical measurement endpoint. Therefore, all procedures used to prepare sediment samples should be explicitly described in the study plan and fully documented. Generally, manipulation procedures should be designed to maintain sample representativeness in terms of toxicity and chemistry by minimizing procedural artifacts. Under certain programs, some analytical procedures and toxicity test protocols necessitate specific manipulations (e.g., seawater or solvent extractions for effluent toxicity tests, USEPA/ACOE, 1991, 1998). The reader should always consult and follow any program or test-specific guidance.

This chapter discusses methods for several common manipulations performed in the laboratory including sieving, spiking, organic carbon modification and formulated sediments, sediment dilution, and elutriate preparation. Other sediment manipulations, such as salinity adjustments or pre-treatment of sediment ammonia or sulfides (often done in conjunction with toxicity testing in certain regulatory programs) are not discussed in this manual as these are well documented elsewhere (e.g., PSEP, 1995; USEPA/ACOE, 1998). The reader should consult these references for further information on these procedures. Figure 5-1 presents a flowchart summarizing the laboratory manipulations discussed in this section, illustrating important issues to be considered for each manipulation.

5.1 Sieving

In general, sieving is not recommended because it can substantially change the physicochemical characteristics of the sediment sample. For example, wet sieving of sediment through fine mesh (≤500 µm openings) has been shown to result in decreased percent total organic carbon and decreased concentrations of total PCBs, which might have been associated with fine suspended organic matter lost during the sieving process (Day et al., 1995). Sieving can also disrupt the natural chemical equilibrium by homogenizing or otherwise changing the biological activity within the sediment (Environment Canada, 1994).

In some cases, however, sieving might be necessary to remove indigenous organisms, which can interfere with subsequent toxicity testing and confound

Checklist

Sediment samples are sieved for the following reasons:

- ✓ To remove unrepresentative material, such as shells, stones, trash, and twigs.
- ✓ To increase homogeneity and replicability of samples.
- ✓ To remove indigenous organisms prior to toxicity testing.
- ✓ To facilitate organism counting, sediment handling, and subsampling.
- ✓ To examine the effects of particle size on toxicity, bioavailability, or contaminant partitioning (ASTM, 2000a).

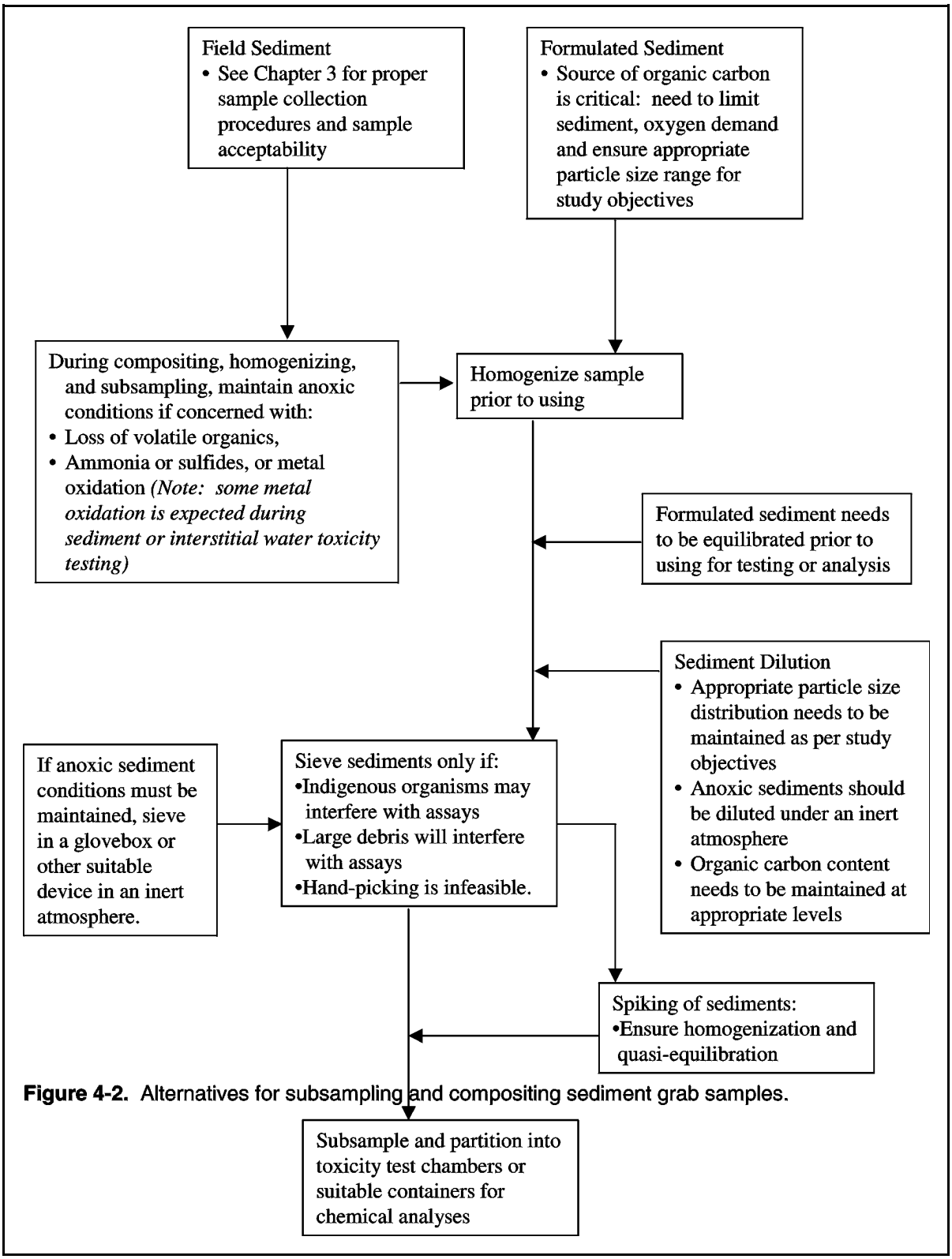


Figure 4-2. Alternatives for subsampling and compositing sediment grab samples.

Figure 5-1. Flowchart depicting relationships between common sediment manipulations including important considerations.

interpretations of analytical results (USEPA, 1994; 2000d; ASTM, 2000e). Indigenous organisms can be problematic in toxicity testing because they might be similar in appearance to test organisms or they might prey on the test organisms.

If sieving is performed, it should be done for all samples to be tested, including control and reference sediments if the objective of the study is to compare results among stations (ASTM, 2000a). It might be desirable to obtain certain measurements (e.g., dissolved and total organic carbon, acid volatile sulfide [AVS], and simultaneously extracted metals [SEM]) both before and after manipulation, to document changes associated with sieving (USEPA, 2000d). In addition, it might be desirable to document the effect of sieving on the sediment sample by conducting comparative toxicity tests using sieved and unsieved sediment (Environment Canada, 1994).

Recommendation Box #1
Should sediment be sieved prior to analyses?

- In general, sieving is not recommended because it can substantially change the physicochemical characteristics of the sediment sample. However, sieving might be necessary in preparing samples for some sediment toxicity testing (i.e., marine amphipod tests; USEPA, 1994).
- Unwanted materials (e.g., large particles and indigenous organisms) can be removed from the sediment sample using forceps as a preferred alternative to sieving.

5.1.1 Sieving Methods

Press Sieving

If sieving is necessary, press sieving is the preferred method. In this method, sediment particles are hand-pressed through a sieve using chemically inert paddles (Giesy et al., 1990; Johns et al., 1991). Matter retained by the screen, such as organisms, shell fragments, gravel, and debris, should be recorded in a log book and discarded (USEPA/ACOE, 1991). Samples with high debris, vegetation, or clay content might be difficult to press through a single sieve with a mesh size less than 1 mm; such samples might need to be pressed through a series of sieves with progressively smaller openings. Water should not be added to sediment when press sieving, as this could result in changes in contaminant concentration and bioavailability. Samples that are going to be used for both chemical analysis and toxicity tests should be sieved together, homogenized, and then split for their respective analyses.

Wet Sieving

If sediments cannot be press sieved without the addition of pressure, wet sieving might be required, however, this type of sieving increases the likelihood of contaminant loss. Wet sieving involves swirling sediment particles within a sieve using water to facilitate the mechanical separation of smaller from larger particles. A slurry made with water that has separated from the sediment during storage or transport might be sufficient to wash particles through the sieve. Wet samples that might have settled during transit should be stirred to incorporate as much field water as possible. In some cases, addition of a small volume of running site or deionized water might be required (ASTM,

Photo courtesy of Allen Burton

Sieving a sediment sample for toxicity testing

2000a). Mechanical shakers or stirring with a nylon brush can also facilitate wet sieving (Mudroch and MacKnight, 1994).

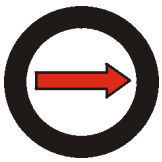
Recommended Sieves

In general, smaller mesh sieves are preferred to reduce loss of fines. Stainless steel, brass, or plastic woven polymer sieves (e.g., polyethylene, polypropylene, nylon, and Teflon) with mesh sizes that vary from 0.24 to 2.0 mm have been used to sieve sediment for toxicity tests (Keilty et al., 1988a;b; Giesy et al., 1990; Lydy et al., 1990; Stemmer et al., 1990a;b; Johns et al., 1991; Landrum and Faust, 1991). Non-metallic sieves are preferred if metals are of interest. Stainless steel sieves are acceptable if organic compounds are of interest. Stainless steel (provided the mesh is not soldered or welded to the frame), nylon, or Nitex-type plastic sieves are recommended when other inorganic constituents are of concern or are to be analyzed (ASTM, 2000a; PSEP, 1995).

Considerations

The mesh type and size should be chosen based on the following considerations...

- ! The type of toxicity test and test organisms to be used.
- ! Potential predators and/or competitors present in the sample.
- ! Potential adsorption or contamination of the chemical of interest due to sieving.
- ! The nature of the sample, including its particle size distribution, volume, and size of debris.



Recommendation Box #2

What type of sieve should be used?

- ➡ Stainless steel or brass sieves are not recommended when metals are a concern or are analyzed (ASTM, 2000a).
- ➡ Smaller mesh sieves (≤2.0 mm mesh openings) are recommended to reduce loss of fine particle sizes.
- ➡ Nylon or nitex mesh sieves are recommended for inorganics analyses (e.g., metals).

Generally, sieving through a 10-mesh (2-mm openings) sieve is acceptable as a basis to discriminate between sediment and other materials (ASTM, 2000a). For toxicity testing, the most frequently used mesh size is 1.0 mm (Environment Canada, 1994), which will remove most adult amphipods. However, a mesh of 0.25 mm might be needed to remove immature amphipods and most macrofauna (Landrum et al., 1992; Robinson et al., 1988; Day et al., 1995). In marine sediments, sieves with a mesh size of 0.5 mm are effective in removing most of the immature amphipods (Swartz et al., 1990; PSEP, 1995).

5.1.2 Alternatives to Sieving

Unwanted materials (e.g., large particles, trash, and indigenous organisms), can be removed from the sediment sample using forceps, prior to or, as an alternative to, sieving. If anerobic integrity of the sample is not a concern, the sediment could be spread on a sorting tray made of cleaned, chemically-inert material, and should be hand-picked with forceps. A stereomicroscope or magnifying lens might facilitate the process, or may be used to determine if sieving is necessary. Hand-picking is

preferable to sieving because it is less disruptive, but it typically is not practical for large volumes of sediment. Of course, this process oxidizes the sediment and might alter contaminant bioavailability.

Autoclaving, freezing, and gamma irradiation of sediments are alternatives to physical removal for inhibiting endemic biological activity in field-collected sediments. These are not generally recommended procedures. Each method has unique effects on the physicochemical and biological characteristics of the sediment, and a careful evaluation with respect to the study objectives is warranted when these methods are considered.

Considerations

In preparing formulated sediments, the following should be noted...

- ! Specific material sources should be carefully selected, as characteristics can vary significantly among product types. A number of suppliers of various sediment components are listed in ASTM (2000a) and USEPA (2000d).
- ! A critical component of formulated sediments is the source of organic carbon. It is not clear that any one source of organic carbon is routinely superior to another. Alpha cellulose appears to be a promising carbon source for formulated sediments.
- ! A variety of formulations have been used successfully in sediment toxicity testing (see ASTM [2000a] and USEPA [2000d]). At this time, no one formulation appears to be universally better than others.

5.2 Formulated Sediment and Organic Carbon Modification

5.2.1 General Considerations

Formulated sediments (also called reconstituted, artificial, or synthetic sediments) are mixtures of materials that mimic the physical components of natural sediments. While they have not been used routinely, formulated sediments potentially offer advantages over natural sediments for use in chemical fate and biological effects testing.

Formulated sediments also have limitations, however. They do not possess the natural microbial, meiofaunal, and macrofaunal communities or the complex organic and inorganic gradients prevalent in natural sediments. The lack of biological activity, diagenesis, and oxidation-reduction (redox) potential gradients undoubtedly alters some sorption and desorption properties, which

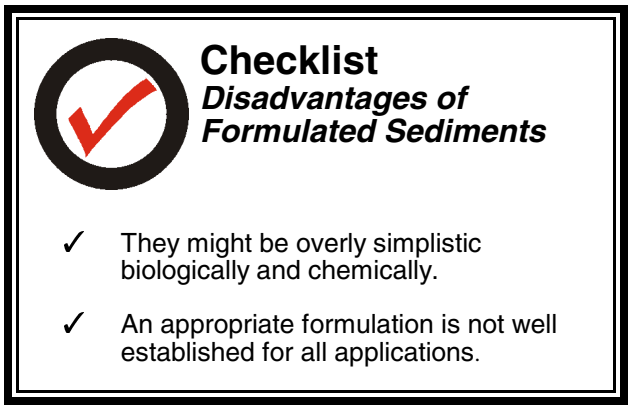
Checklist

Advantages of Formulated Sediments

- ✓ They provide a consistent, reproducible medium which facilitates comparisons between different sets of tests.
- ✓ Eliminates interferences caused by the presence of indigenous organisms.
- ✓ Components of the formulated sediment can be altered to measure the effect of certain physicochemical characteristics on chemical fate and bioavailability.
- ✓ They are useful in spiking experiments to obtain effect concentrations for chemicals.

might in turn alter contaminant fate and effects. The current lack of understanding of physicochemical controls on bioavailability in different sediment environments precludes broad-scale use of formulated sediments in definitive ecological risk assessments.

A formulated sediment should: (1) support the survival, growth, or reproduction of a variety of benthic invertebrates, (2) provide consistent acceptable biological endpoints for a variety of species, and (3) be composed of materials that have consistent characteristics (USEPA, 2000d; ASTM, 2000a). Characteristics should include: (1) consistency of materials from batch to batch, (2) contaminant concentrations below concentrations of concern, and (3) availability to all individuals and facilities (Kemble et al., 1999). Physicochemical characteristics that might be considered when evaluating the appropriateness of a sediment formulation include percent sand/clay/silt, organic carbon content, cation exchange capacity (CEC), redox potential, pH, and carbon:nitrogen:phosphorous ratios (USEPA, 2000d; ASTM, 2000a).



5.2.2 Sediment Sources

The specific material source should be carefully selected, as characteristics can vary significantly among product types. For example, USEPA (2000d) found that for three different sources of kaolinite clay, the percentage of clay ranged from 56.5 to 88.5%, depending on individual product specifications. There are a number of suppliers of various sediment components (see USEPA, 2000d).

A critical component of formulated sediments is the source of organic carbon. It is not clear that any one source of organic carbon is routinely superior to another source.

5.2.3 Organic Carbon Modification

Organic carbon content of natural as well as formulated sediments can be modified to assess the effect on contaminant fate and bioavailability. Many studies employ sediment carbon modifications because total organic carbon (TOC) content has been shown to be a major determinant of nonionic organic chemical bioavailability (DiToro et al., 1991; DeWitt et al., 1992; and Kosian et al., 1999). While TOC modifications might be necessary to achieve study objectives, it should be recognized that organic carbon manipulations can change the particle composition and size distribution, thereby potentially affecting contaminant equilibrium. Thus, results from such experiments should be interpreted with care. Also, the sample needs to be equilibrated (see Section 5.3.3) following addition of the new source of organic carbon, prior to conducting analyses.

Many recipes have used peat as the source of organic carbon, however, the quality and characteristics of peat moss can vary from bag to bag. Other sources of organic carbon include humus, potting soil, maple leaves, composted cow manure, rabbit chow, cereal leaves, chlorella, trout chow, Tetramin®, Tetrafin®, and alpha cellulose. Of these, only peat, humus, potting soil, composted cow manure, and alpha cellulose have been used successfully in sediment testing without fouling the overlying water;

other sources have caused dissolved oxygen concentrations to fall to unacceptable levels (Kemble et al., 1999).

More about organic carbon modification:

Five studies compared organic carbon sources in formulated sediments. A study of 31 different organic carbon recipes by Environment Canada (1995) compared effects on sediment homogeneity, density, and turbidity. Cerophyll and trout chow were selected as the optimal organic carbon sources with high clay (kaolin at 50 or 75% total concentration) and fine sand.

Ribeiro et al. (1994) recommended use of synthetic alpha-cellulose as a carbon source amended with humic acid. This compound has since been tested by Kemble et al (1999), Sawyer and Burton (1994), and Fleming and Nixon (1996). Ribeiro et al. (1994) found that sorption was dependent on the amount of organic carbon present. Kemble et al. (1999) found that growth and survival of *Chironomus tentans* and *Hyalella azteca* was better in 10% than in 2% alpha-cellulose. Both alpha-cellulose and conditioned red maple leaves were found to be suitable as organic carbon amendments for reference toxicant testing with *Hyallela azteca* (96 hr) when spiked with cadmium, zinc, or anthracene (Sawyer and Burton, 1994).

Use of alpha cellulose as a carbon source for sediment-spiking studies has not been adequately evaluated, but it appears to be promising. Alpha cellulose is a consistent source of organic carbon that is relatively biologically inactive and low in concentrations of chemicals of concern. Furthermore, Kemble et al. (1999) reported that conditioning of formulated sediment was not necessary when alpha cellulose was used as a carbon source for a negative control sediment. Compared with other sources of organic carbon, alpha cellulose is highly polymerized and would not serve as a food source, but rather would serve to add texture or provide a partitioning compartment for chemicals.

Reductions in organic carbon content have been achieved by diluting sediment with clean sand (See Section 5.4; Clark et al., 1986; Clark et al., 1987; Tatem, 1986; Knezovich and Harrison, 1988). However, this can change sediment characteristics resulting in non-linear responses in toxicity (Nelson et al., 1993). Combustion has also been used to remove fractions of organic carbon (Adams et al., 1985; IJC, 1988). However, this method results in substantial modification of the sediment characteristics, including oxidization of some inorganic components.

The ratio of carbon to nitrogen to phosphorous might be an important parameter to consider when selecting an organic carbon source. This ratio can vary widely among carbon sources (ASTM, 2000a; USEPA, 2000d). For example, carbon can range from 30 to 47%, nitrogen from 0.7 to 45 mg/g, and phosphorous from below detection limits to 11 µg/g for several different carbon sources (USEPA, 2000d).

A variety of formulations have been used successfully in sediment toxicity testing (see ASTM, 2000a and USEPA, 2000d). At this time, no one formulation appears to be universally better than others.

5.3 Spiking

Spiking involves adding one or more chemicals to sediment for either experimental or quality control purposes. Spiking environmental samples is used to document recoveries of an analyte and thereby analytical bias. Spiked sediments are used in toxicity tests to determine effects of material(s) on test species. Spiking tests can also provide information concerning chemical interactions and transformation rates. The design of spiking experiments, and interpretation of results, should always consider the ability of the sediment to sequester contaminants, recognizing that this governs many chemical and biological processes (O'Donnel et al., 1985; Stemmer et al., 1990a;b; ASTM, 2000a;

Northcott and Jones, 2000). In preparation for toxicity and bioaccumulation tests, references regarding the choice of test concentrations should be consulted (USEPA, 2000d; ASTM, 2000a; Environment Canada, 1995). Program specific guidance documents should also be consulted as appropriate.

Several issues regarding sediment spiking are addressed in this section. First, several methods have been used to spike sediments but the appropriate method needs to be selected carefully depending on the type of material being spiked (e.g., soluble in water or not), its physical-chemical form, and objectives of the particular study. Second, spiked material should be uniformly distributed throughout the sediment. Otherwise, analyses or toxicity tests are likely to yield highly variable results, depending on the concentration of spiked material present. Third, the spiked material needs to be at equilibrium between the sediment and the interstitial water to ensure that all relevant exposure phases are appropriately considered in chemical analyses or toxicity testing. The time it takes to reach this equilibrium is a critical factor that needs to be considered and documented.

Recommendation Box #3

How should sediments be spiked with a chemical or other test material?

- Regardless of the spiking technique used, care should be taken to ensure complete and homogenous mixing.
- Replicate subsamples should be analyzed to confirm homogeneous mixing.
- Moisture content should be determined on triplicates for each sample so that the spike concentration can be normalized on a dry weight basis.
- Wet spiking is recommended over dry spiking methods.
- Generally speaking, the jar rolling method is more suitable than hand mixing for spiking larger batches of sediment.
- To ensure chemical equilibrium between the sediment and pore water in toxicity testing, spike sediments should be stored for at least one month, unless other information is available for the spiking material and sediment type.
- Direct addition of organic solvent carriers should be avoided because they might alter sediment chemistry and affect contaminant bioavailability. Shell coating methods should be used instead as this eliminates many of the disadvantages of solvent carriers.

5.3.1 Preparation for Spiking

Debris and indigenous organisms should be removed from sediment samples as soon as possible after collection to reduce deterioration of sediment quality due to decomposition of organic debris and dying infauna. If sediments are to be stored prior to spiking, they should be kept in sealed containers at 4 °C.

Regardless of the spiking technique used, care should be taken to ***ensure complete and homogenous mixing*** (See Section 4.4). It is recommended that chemical analyses be conducted to verify that concentrations of the spiked contaminants are uniform throughout the mixed material. Three or more subsamples of the spiked sediment should be randomly collected to determine the concentration of

the substance being tested. In general, the coefficient of variation (CV) should be ≤20% for homogeneity of mixing to be considered sufficient (ASTM, 2000a; Northcott and Jones, 2000).

Temperatures should be kept cool during spiking preparation (e.g., 4° C) due to rapid physicochemical and microbiological alterations which might occur in the sediment that, in turn, might alter bioavailability and toxicity (ASTM, 2000a; Environment Canada, 1995). If spiking PAH compounds, it might be important to conduct spiking in the dark, or at least under low light as PAH toxicity has been shown to increase under ultraviolet light (Ankley et al., 1994).

It is recommended that a subsample of the spiked sediment be analyzed for at least the following parameters: moisture content, pH, ammonia, total organic carbon (TOC), acid volatile sulfide (AVS), particle size distribution, and background levels of the chemical(s) to be spiked. Further characterization may include analyses of total volatile residue, pore water salinity (before and after any sieving), chemical oxygen demand, sediment oxygen demand, oxidation-reduction potential (Eh), metals, total chlorinated organic content, chlorinated organic compounds, and polycyclic aromatic hydrocarbons (see Appendix G for more information on physicochemical parameters often measured on sediments). It is particularly important to determine the TOC concentration if the sediment is to be spiked with a nonionic organic compound, as organic carbon is the primary binding phase for such compounds (DiToro et al., 1990). Similarly, the concentration of AVS (the primary binding phase for cationic metals in anoxic sediments) and TOC should be measured after spiking with a cationic metal (Ankley et al., 1996; Leonard et al., 1999).

The sediment moisture content measurement is used to standardize the amount of chemical spiked on a dry weight basis (see Appendix G). Generally, the moisture content should be determined on triplicates for each sample by measuring the weight lost following 24 h of oven-drying at 105 °C. After drying, the samples should be cooled to room temperature in a desiccator before taking dry weight measurements (Yee et al., 1992). The mean wet density, expressed as mg water/cm^3, is measured by using the same drying method on known sediment volumes. This allows spiking to be normalized from a volume basis to an equivalent dry weight basis.

5.3.2 Methods for Spiking

Spiking of both wet and dry sediments is common, but wet spiking is recommended because drying might reduce the representativeness of the sample by changing its physicochemical characteristics (ASTM, 2000a). Methods differ mainly in the amount of water present in the mixture during spiking, the solvent used to apply the toxicant, and the method of mixing. Generally speaking, the jar rolling method is more suitable than hand mixing for spiking larger batches of sediment.

In addition to the above techniques, sediments may be spiked by hand stirring using a scoop or spatula, as long as the homogeneity of the mixture is verified. Eberbach and gyro-rotary shakers have also been used effectively to mix spiked sediments (Stemmer et al., 1990a). Less commonly, chemical(s) are added to the water overlying the sediment and allowed to sorb with no mixing (Stephenson and Kane, 1984; O'Neill et al., 1985; Crossland and Wolff, 1985; Pritchard et al., 1986).

Sediment Rolling

One of the recommended wet sediment rolling techniques requires a specific jar-rolling apparatus, first described by Ditsworth et al. (1990). Many other jar-rolling apparatuses are available, ranging in size and options available. This "rolling mill" method has been used to homogenize large volumes of sediments spiked with metals and non-ionic organic compounds. The primary disadvantage of this method is that the mixing apparatus must be constructed or purchased.

The jar-rolling apparatus used by Ditsworth et al. (1990) consists of eight parallel, horizontal rollers powered by an electric motor through a reduction gear, belts, and pulleys, which rotate cylindrical vessels containing the substrate mixtures. Mixing is accomplished gravimetrically by slowly rolling the jars (gallon-sized jars can be rolled at approximately 15 rpm). Optimally wetted, individual substrate particles adhere to each other and to the wall of the revolving jar until they cascade or tumble down the surface of the substrate mass. Dilution water may be added to the substrate before rolling to adjust the sediment-to-water ratio for optimal mixing. If oxidation is a concern (for example, if the sample will be analyzed for metals), jar contents might need to be maintained in an inert atmosphere. If PAHs are of concern then jars should be shielded from light (Ankley et al., 1994).

Considerations
When rolling sediment:

- Jars should not be overfilled, as this will reduce mixing efficiency.
- Prolonged rolling (e.g., > 1 wk) should be avoided to minimize physicochemical changes to the sediment.

Each jar should be loaded with the required amount of wet base sediment (with a calculated mass of dry sediment required for the test) prior to introduction of the toxicant. Several 1-cm diameter holes of different depths should be punched into the sediment to provide more surface area for the initial distribution of the test material. A predetermined volume of the stock solution or a serial dilution of the stock should be used to spike each jar load of sediment. A volumetric pipette should be used to distribute each aliquot onto the top surface and into the holes of the sediment in each jar. Sediments should be spiked sequentially, proceeding from low to high concentrations of test material, to minimize cross-contamination. Control substrates should be prepared by adding an equivalent volume of dilution water to a jar loaded with unspiked sediment. After spiking, all jars and their contents should be processed identically.

Typically, jars should be rolled for greater than two hours to achieve sample homogeneity. Jars should be closely monitored during the first hour of rolling to ensure proper mixing of substrates. After rolling for approximately 15 min, mixing efficiencies of the substrates can be judged visually. If a sediment displays excessive cohesiveness, as indicated by agglomerating or balling, the jars should be opened and an aliquot of appropriate dilution water (50 mL of either saltwater or freshwater depending on the source of the sediment) added to each substrate to increase the fluidity. This procedure should be repeated as necessary until the operator visually observes that all substrates are tumbling without forming balls. Adding water in small rather than large aliquots can prevent over-saturation of the sediment. Over-saturation is undesirable because excess water must be decanted following rolling, prior to sediment testing.

After rolling, the jars should be gently shaken to settle sediment that adhered to the walls. They may be set upright and stored overnight in the dark at room temperature or at an alternate temperature (e.g., 4° C) depending on the study objectives. After equilibration (see Section 5.3.3) and prior to distributing the sample to test chambers, additional rolling for two hours will help integrate interstitial water into the sediment.

Sediment Suspension Spiking

The sediment suspension technique (Cairns et al., 1984; Schuytema et al., 1984; Stemmer et al., 1990a; b; Landrum and Faust, 1991; Landrum et al., 1992) is the simplest of the three spiking techniques and requires the least equipment. The method involves placing dilution water and sediment together in a 1-L beaker. The desired amount of toxicant, dissolved in dilution water, is

added to the beaker. The mixture should be stirred at a moderate speed with a stir bar, or mechanical stirrer, for a minimum of four hours. The sediment in the beakers should then be allowed to settle and equilibrated at the appropriate test temperature as specified in the test method. The excess water overlying the sediment is decanted and discarded, and the sediment is distributed to the test containers (Environment Canada, 1995).

Slurry Spiking

The slurry technique (Birge et al., 1987; Francis et al., 1984; Landrum and Faust, 1991; Landrum et al., 1992) requires a minimum of equipment and involves less water than the sediment suspension technique. A 250-g dry weight sample of sediment is placed in a 500-mL Erlenmeyer flask. Via a 25-mL aliquot of distilled, deionized water, a sufficient concentration of the materials of interest is added to obtain the desired sediment concentration (mg/kg, dry weight basis). Control (unspiked) sediment receives a 25-mL aliquot of distilled, deionized water having no added materials. The sealed flask may be mixed using various methods such as continuous agitation in a shaker for five days (Birge et al., 1987) or vigorous shaking for 60 seconds, twice daily for seven days (Francis et al., 1984). Following mixing, the sediment suspensions should be centrifuged to remove water. The moisture content of the sediment should be approximately 15% to 20% after centrifugation. After removal of excess water, the prepared sediment can be placed in the exposure chambers and covered with dilution water according to the specific test methods. This procedure often yields sediment having its original moisture content.

5.3.3 Equilibration Times

Prior to distributing the spiked sediment to containers for toxicity testing or chemical analyses, ***the spiked sediments should be stored for a sufficient time to approach chemical equilibrium in the test material between the sediment and interstitial water.*** Equilibration times for spiked sediments vary widely among studies (Burton, 1991), depending on the spiking material and sediment type. For metals, equilibration time can be as short as 24 h (Jenne and Zachara, 1984; Nebecker *et al*., 1986), but one to two weeks is more typical (ASTM, 2000a). For organic compounds with low octanol-water partition coefficients (K_{ow}), equilibration times as short as 24 h have been used (Dewitt *et al*., 1989). Some organic contaminants might undergo rapid microbiological degradation depending on the microbial population present in the sample. In these cases, knowledge of microbial effects might be important in defining an appropriate equilibration period. Organic compounds with a high partition coefficient might require two months or more to establish equilibrium (Landrum et al., 1992). Boundaries for the sorption time can be estimated from the partition coefficient, using calculations described by Karickhoff and Morris (1985a, b). It is important to recognize that the quantity of spiked chemical might exceed the capacity of the test sediment system, prohibiting equilibrium.

For research purposes, unless definitive information is available regarding equilibration time for a given contaminant and sediment concentration, a one-month equilibration period is recommended, with consideration that two months might be needed in some instances (USEPA, 2000d). For regulatory programs, however, sample holding time should not exceed 2 weeks. Therefore, for these programs spiking equilibration time should not exceed 2 weeks. Periodic monitoring during the equilibration time is highly recommended to empirically establish stability of interstitial water concentrations (USEPA, 2000d). Sediment and interstitial water chemical concentrations should also be monitored during long-term bioassay tests to determine the actual chemical concentrations to which test organisms are exposed, and to verify that the concentrations remain stable over the duration of the test.

5.3.4 Use of Organic Solvents

Direct addition of organic solvents should be avoided if possible, because they might dramatically affect sediment geochemistry and alter bioavailability (USEPA, 2000d). However, many organic materials require use of a solvent to adequately mix with the sediment. If an organic solvent is to be used, the solvent should be at a concentration that does not affect test organisms and should be uniform across treatments. Further, both solvent control and negative control sediments should be included in tests with solvents. The solvent concentration in the control should equal the treatment concentration and should be from the same batch used to make the stock solution (ASTM, 2000a).

To reduce the possibility of solvent-related artifacts, the spiking process should include a step which allows the solvent to evaporate before addition of sediment and water followed by rolling (McLeese et al., 1980; Muir et al.,1982; Adams et al., 1985). Highly volatile organic compounds have been spiked into sediments using co-solvents followed by shaking in an aqueous slurry. When highly volatile compounds are used, immediate testing in covered flow-through systems is recommended (Knezovich and Harrison, 1988).

There is some uncertainty concerning artifacts introduced by the use of solvents. The use of a polar, water soluble carrier such as methanol was found to have little effect on the partitioning of nonpolar compounds to dissolved organic matter at concentrations up to 15% carrier by volume (Webster et al., 1990). However, another study showed that changes in partitioning by a factor of approximately two might occur with 10% methanol as a co-solvent for anthracene sorption (Nkedi-Kizza et al., 1985). The effect of carrier volume on partitioning of organic chemicals in sediments is equivocal. However, because solvents might be either directly or indirectly toxic to the test organisms, caution should be taken to minimize the amount of carrier used. In addition, the use of a carrier such as acetone might result in faster equilibration of spiked organic compounds (Schults et al., 1992).

Shell coating techniques which introduce dry chemical(s) to wet sediment have also been developed, principally to eliminate the potential disadvantages of solvent carriers. The chemical may be either coated on the inside walls of the container (Ditsworth et al., 1990; Burgess et al., 2000) or coated onto silica sand (Driscoll et al., 1997; Cole et al., 2000). In each shell coating method, the chemical is dissolved in solvent, placed in a glass spiking container (with or without sand), and the solvent is slowly evaporated prior to addition of the wet sediment. Wet sediment then sorbs the chemical from the dry surfaces. It is important that the solvent be allowed to evaporate prior to adding sediment or water.

5.4 Preparation of Sediment Dilutions

Spiked or field-contaminated sediments can be diluted with whole sediment to obtain different contaminant concentrations for concentration-effects testing. The diluent sediment should have physicochemical characteristics similar to the test sediment, including organic carbon content and particle size, but should not contain concentrations of contaminants above background levels (ASTM, 2000a; Burton, 1991). Diluent sediment has included formulated sediment as well as known reference site sediment. Diluted sediment samples should be homogenized and equilibrated in accordance with procedures described in Sections 4.4 and 5.3.3, respectively.

The diluent sediment should be combined with the test sediment in ratios determined on a dry weight basis to achieve the desired nominal dilution series (DeWitt, personal communication). Volume to volume dilutions have also been performed (e.g., Schlekat et al.,1995; Johns et al., 1985), but weight to weight dilutions are preferred because they provide more accurate control and enable a more straightforward calculation of dose-response curves.

Results from dilution experiments should be interpreted with care. There are often non-linear responses due to non-equilibrium, non-linear sorption-desorption processes that cannot always be adequately controlled (Nelson et al., 1993). Nelson et al. (1993) found that analyses of diluted sediments did not match nominal concentrations as estimated by physical characteristics. They suggested that chemical characterization is needed to determine effects of manipulations (i.e., mixing) and resulting changes (i.e., oxygenation of complexing agents such as acid volatile sulfides).

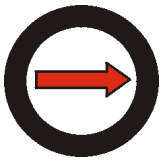
5.5 Preparation of Sediment Elutriates

Many studies of sediment toxicity have evaluated aqueous extractions of suspended sediment called elutriates. The elutriate method was initially developed to assess the effects of dredging operations on water quality (U.S. ACOE, 1976). Elutriate manipulations are also applicable to any situation where the resuspension of sediment-bound toxicants is of concern, such as bioturbation and storms, that might disturb sediments and affect water quality (USEPA/ACOE, 1991, 1998; Ankley et al., 1991). USEPA/ACOE (1998) lists eighteen freshwater and saltwater aquatic organisms as candidates for elutriate toxicity testing. Standard effluent toxicity test procedures are also appropriate for elutriates, including tests with various vascular and non-vascular plant species (Ingersoll, 1995).

Elutriate tests are not intended to reflect the toxicity of interstitial waters or whole sediments, as there are differences in contaminant bioavailability in the two types of media (Harkey et al., 1994). In general, elutriates have been found to be less toxic than bulk sediments or interstitial water fractions (Burgess et al., 1993; Ankley et al., 1991), although in some studies elutriates have been found to be more toxic (Hoke et al., 1990) or equally as toxic (Flegel et al., 1994) relative to interstitial water.

While there are several procedural variations, the basic method for elutriate preparation involves combining various mixtures of water and sediment (usually in the ratio of 4 parts water to 1 part sediment, by volume) and shaking, bubbling or stirring the mixture for 1 hour (Ross and Henebry, 1989; Daniels et al., 1989; Ankley et al., 1991; Burgess et al., 1993; USEPA/USACOE, 1991, 1998). It is likely that chemical concentrations will vary depending on the elutriate procedure used. Specific program guidance should be consulted as appropriate. The water phase is then separated from the sediment by settling and/or centrifugation (Note: the dredging remediation program does not always require centrifuging elutriates). Once an elutriate has been prepared, it should be analyzed or used in biological tests immediately, or as soon as possible thereafter. It should be stored at 4 °C for not longer than 24 h, unless the test method dictates otherwise (Environment Canada, 1994; USEPA/ACOE, 1991, 1998). For toxicity test exposures exceeding 24 h, fresh elutriate should be prepared daily.

Filtering the elutriate is generally discouraged, but it might be prescribed for some toxicity tests. Filtration can reduce the toxicity of sediment elutriates due to sorption of dissolved chemicals on the filtration membrane and retention of colloids. If colloidal material needs to be removed, serial or double centrifugation is generally a preferred alternative. If an elutriate must be filtered, it is recommended that only pre-treated filters be used and that the first 10 to 15 mL of the elutriate to pass through the filter be discarded (Environment Canada, 1994). Testing with a filtered elutriate should include an assessment to determine the extent of analyte adsorption/desorption to/from the filter.



Recommendation Box #4

How should sediment elutriates be performed?

- ➡ Combine 1 part sediment with 4 parts water unless a specific program stipulates otherwise.
- ➡ The sediment-water mixture should be vigorously shaken, bubbled or stirred for 1 hour.
- ➡ Centrifugation is a useful means for isolating the water phase (elutriate).
- ➡ Once prepared, the elutriate should be analyzed or tested as soon as possible.
- ➡ Store elutriate at 4° C with little or no headspace until analysis.
- ➡ Filtering the elutriate (to remove colloidal material) is generally not recommended. Use double (serial) centrifugation if appropriate.

CHAPTER 6 Collection of Interstitial Water

Sediment interstitial water, or pore water, is defined as the water occupying the spaces between sediment particles. Interstitial water might occupy about 50% (or more) of the volume of a depositional (silt-clay) sediment. The interstitial water is in contact with sediment surfaces for relatively long periods of time and therefore, might become contaminated due to partitioning of the contaminants from the surrounding sediments. In addition, interstitial waters might reflect ground water – surface water transition zones in upwelling or downwelling areas. In these areas their chemistry might be more reflective of ground or surface waters at the site. Therefore, flow, residence time and other physicochemical factors (e.g., pH, temperature, redox potential, organic carbon, sulfides, carbonates, mineralogy) might have varying roles in determining whether interstitial waters are contaminated.

In many depositional sediments, interstitial waters are relatively static, and therefore contaminants in the interstitial water and in the solid phase are expected to be at thermodynamic equilibrium. This makes interstitial waters useful for assessing contaminant levels and associated toxicity. Interstitial water is often isolated to provide either a matrix for toxicity testing and/or to provide an indication of the concentration and/or partitioning of contaminants within the sediment matrix.

6.1 General Procedures

Interstitial water sampling has become especially important in regulatory programs because interstitial water toxicity tests yield additional information not currently provided by solid-phase, elutriate, or sediment extract tests (Carr and Chapman, 1992; SETAC, 2001). Furthermore, interstitial water toxicity tests have proven to be useful in sediment toxicity identification evaluation (TIE) studies (e.g., Burgess et al., 1996; Carr, 1998; Burton, 2001) as test procedures and sample manipulation techniques are generally cheaper, faster, and easier to conduct than solid-phase tests (SETAC, 2001). Thus, the collection of interstitial water has become increasingly important in sediment quality monitoring and remediation programs.

Interstitial water sampling is most suitable for sediment types ranging from sandy to uncompacted silt-clays (Sarda and Burton, 1995; SETAC, 2001). Such sampling is not typically performed on sediments with coarse particle size (such as gravel) or on hard, compacted clays, as the potential for interstitial water contamination in these sediment types is relatively low.

As with all sampling discussed in this manual, the principle aim is to use procedures that minimize changes to the *in situ* condition of the water. It should be recognized that most sediment collection and processing methods have been shown to alter interstitial water chemistry (e.g., Schults et al., 1992; Bufflap and Allen, 1995; Sarda and Burton, 1995), thereby potentially altering contaminant bioavailability and toxicity.

Laboratory-based methods (e.g., centrifugation, pressurization, or suction) are commonly used as alternatives to *in-situ* interstitial water collection (see Section 6.2). While these methods have been shown to alter interstitial water chemistry, they're sometimes necessary or preferred, especially when larger sample volumes are required (e.g., for toxicity testing).

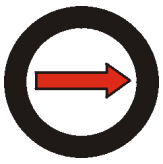
As both *in-situ* and laboratory-based or *ex-situ* (e.g., methods might be appropriate for many study objectives, ***it is critical that the same procedures are used for all stations sampled in a study, or program, so that appropriate sample comparisons can be made.*** Furthermore, the ***sediment depth at which interstitial water is sampled (either using in-situ or ex-situ extraction methods) should match the depth of interest in the study*** (SETAC, 2001). For example, samples for dredging remediation should be sampled to the depth to be disturbed by dredging activity, whereas samples for a status and trends survey should be collected at the biologically active depth (often < 15 cm). Figure 6-1 summarizes the major considerations for selecting *in-situ* or *ex-situ* procedures in a given study.

The two major issues of concern regarding interstitial water sample integrity are: 1) the ability of the sampling device to maintain physicochemical conditions in the natural state by minimizing adsorption/leaching of chemicals to/from the device, and 2) the ability to maintain the sample in the redox state existing at the site. Precautions required to reduce the likelihood of sample artifacts will vary with each study as indicated in the following sections.

6.2 *In-situ* Collection

In situ methods might be superior to *ex-situ* methods for collecting interstitial water, as they are less subject to sampling/extraction related artifacts and therefore, might be more likely to maintain the chemical integrity of the sample (Sarda and Burton, 1995; ASTM 2000a; SETAC, 2001). However, *in situ* methods have generally produced relatively small volumes of interstitial water, and often limited to wadeable or diver-accessible water depths. These logistical constraints have limited their use and applicability in sediment monitoring studies.

The principal methods for *in situ* collection of interstitial water involve either deployed "peepers" (Bufflap and Allen, 1995; Brumbaugh et al., 1994; Adams, 1991; Carignan and Lean, 1991; Carignan et al., 1985; Bottomley and Bayly, 1984) or suction techniques (Watson and Frickers, 1990; Knezovich and Harrison, 1988; Howes et al., 1985). A summary of these methods is provided in Table 6-1. Both methods have a high likelihood of maintaining *in situ* conditions. In cases where *in situ* deployment is impractical, peepers or suction devices can be placed in relatively undisturbed sediments collected by core or grab samplers (see Chapter 3).



Recommendation Box #1
In-situ interstitial water collection

- Use peepers for sampling interstitial waters, rather than (or in addition to) grab or core sediment extractions if site conditions, volume requirements, and logistical considerations allow.
- Reduce potential for oxygenation of samples by proper deployment and retrieval procedures.
- Allow adequate equilibration of peepers prior to sampling.
- Minimize handling and processing of field-collected interstitial waters.
- Field collected interstitial water samples should be stored in containers, without headspace at 4° C in the dark, until analyzed/tested. Samples for certain chemical analyses (e.g., pesticides, phenols), should be frozen or preserved immediately.

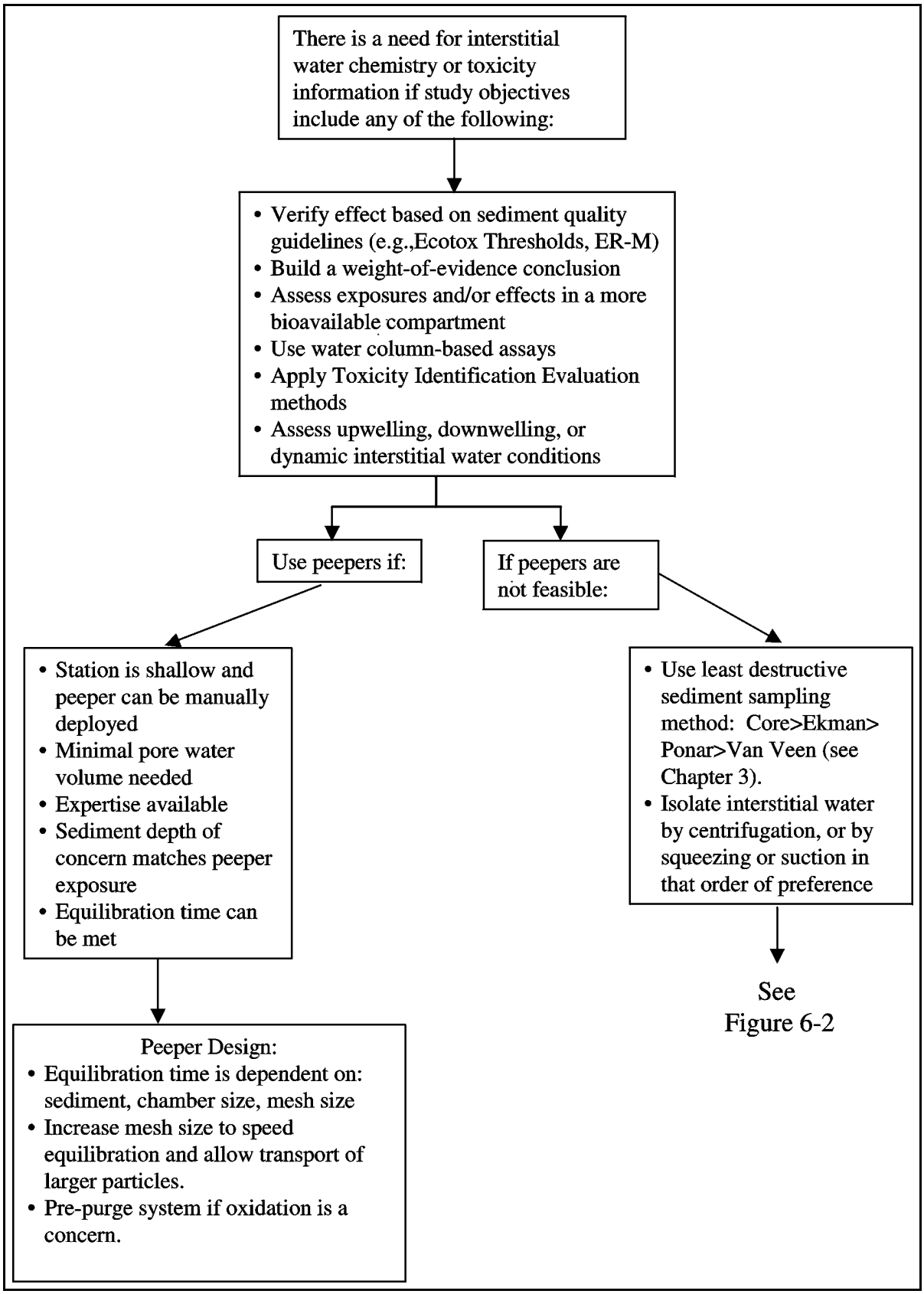
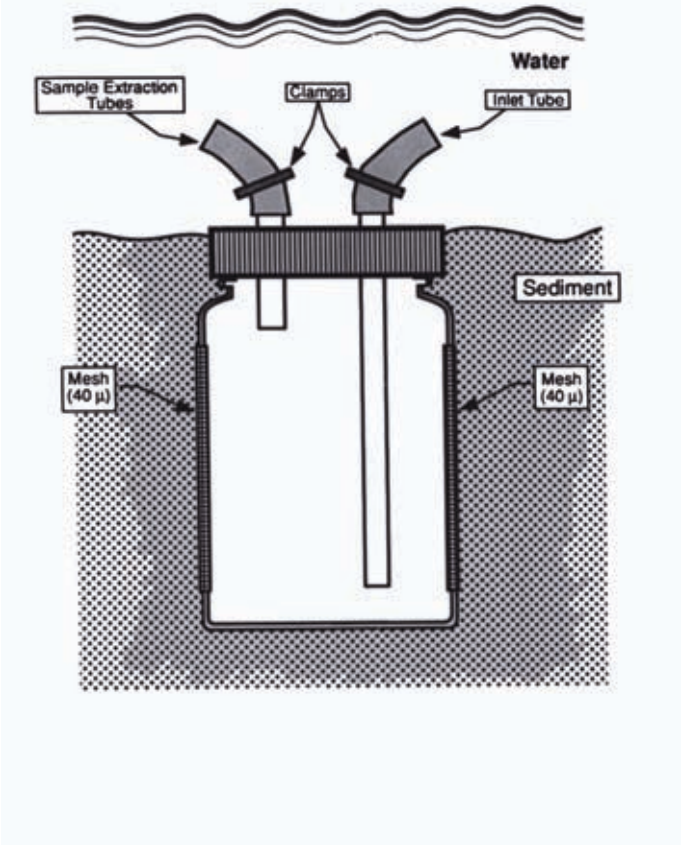


Figure 6-1. Considerations for selecting the appropriate type of interstitial water sampling method.

Photo and illustration on this page, courtesy of Allen Burton

Peepers deployed in the field



General peeper design with *in-situ* sample extraction

6.2.1 Peeper Methods

Peepers are small chambers with membrane or mesh walls containing either distilled water or clean water of the appropriate salinity or hardness. Samples are collected by burying the devices in sediments and allowing surrounding interstitial waters to infiltrate. In principle, dissolved solutes will diffuse through the porous wall into the peeper and the contained water will reach equilibrium with the ambient interstitial water. The design concept for sediment peepers originated as modifications of the dialysis bag technique used by Mayer (1976) and Hesslein (1976), and has been modified successfully for use in laboratory sediment toxicity tests (Doig and Liber, 2000). The initial designs consisted of either a flat base plate or a cylindrical dialysis probe (Bottomley and Bayly, 1984) with compartments covered by dialysis membranes and a manifold for collection of multiple samples at various depths in the sediment profile (Figure 6-2). Further modifications to these designs have incorporated sampling ports, large sample compartments, and various types of membranes with different pore sizes. These modifications are usually required based on specific project objectives regarding sample volumes and contaminants of interest.

Table 6-1. *In-situ* interstitial water collection methods (Sarda and Burton, 1995; SETAC, 2001).

Device	Sediment Depth (cm)	Sample Volume (L^3)	Advantages	Disadvantages
Peeper	0.2 - 10	≤ 0.5	Most accurate method, reduced artifacts, no lab processing; relatively free of effects from temperature, oxidation, and pressure; inexpensive and easy to construct; some selectivity possible depending on nature of sample via specific membranes; wide range of membrane/mesh pore sizes, and/or internal solutes or substrates available.	Requires deployment by hand, thus requiring diving in > 0.6 m depth water; requires hours to days for equilibration (varies with site and chamber); methods not standardized and used infrequently; some membranes such as dialysis/cellulose are subject to biofouling; must deoxygenate chamber and materials to prevent oxidation effects; some construction materials yield chemical artifacts; some chambers only allow small sample volumes; care must be used on collection to prevent sample oxidation.
In situ Suction	0.2 - 30	≤ 0.25	Reduced artifacts, gradient definition; rapid collection, no lab processing; closed system which prevents contamination; methods include airstone, syringes, probes, and core-type samplers.	Requires custom, non-standard collection devices; small volumes; limited to softer sediments; core airstone method; difficult in some sediments and in deeper water (>1 m); method might require diving for deployment in deep waters; methods used infrequently and by limited number of laboratories.

Note: Incorporation of filtration into any collection method might result in loss of metal and organic compounds.

Various peeper devices have been recently used effectively to collect interstitial water. For example, a simplified design using a 1 µm polycarbonate membrane over the opening of a polyethylene vial was successful in capturing elevated levels of copper and zinc (Brumbaugh et al., 1994). Other

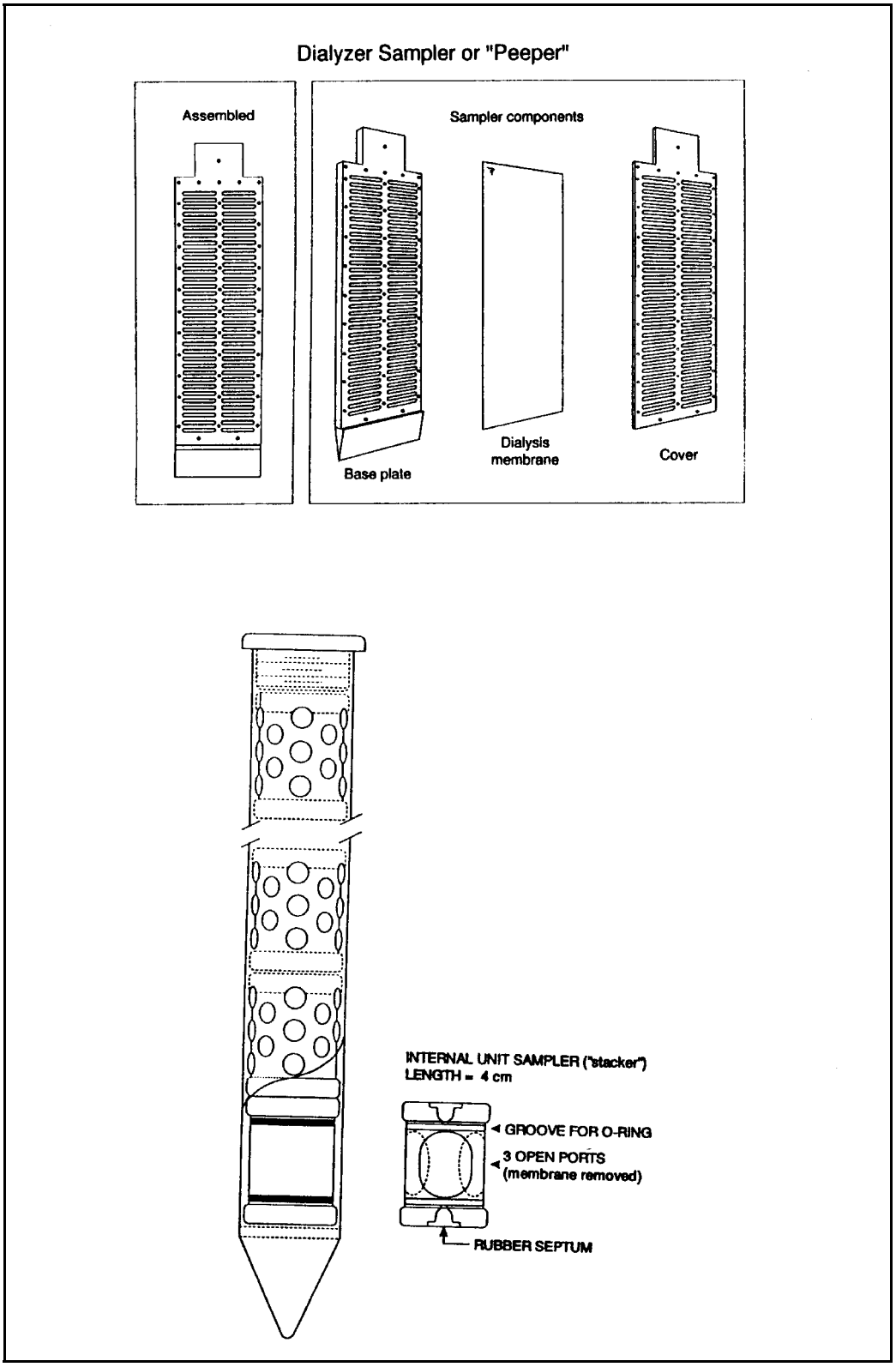


Figure 6-2. Front view and components of peeper sampling devices (top: plate device; bottom: cylindrical probe)

designs have been used to collect nonpolar organic compounds in a variety of aquatic systems (Bennett et al., 1996; Axelman et al., 1999) and in overlying water (Huckins et al., 1990).

Peepers have also been used to expose organisms to sediments *in situ* (Burton et al., 2001). Burton et al. (1999) successfully introduced organisms to aerobic sediments using peepers. However, anoxic sediments are not amenable to *in situ* organism exposure.

Different materials might be advisable in constructing peepers depending on the contaminants of concern. For example, for many contaminants, peepers constructed from acrylic material appear to yield interstitial water samples with minimal chemical artifacts (Burton et al., 2001). Some polymer materials might be inappropriate for studies of certain nonpolar organic compounds. Cellulose membranes are also unsuitable, as they decompose too quickly. Plastic samplers can contaminate anoxic sediments with diffusible oxygen (Carignan et al., 1994).

In preparation for interstitial water collection, peeper chambers should be filled with deoxygenated water, which can be prepared by nitrogen purging for 24 hours prior to insertion. If sediment oxidation is a concern, the peepers should be transported to the deployment site in a sealed oxygen-free water bath to avoid potential changes to the sediment-water equilibrium caused by dissolved oxygen interactions. However, during peeper equilibration periods, anoxic conditions are likely to be quickly reestablished. In addition, when samples are collected and processed, exposure to oxygen should be minimized.

Following initial placement, the equilibration time for peepers may range from hours to a month, but a deployment period of one to two weeks is most often used (Adams, 1991; Call et al., 1999; Steward and Malley, 1999). Equilibration time is a function of sediment type, study objectives, contaminants of concern, and temperature (e.g., Skalski and Burton, 1991; Carr et al., 1989; Howes et al., 1985; Simon et al., 1985; Mayer, 1976). Membrane pore size also affects equilibration time, with larger pore sizes being used to achieve reduced equilibration times (Sarda and Burton, 1995). For example, using a peeper with a 149-µm pore size, Adams (1991) reported equilibration of conductivity within hours of peeper insertion into the sediment. Thus, it appears that equilibration time is a function of the type of contaminant, sediment type, peeper volume, and mesh pore size.

Peepers with large-pored membranes, while shortening equilibration time, also allow particulates to enter the chamber. The larger solids tend to settle to the bottom of the peeper chamber, and caution should be used to avoid collecting the solids when retrieving the water sample from the chamber. Colloidal particles will remain suspended in the sample and thereby present an artifact, but the concentration of such particles is typically lower than that found in laboratory- centrifuged samples (Chin and Gschwend, 1991).

In several studies, analysis of interstitial water from replicate peepers has demonstrated from low to high heterogeneity in water quality characteristics (Frazier et al., 1996; Sarda and Burton, 1995). The potential for high variability in interstitial water chemical characteristics should be taken into account when developing the sampling design.

6.2.2 Suction Methods

There are a variety of suction devices for collecting interstitial water. A typical suction device consists of a syringe or tube of varying length, with one or more ports located at the desired sampling positions (ASTM, 2000a). The device is inserted into the sediment to the desired depth and a manual, spring-operated, or vacuum gas suction is applied to directly retrieve the water sample. A

variation on this approach employs a peeper-like porous cup or perforated tube with filters. The unit is inserted into the sediment for a period of time, allowing interstitial water to infiltrate the chamber before suction is applied. The samples are then retrieved by suction. Another variation that has been used successfully employs an airstone embedded into the sediment which forces interstitial water upward where it can be collected via syringe or tube. All of these suction methods generally yield smaller quantities of interstitial water than peepers and chemical (toxicological) artifacts are more likely due to greater potential exposure of interstitial water to oxygen (ASTM, 2000a).

6.2.3 Processing of Field-Collected Interstitial Water Sample

Following sample retrieval, interstitial water might need to be recovered and stabilized quickly to prevent oxidative changes or volatilization (Carignan, 1984). Containers should be filled, with no headspace to minimize changes in dissolved oxygen and contaminant bioavailability. Procedures for stabilization are dependent on the analyses to be performed. When non-volatile compounds are the target analytes, acidification is often stipulated, while organic carbon and methane may be stabilized with saturated mercury chloride (Mudroch and MacKnight, 1994).

Samples to be analyzed for toxicity, are normally cooled to 4° C as soon as possible for transport to the laboratory. EPA methods for toxicity testing of surface waters and effluents (USEPA 1991) recommend that samples not be frozen in storage or transport. However, recent information suggests that freezing of interstitial water may not affect toxicity in some cases (Ho et al., 1997; Carr and Chapman, 1995; SETAC, 2001). Unless a demonstration of acceptability is made for the sites of interest, interstitial water samples should not be frozen prior to biological testing. Samples for chemical analyses should be preserved immediately, if appropriate, or cooled to 4° C as soon as possible.

6.3 *Ex-situ* Extraction of Interstitial Water

Ex-situ interstitial water collection methods are often necessary when relatively large volumes of interstitial water are required (such as for toxicity testing), when *in-situ* collection is not viable or when a brief sampling time is critical. While these extraction methods can be done in the field or in the laboratory, extraction in the laboratory, just prior to analysis or testing, is preferable so that the sample is maintained as close to its original state as much as possible during transport and storage (SETAC, 2001). Guidance in this chapter reflects recommendations presented in several recent publications including proceedings from two workshops devoted entirely to interstitial water extraction methods, water handling, and use in toxicity applications: (1) a dredged materials management program workshop on interstitial water extraction methods and sample storage in relation to tributyltin analysis (Hoffman, 1998) and (2) a Pellston workshop on interstitial water toxicity testing including interstitial water extraction methods and applications (SETAC, 2001). Figure 6-3 summarizes many of the issues associated with laboratory isolation of interstitial water discussed in this section.

6.3.1 General Procedures

Centrifugation and squeezing are the two most common techniques for collecting interstitial water, and are generally preferred when large volumes are required. Other methods include pressurization (e.g., vacuum filtration) devices, which can be used to recover small volumes of interstitial water.

Regardless of the method used, interstitial water should be preserved immediately for chemical analyses, if appropriate, or analyzed as soon as possible after sample collection if unpreserved (such as for toxicity testing; Hoffman, 1998; SETAC, 2001). Significant chemical changes can occur even

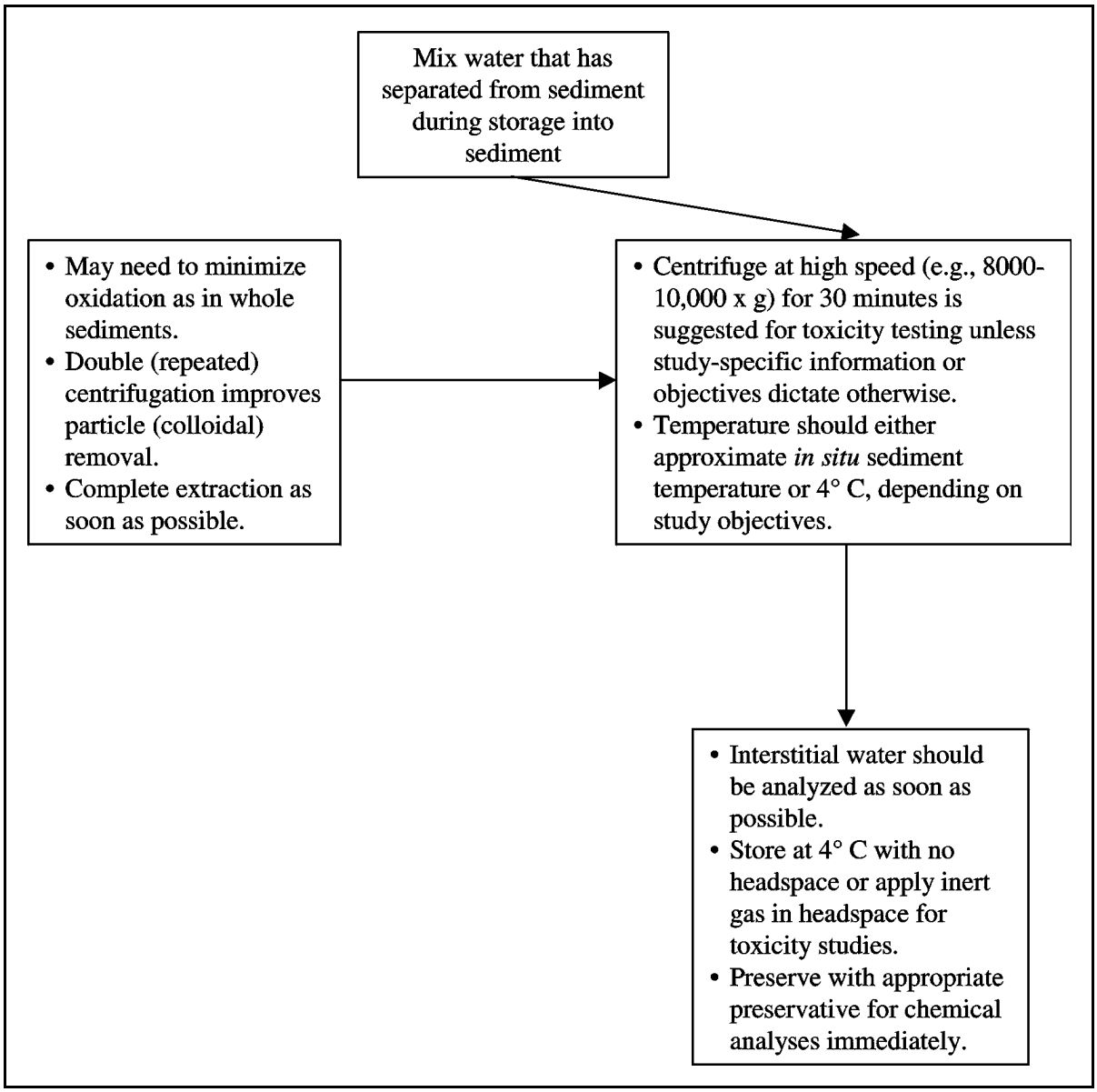


Figure 6-3. Summary of recommended procedures and considerations for laboratory isolation of interstitial water*

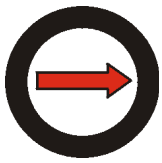
**Note: Emphasis should be placed on minimizing the duration of all sample manipulations whenever possible*

when interstitial water is stored for periods as short as 24 h (Hulbert and Brindle, 1975; Watson et al., 1985; Kemble et al., 1999; Sarda and Burton, 1995; SETAC, 2001).

If sediments are anoxic, as most depositional sediments are, sample processing, including mixing of interstitial water that has separated from the sediment, should be conducted in an inert atmosphere or with minimal atmospheric contact. Exposure to air can result in oxidation of contaminants, thereby altering bioavailability (Bray et al., 1973; Lyons et al., 1979; Howes et al., 1985). Air exposure can also result in loss of volatile sulfides, which might increase the availability of sulfide-bound metals (Allen et al., 1993; Bufflap and Allen, 1995). In addition, iron and manganese oxyhydroxides are quickly formed upon exposure to air. These compounds readily complex with trace metals, thus

altering metals-related toxicity (Bray et al., 1973; Troup et al., 1974; Burton, 1991; Bufflap and Allen, 1995). Maintaining anoxic processing conditions is not necessary when study objectives are concerned with exposures to aerobic sediments, or if target contaminants are unaffected by oxidation in short-term toxicity or bioaccumulation testing.

Interstitial water filtration should be avoided (SETAC, 2001). Numerous studies have shown that filters reduce toxicity and contaminant concentrations by retaining contaminant-associated particles and also by contaminant sorption onto the filter matrix (Bray et al., 1973; Troup et al., 1974; Sasson-Brickson and Burton, 1991; Schults et al., 1992). If filtration is stipulated by a test method, treated filters (e.g., pre-soaked in distilled, deionized water, or combusted at 400° C overnight for glass fiber filters) should be used, and an unfiltered sample should also be tested for toxicity and contaminant concentrations. The characteristics of filters and the filtering apparatus should also be carefully considered, as different filters have different sorptive capacities for different contaminants.



Recommendation Box #2
Extraction of interstitial water

- ➡ Centrifugation is the generally preferred laboratory method for the extraction of interstitial water.
- ➡ Extraction of interstitial water should be completed as soon as possible.
- ➡ Interstitial water that has accumulated on the surface of the homogenized sediment sample should be mixed into the sediment before the sample is partitioned among centrifuge bottles.
- ➡ Unless other program-specific guidance is available, sediments should be centrifuged at high speed (e.g., 8000-10,000 x g) for 30 minutes.
- ➡ Unless site-specific information suggests otherwise, centrifuging should be at 4° C to minimize temperature-mediated biological and chemical processes.
- ➡ Interstitial water should be preserved immediately for chemical analyses or analyzed as soon as possible after extraction, unpreserved. For toxicity testing, interstitial water should be stored at 4° C for not longer than 24 hours, unless the test method dictates otherwise.
- ➡ Filtration should be avoided unless required by a test method because it might reduce interstitial water toxicity. Double (serial) centrifugation (low speed followed by high speed) should be used instead.
- ➡ If filtering is required by a test method, pre-treated filters should be used to reduce potential contamination.

6.3.2 Centrifugation

Centrifugation is the generally preferred laboratory method for collection of interstitial water (SETAC, 2001). It is a relatively simple procedure that allows rapid collection of large volumes of interstitial water. It also facilitates the maintenance of anoxic conditions (if required). However, centrifugation, like other *ex-situ* procedures might yield chemical and/or toxicological artifacts due to

the extraction procedures themselves, which might alter the natural equilibrium between interstitial water and sediment.

Prior to centrifugation, the sediment sample is homogenized (see Section 4.3) and partitioned among centrifuge bottles. If the homogenized sample is stored prior to centrifugation, interstitial water might accumulate on the surface of the sediment. This overlying water should be mixed into the sediment before subsampling for centrifugation. Samples are then partitioned among centrifuge bottles. In general, approximately 50% of sediment moisture content can be extracted as interstitial water. If interstitial water volume requirements are lower, smaller sediment subsamples may be used.

For more information about centrifugation:

Interstitial waters have been isolated over a range of centrifugal forces and durations (Landrum et al., 1987; Giesy et al., 1988; Schults et al., 1992; Burgess et al., 1993; Ankley et al., 1990; Schubauer-Berigan and Ankley, 1991; Ankley and Schubauer-Berigan, 1994). For toxicity testing of interstitial waters, some sources recommend that sediments be centrifuged at 10,000 x g for a 30 min period (ASTM, 2000a; Environment Canada, 1994). Such high speed centrifugation is often necessary to remove most colloids and dispersible clays (Adams, 1991; Chin and Gschwend, 1991; Brownawell and Farrington, 1986; Ankley and Schubauer-Berigan, 1994), which can introduce interferences to chemical or toxicological analysis. However, such high speed centrifuges are not commonly available. Furthermore, many materials (glass, plastic) are not able to withstand high centrifugation speeds. Finally, it should be noted that toxicity is typically reduced with high speed centrifugation due to the removal of particle-associated contaminants (Sasson-Brickson and Burton 1991; Schults et al., 1992; Ankley and Schubauer-Berigan, 1994; Bufflap and Allen, 1995).

Based on research to date, both slower and faster centrifugation speeds (and associated differences in colloid/suspended solids removal) may be appropriate depending on the study objectives. For many programs that are interested in characterizing site toxicity, high speed centrifugation may not be appropriate because one is interested in toxicity potential of the interstitial water in its entirety (i.e., including colloidal material). However, if one is interested in comparing interstitial water contaminant concentrations to specific sediment quality values, or model exposure compartments for example (EPRI, 2000), then high speed centrifugation might be necessary. As our knowledge is still limited in this area, it is perhaps most important to note that centrifugation speed often has a dramatic effect on observed sample toxicity and chemical characteristics. Therefore, in any sediment monitoring study, ***one centrifugation protocol (including speed and time) should be identified and used throughout for all samples***.

Centrifugation has been performed at various temperatures. ASTM (2000a) recommends that the centrifugation temperature reflect the *in situ* sediment temperature to ensure that the equilibrium between the particulate and interstitial water is not altered. Alternatively, a temperature of 4° C may be preferred to minimize temperature-mediated chemical and biological processes (Environment Canada, 1994).

When centrifuging coarse sand, it might be desirable to use a modified centrifuge bottle to aid interstitial water recovery (USEPA/ACOE, 1998). The modified bottle is equipped with an internal filter that can recover 75% of the interstitial water, as compared to 25 - 30% recovery from squeezing (Saager *et al*., 1990).

As discussed in Section 4.2, all containers have limitations with regards to adsorption or leaching of chemicals, ease of use, and reliability. For example, polytetrafluororthylene (PTF) bottles have been used successfully up to 2500 x g when filled to 80% of capacity, but collapse at 3000 g (Burgess et al., 1993). Polycarbonate bottles have been used successfully for tributytin analyses in interstitial water (Hoffman, 1998). If small volumes of water are required for testing, higher speed centrifugation can be performed with glass tubes (up to 10,000 g, Word et al., 1987). Larger glass tubes, however, can not be centrifuged at such high speeds. If metal toxicity is not a concern, then high speed centrifugation in larger stainless steel centrifuge tubes is suitable. If test samples are contaminated with photoreactive compounds such as PAHs, exposure of the sample to light should be minimized to limit degradation or alteration of potentially toxic compounds. This can be accomplished by using reduced lighting.

6.3.3 Sediment Squeezing

Isolation of interstitial water by squeezing has been performed using a variety of procedures and devices (Reeburgh, 1967; Kalil and Goldhaker, 1973; Jahnke, 1988; Carr et al., 1989; Long et al., 1990; Watson and Frickers, 1990; Adams, 1991; Carr and Chapman, 1995; Carr, 1998). Inexpensive low pressure mechanical squeezers can be constructed, and may provide specialized capacities such as collection of interstitial water profiles from core samples (Bender, *et al*, 1987). In all cases, the interstitial water is passed through a filter that is a part of the squeezing apparatus.

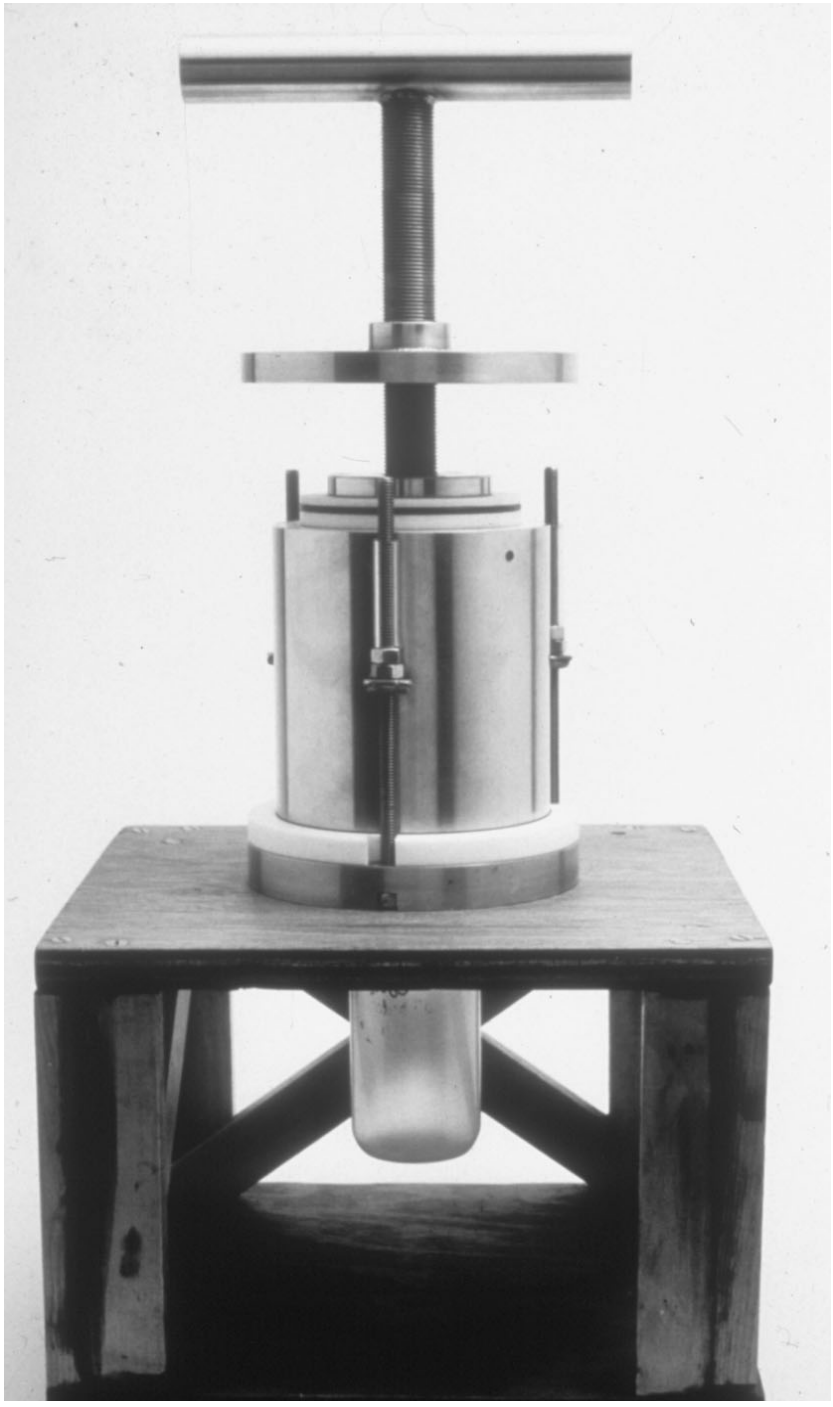
Squeezing has been shown to produce a number of artifacts due to shifts in equilibrium from pressure, temperature, and gradient changes (e.g., Froelich et al., 1979; Kriukov and Manheim, 1982; Bollinger et al., 1992; Schults, 1992). Squeezing can affect the electrolyte concentration in the interstitial water particularly with a decrease in chemical concentrations near the end of the squeezing process. However, others reported that squeezing did not produce artifacts in interstitial water toxicity studies (Carr and Chapman, 1995; Carr, 1998; SETAC, 2001). It is therefore recommended that if squeezing is performed, moderate pressures be applied along with electrolyte (conductivity) monitoring during extraction (Kriukov and Manheim, 1982). Squeezing should also be performed at *in situ* ambient temperatures, as significant alterations to interstitial water composition can occur when squeezing is conducted at temperatures different from ambient conditions (e.g., Mangelsdorf et al., 1969; Bischoff et al., 1970; Sayles et al., 1973).

Other sources of interstitial water alteration during squeezing are: contamination from overlying water; internal mixing of interstitial water during extrusion; and solid-solution reactions as interstitial water is expressed through the overlying sediment. As interstitial waters are displaced into upper sediment zones, they come in contact with solids with which they are not in equilibrium. This inter-mixing causes solid-solution reactions to occur. Most interstitial water chemical species are rapidly transformed, as observed with ammonia and trace metals (Rosenfield, 1979; Santschi et al., 1997). Bollinger et al. (1992) found elevated levels of several ions and dissolved organic carbon in squeezed samples as compared to samples collected by *in situ* peepers. The magnitude of the artifact will depend on the pollutant sediment characteristics and redox potential.

6.3.4 Pressurized and Vacuum Devices

Other methods for extraction of interstitial water from sediment samples can include vacuum filtration (Jenne and Zachara, 1987; Knezovich and Harrison, 1987; Winger and Lasier, 1991), gas pressurization (Reeburgh, 1967), and displacement (Adams, 1991). These methods typically recover only small volumes of interstitial water and are not commonly used.

Photo courtesy of Allen Burton



Sediment squeezing apparatus for extracting interstitial water

Use of a hand vacuum with an aquarium stone is an effective vacuum filtration method (Winger and Lasier, 1991; Sarda and Burton, 1995). The procedure typically involves attaching the air stone to a 50 mL syringe via plastic tubing, inserting it into the sediment to the desired depth, and then applying suction. This method can recover relatively large volumes of interstitial water; Santschi et al. (1997) used this procedure to extract up to 1,500 mL from 4 L of sediment. Sarda and Burton (1995) found that ammonia concentrations in water obtained by this procedure were similar to those collected by *in situ* peepers. Drawbacks to this method include loss of equilibrium between the interstitial water and the solids, filter clogging, and oxidation (Brinkman et al., 1982).

CHAPTER 7 Quality Assurance and Quality Control

7.1 General Procedures

Quality assurance activities provide a formalized system for evaluating the technical adequacy of sample collection and laboratory analysis activities. These quality assurance activities begin before samples are collected and continue after laboratory analyses are completed, requiring ongoing coordination and oversight. The quality assurance program should integrate management and technical practices into a single system to provide data that are sufficient, appropriate, and of known and documented quality.

Checklist

QA practices within a laboratory should address all activities that affect the quality of the final data, such as

- ✓ sediment sampling and handling
- ✓ condition and operation of equipment
- ✓ instrument calibration
- ✓ replication
- ✓ use of standards
- ✓ record keeping
- ✓ data evaluation

Developing and maintaining a quality assurance (QA) program requires an ongoing commitment by project management and also includes the following: (1) appointment of a quality assurance officer with the responsibility and authority to develop and maintain a QA program, (2) preparation of a Quality Assurance Project Plan with Data Quality Objectives, (3) preparation of written descriptions of Standard Operating Procedures (SOPs) for sediment sampling and manipulations, instrument calibration, sample chain-of-custody, laboratory sample tracking system, and (4) provision of adequate, qualified technical staff and suitable space and equipment to assure reliable data. Program specific guidance for developing and maintaining a QA program should be followed as appropriate. Examples of program guidance for developing a quality assurance program can be found in USEPA (1994; 1995; 2000d), PSEP (1997a), WDE (1995), and USEPA/ACOE (1991, 1998).

Quality control (QC) practices consist of more focused, routine, day-to-day activities carried out within the scope of the overall QA program. QC is the routine application of procedures for obtaining data that are accurate (precise and unbiased), representative, comparable, and complete. QC procedures include activities such as identification of sampling and analytical methods, calibration and standardization, and sample custody and record keeping. Audits, reviews, and complete and thorough documentation are used to verify compliance with predefined QC procedures. Project-specific QA plans (QAPP; see Section 7.3 below) provide a detailed plan for activities performed at each stage of the study and outline the data quality objectives that should be achieved. Through periodic reporting, QA activities provide a means to track progress and milestones, performance of measurement systems, and data quality. A complete project-specific QA/QC effort has two major components: a QA program implemented by the responsible agency (i.e., the data

user) and QC programs implements by the parties responsible for collection and analyses (i.e., the data generators).

7.2 QA/QC Procedures for Sediment Collection and Manipulation

To ensure the appropriateness of the sample collection protocol for sample integrity and data of suitable quality, a program of scheduled field QC samples, such as field replicates (duplicates, splits, field spikes), field blanks (rinsate equipment), bottle, trip, and background (upgradient) samples is critical. All field QC samples should be handled exactly as the sediment samples and should be treated as blind samples so as to minimize bias in the analysis. A random portion of the samples should also be analyzed by a third party to evaluate the primary laboratory's performance. QC replicates (duplicates, splits) should be collected for analysis by the primary laboratory to determine analytical variability (USEPA 1995).

Checklist

QA/QC procedures for sample collection should include the following principal elements:

- ✓ implementing a sound sampling approach based on the intended use of the data.
- ✓ use of sampling methodologies which allow the collection of representative samples based upon data needs.
- ✓ use of sampling devices that minimize the disturbance or alteration to the media's chemical composition.
- ✓ employing decontamination procedures which reduce cross-contamination potential between sampling points.
- ✓ use of proper sample containers and preservation techniques that maximize the integrity of samples.

The procedures for sediment manipulations described in Chapter 4 should maintain the sample in a chemical condition as similar as possible to that at the time of collection. QA procedures are established to assure that SOPs are followed and that contamination is neither introduced to nor lost from the manipulated sample. For example, samples to be analyzed for trace metals should not come in contact with metal surfaces (except stainless steel). Sample tracking sheets should document date, time, and investigator related to removal and replacement of samples from storage. Specific manipulation procedures should follow established SOPs that minimize chemical alteration of the sample (excepting chemical spiking), maintain sediment physical properties, and include replication and blank samples.

7.3 The Quality Assurance Project Plan (QAPP)

The Quality Assurance Project Plan (QAPP) is a project-specific document that specifies the data quality and quantity requirements needed for the study as well as all procedures that will be used to collect, analyze, and report those data.

The QAPP uses input from the sampling design derived from the Data Quality Objectives Process (see Chapter 2 specifically Measurement Quality Objectives discussion, Section 2.4, and USEPA, 2000a) to specify the above elements. This Plan should be reviewed by an independent person (e.g., quality assurance officer or staff member not involved in the project directly) for accuracy and completeness. A key element of a QAPP is Standard Operating Procedures (see Section 7.4). Further information on preparing a QAPP and resources necessary can be found in USEPA (2000e).

7.4 Standard Operating Procedures

Standard operating procedures are written descriptions of routine methods and should be provided for all methods used. A large number of field and laboratory operations can be standardized and presented as standard operating procedures. General types of procedures that benefit from standard operating procedures include field measurements ancillary to sample collection (e.g., water quality measurements or mixing model input measurements); chain-of-custody, sample handling, and shipment; and routine analytical methods for chemical analyses and toxicological 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 might affect data quality and integrity. If it is necessary to deviate from approved standard operating procedures, these deviations must be documented and approved through an appropriate chain-of-command.

7.5 Sediment Sample Documentation

Bound field logbooks should be used for the maintenance of field records. All entries should be dated and time of entry recorded. All aspects of sample collection and handling as well as visual observations should be documented in the field logbooks. Documentation should be recorded in pre-numbered bound notebooks using indelible ink pens in sufficient detail so that decision logic may be traced back, once reviewed.

Checklist

Quality Assurance Project Plans vary in content depending on program needs, but should address the following elements:

- ✓ a description of the project organization and responsibilities
- ✓ definition of data quality objectives (see Section 2.1)
- ✓ sampling, analysis, and measurement procedures
- ✓ instrument calibration procedures
- ✓ procedures for recording, reducing, validating, and reporting data
- ✓ procedures for performing quality assurance verification and internal quality control checks
- ✓ preventive maintenance schedules
- ✓ specific routine procedures to evaluate precision, accuracy, and completeness
- ✓ definitions of deviations and appropriate corrective actions
- ✓ information on appropriate training

Proper field sheet, sample labeling, chain-of-custody, and sample tracking documentation should be maintained as appropriate. Specific details concerning sample documentation and sample management should be included in planning documents and reviewed by the sampling team prior to initializing the sampling program.

7.6 Sample Tracking Documentation

Samples delivered to the laboratory should be accompanied by a chain-of-custody record that includes the name of the study, location of collection, date and time of collection, type of sample, sample name or number, number of containers, analysis required, and the collector's signatures. When turning over possession of samples, the relinquisher and the receiver sign, date and record the time on the record sheet. The record sheet allows the transfer of a group of samples at one time. When the laboratory takes possession of the samples, each should be assigned a unique laboratory identification designation. This assures a consistent system for tracking within the laboratory. If the samples arrive at the laboratory when designated personnel are not there to receive them, the samples are put into a secure location and the transfer is conducted when the appropriate personnel are present.

Upon arrival at the laboratory, samples are inspected for condition and temperature, and sample container labels are verified against the chain-of-custody record or sample tracking form. Sample information is entered on a laboratory log-in data sheets used to maintain information regarding sample: receipt, shipping, collection date, and storage. To allow for accurate identification of samples, information contained on sample tracking forms must match identically with information contained on the sample container labels. The tracking form lists both the collector's and the laboratory's identification designations. Verified tracking forms are signed by the laboratory personnel with date and time in ink. Missing and/or compromised samples (e.g., inappropriate preservation to maintain integrity, inappropriate containers, and unlabeled or mislabeled containers) are documented on the tracking forms.

When samples are removed from storage, the sample tracking form accompanies it and documents data, time, and investigator associated with any manipulations. The manipulation type is noted on the form in detail or by reference to an approved laboratory SOP. Any deviation from the SOP are also noted. Should the sample be

Checklist
Sample documentation should include:

- ✓ project name, and analysis or test to be performed
- ✓ sampling locations
- ✓ dates and times
- ✓ sampling personnel present
- ✓ level of personal protective equipment worn
- ✓ weather or any environmental condition that might affect samples
- ✓ equipment used to collect samples, and sample container preparation
- ✓ calibration data
- ✓ deviations from approved work plans or SOPs
- ✓ sketch of sampling area
- ✓ notation of the system identifying and tracking samples
- ✓ notation of any visitors to the site
- ✓ initials and date on each page

modified in such a way that additional subsamples are created, additional tracking forms must also be created.

7.7 Record Keeping

Proper record keeping is essential to the scientific defensibility of a sediment sampling and manipulation program. A separate file should be maintained for each sampling/manipulation event or closely related events. This file should contain field logs, chain-of-custody forms, sample tracking forms, storage records, and any QA/QC documentation and records. Original documentation should be signed and dated by the originator.

7.8 QA Audits

In addition to the QA/QC procedures conducted on a routine basis, quality audits (i.e., performance and quality systems audits) might be conducted. Performance audits refer to independent checks to evaluate the quality of data produced during testing. There are three types of performance audits: sampling; test; and data processing. These audits are independent of normal quality control checks performed by the operator.

A systems audit is an on-site inspection and review of the quality assurance system. The systems audit is performed to verify that the organization is following the policies and procedures described in its QA/QC plan and in appropriate SOPs. Systems audits are performed by an auditor typically from an accrediting body.

Checklist
Performance auditing procedures are:

- ✓ sample auditing - the auditor uses a separate set of calibrated standards to check the sample collection system.
- ✓ test auditing - the auditor is provided with set of a duplicate sample or split portion.
- ✓ data processing audit - the auditor spot checks calculations or a dummy set of raw data is inserted followed by review of validated data.

7.9 Corrective Action (Management of Non-conformance Events)

The QA Officer and the responsible manager are responsible for reviewing the circumstances of all instances of occurrence of nonconformities, to determine whether corrective action should be taken. The manager is responsible for determining if new samples are required, if the customer should be notified, if additional testing is necessary, or whether the results should be confirmed. A good communication plan is invaluable in helping to identify interactions among labs, clients, and agencies during corrective actions.

Corrective action might take two forms: that of addressing technical problems associated with project activities and that of addressing QA/QC infractions based upon performance. Technical problems in meeting project objectives may range in magnitude from failure to meet minor procedural requirements, to major problems associated with inappropriate methods or data loss.

Established procedures for corrective action of minor technical problems are often included in the SOPs for cases where performance limits or acceptance criteria have been exceeded. On-the-spot corrective actions are noted on data sheets. Major or recurrent QA/QC problems which require long-term corrective action, such as modification of SOPs, are reported. Depending upon the nature and

severity of the problem, an approach might be developed. Any corrective action is documented by management.

Infractions of QA/QC policies by staff are identified and addressed by the management. Minor infractions are corrected through additional training and/or closer supervision. Major or recurrent infractions are corrected through re-assignment of technical personnel.

Corrective actions relative to sample collection and manipulation may include, but are not limited to, review of the data and calculations, flagging and/or qualification of suspect data, or possible re-sampling. A review that provides a preliminary check of all "out of limit" events is performed as soon as the data for a given parameter or test is tabulated and verified for accuracy. "Out of limit" events are flagged to determine whether new samples are required.

7.10 Data Reporting

In addition to reporting the raw data from a given sediment quality study or analysis, the data report should include additional quality assurance information to ensure the data user that sample handling and analyses are in accordance with the project plan. The quality assurance information also documents procedures taken to ensure accurate data collection. Data are to be presented electronically as well as in hardcopy for many regulatory programs. Required electronic format should be explicitly outlined as a data quality objective during the planning process.

Checklist
Quality Assurance Reporting

- ✓ A copy of the sample chain of custody record, including documentation of sample collection date and time
- ✓ Documentation of the laboratory certification number
- ✓ Documentation of the analysis method used
- ✓ Documentation of analysis date and time (or testing period in the case of toxicity tests)
- ✓ Documentation that data for spikes, duplicates, standards, etc meets laboratory QA/QC requirements for chemical analytes
- ✓ Documentation that reference toxicant test data meets laboratory QA/QC requirements for toxicity tests.
- ✓ Documentation of any deviations in sample preparation or analysis protocols

CHAPTER 8 References

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APPENDIX A

EXAMPLES OF SEDIMENT QUALITY SAMPLING DESIGNS USING THE DATA QUALITY OBJECTIVES (DQO) PROCESS

The Data Quality Objectives (DQO) process is a logical progression of steps that define the question to be answered and identifies qualitatively and quantitatively the procedures and decisions necessary to address the question posed. USEPA (2000a) discusses a 7-step DQO process that leads one through each of the decision points to help ensure a successful study or program outcome.

Sediment quality monitoring studies, whether for regulatory or non-regulatory purposes, would benefit from following USEPA's DQO process in order to:

- reduce the likelihood of collecting improper or inappropriate samples
- increase the likelihood of collecting representative samples for the question asked
- decrease the chances of introduced measurement artifacts or interference due to sampling or sample processing techniques
- increase the likelihood that data, and decisions based on those data, will be scientifically defensible and accepted by those involved.

The following tables are hypothetical examples demonstrating how the DQO process could be used in addressing a few common purposes for collecting sediment quality data. The purpose of the study, or question needing to be answered, drives the input for all subsequent steps in the DQO process. Thus, sampling design, how samples are collected and manipulated, and the types of analyses chosen, should all stem from the overall purpose of the study. Many national and regional programs (e.g., NOAA's Status and Trends, USEPA's Dredge Materials Management Program, or Puget Sound Estuary Program) already have a particular purpose identified, thus giving rise to the particular sampling protocols they each use.

Example 1. Objective: Determine whether certain point and nonpoint sources are associated with sediment contamination in a lake, estuary, or river segment

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Certain point and nonpoint sources of concern • Enough resources for a small-moderate survey depending on number of analyses per station
2. Identify questions to be addressed	• How does sediment quality near these sources compare with other locations and with Ecotox Thresholds (USEPA, 1996)? How toxic are they?
3. Identify information/ measurements needed	• Use available data, source information, BPJ to identify contaminants of concern Measurements could include the following: • 10d whole sediment toxicity tests • Acute or chronic toxicity tests using interstitial water • Benthic macroinvertebrate analyses • Contaminant analyses (e.g., PAHs, PCBs, metals, pesticides) • Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia measured for each sample • Water, pH, oxygen, conductivity/salinity overlying sediment at each site
4. Define spatial/temporal boundaries	• Sample during one index period • Surficial sediment (top 0 to 2 or up to 15 cm) of most interest • Concentrate sampling near suspected contaminant sources with some reference stations (locations removed from potential sources) as well
5. Define thresholds or decision rule for parameters of interest	• Ecotox Thresholds (USEPA, 1996), and/or other sediment threshold values for contaminants • Toxicity effect level: e.g., significantly lower survival than reference stations or survival $\leq$ 50%
6. Limits on decision errors	• Precision: $\leq$ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield $\leq$ 25% C.V. Toxicity test replicates $\leq$ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose targeted sampling design including reference stations • Sample when conditions most favorable for gear efficiency and personnel safety • Use grab sampler - Ponar, VanVeen, or Petersen (see Table E-1 for advantages and disadvantages) • Use GPS for site positioning (± 10m) • Composite several (determined by number of contaminant analyses desired) grabs at each site for a single sample • Take 3 replicate samples at 10% of the sites, selected at random • See flowchart for Selecting a Grab Sampler Based on Site-Specific Factors (Figure 3-2).

Example 2. Objective: Determine the status of sediment quality in a site (e.g., lake, estuary, or river segment)

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Sediment quality unknown or status was determined in the past and there is a need to determine how the quality may have changed. • Enough resources for a moderate survey depending on number of analyses per station.
2. Identify questions to be addressed	• How does sediment quality compare with Ecotox Thresholds (USEPA, 1996)? How toxic are sediments now as compared to historically?
3. Identify information/ measurements needed	• Use available data, source information, BPJ to identify contaminants of concern Measurements could include the following: • 10d whole sediment toxicity tests • Acute or chronic toxicity tests using interstitial water • Benthic macroinvertebrate analyses • Contaminant analyses (e.g., PAHs, PCBs, metals, pesticides) • Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia measured for each sample • Water, pH, oxygen, conductivity/salinity overlying sediment at each site
4. Define spatial/temporal boundaries	• Sample during one season (index period) • Sample surficial as well as deeper sediments to obtain historical record. • Sample stations representative of the entire site or, if site contains different subareas of interest (e.g., areas having very different salinity zones or different geology/sediment particle size), representative samples of each subarea.
5. Define thresholds or decision rule for parameters of interest	• Ecotox Thresholds (USEPA, 1996), and/or other sediment threshold values for contaminants • Toxicity effect level: e.g., significantly lower survival than reference stations or survival $\leq$ 50%
6. Limits on decision errors	• Precision: $\leq$ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield $\leq$ 25% C.V. Toxicity test replicates $\leq$ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose probabilistic sampling design; use stratified random or multi-stage random design if interested in comparing quality with respect to certain habitat features or subareas of site, respectively. • Use a corer sampler to obtain vertical (historical) profiiles of sediment at each station. Collect and analyze samples of strata of interest. Use of a larger corer (e.g., box corer) will mean fewer cores needed per station (see Table E-2 for advantages and disadvantages of different corers.) • Use GPS for station positioning ($\pm$ 10 m). • Take 3 replicates for each type of analysis at 10% of the stations. • See Flowchart for Selecting Core Samplers Based on Site-Specific Factors (Figure 3-3).

Example 3. Objective: Determine the need for or locations of site remediation (e.g., superfund)

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Site known or suspected to contain contaminated sediments that pose an ecological and/or human health risk • Resources are available for a moderate-intensive survey
2. Identify questions to be addressed	• Does the site need to be remediated? Where at the site is sediment remediation warranted?
3. Identify information/ measurements needed	• Use previously collected data, if available, to identify contaminants of concern. If no information is available, a pilot survey, using a random sampling design, may be useful to identify potential contaminants of concern. • Measurements could include: – Contaminants of concern in whole sediment and/or interstitial water – 10 d whole sediment toxicity tests – Acute or chronic interstitial water toxicity tests – Benthic macroinvertebrate analyses – Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia to help interpret chemical or toxicological data.
4. Define spatial/temporal boundaries	• Sample over one or more index periods depending on assumed or measured rates of sediment or contaminant movement. • Surficial as well as deeper sediments may need to be sampled depending on depth of contamination. • Sampling all areas of the site may be necessary to locate areas in need of remediation unless more information is available.
5. Define thresholds or decision rule for parameters of interest	• Contaminant levels exceed Ecotox Thresholds (USEPA, 1996). • Toxicity effect level: e.g., significantly lower survival than reference sediment and < 50%.
6. Limits on decision errors	• Precision: ≤ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield ≤ 25% C.V. Toxicity test replicates ≤ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose systematic or grid sampling design if no previous information available on areas of contamination. • Choose targeted design if information is already available on areas of contamination within the site. • Choose multi-stage design if more than one area of contamination within the site is known but locations of contamination within each area are not precisely known. • Use grab sampler if remediation will involve only surficial sediments, or sediment depth is known to be shallow (see Table E-1 and Figure 3-2). • Use corer if remediation is likely to involve deeper sediments. For areas in which remediation may entail very deep sediments (> 2 m), consider using a vibracorer or piston corer (see Table E-2 and the Flowchart for Selecting Core Samplers Based on Site-Specific Factors (Figure 3-3).

APPENDIX B

EXAMPLES OF MEASUREMENT QUALITY OBJECTIVES USED IN SEDIMENT QUALITY MONITORING STUDIES

In the Data Quality Objectives (DQO) framework (discussed in Chapter 2 and examples presented in Appendix A of this Manual), a key element of this process is defining the thresholds or decision rules (Step 5, Figure 2-2) and the limits on errors pertaining to those decisions (Step 6, Figure 2-2). Both of these steps are critical to the DQO process, and the success of a study, because they explicitly define whether a particular result qualifies as an effect of interest, and when and where something might need to be done to mitigate or address a given observed effect. Also, these steps are critical factors in designing a tiered or phased sampling program. Thresholds, for example, can be initially set to identify problem areas with high accuracy (low decision error). This would be followed by a second sampling, with a lower threshold, to identify emerging or more subtle problems in a cost-effective manner.

The information used to help derive meaningful threshold or decision rules, and the tolerable errors associated with those rules, is collectively referred to as Measurement Quality Objectives (MQOs). MQOs are qualitative or quantitative statements that describe the type of data quality needed to support or refute a given decision. These statements explicitly define acceptable precision, bias, and sensitivity required of all analyses in the study and therefore, should be consistent with the expected performance of a given analysis or test method (ITFM 1995). Thus, if a particular whole sediment toxicity test is expected to yield 80% survival among control replicates, the MQO for control survival should be $\geq$ 80% for that test. Further, if one intends to compare sediment toxicity results between a reference station and test stations, it is important to set the number of replicates and the decision rule appropriately so that the study can determine with reasonable power and confidence whether a given sediment sample is toxic to the test organisms. The number of replicates performed will depend on the expected variability of a given test endpoint and the sensitivity desired in the study.

The following summarizes four different examples of sediment quality studies or programs, each with a different study purpose, and the types of MQOs they used. These examples are for illustrative purposes and are not meant to imply that these are the only acceptable ways in which MQOs can be derived. The examples provided are:

- Shoreline ecology program following the Exxon Valdez oil spill in Alaska
- Great Lakes Assessment and Remediation of Contaminated Sediment (ARCS) Program
- An example of an EMAP study design in the St. Louis River, Minnesota/Wisconsin
- A focused assessment in Burlington Harbor, VT in Lake Champlain
- Excerpts from Washington Department of Ecology's Sampling and Analysis Plan Guidance (WDE, 1995).

This latter guidance demonstrates how a particular program addresses sampling and analysis needs depending on the monitoring objective. The guidance also provides an interesting comparison of overall sampling procedures and sampling design considerations for two programs: WDE's Sediment Management Standards Program and the Puget Sound Dredged Disposal Analysis Program, both of which have some common monitoring objectives.

Example 1: Shoreline Ecology Program for Prince William Sound, Alaska, Following the *Exxon Valdez* Oil Spill

Background

A comprehensive shoreline ecology program was designed to assess recovery in Prince William Sound following the *Exxon Valdez* oil spill on March 24, 1989 (Page et al., 1995a; b; Boehm et al., 1995; Gilfillan et al., 1995; Gillfillan et al., 1999). The spill resulted in the release of about 258,000 barrels of Alaska North Slope crude oil into the marine environment. Nearly 500 miles of shorelines in the sound were oiled to some degree.

Project Objectives

The shoreline ecology program was designed to assess the recovery of hundreds of miles of oiled shorelines in Prince William Sound by using a limited number of sampling stations. The number of sampling stations had to be small enough for a survey to be accomplished in the summer weather window, but large enough to detect important spill effects. The study design consisted of two field components: fixed sampling locations and stratified random sampling locations. The 12 fixed locations provided information on the changes in amount and composition of petroleum residues over the period 1989-1991 to assess the rate of shoreline recovery and oil loss. Stations chosen represented worst-case oiling conditions and reference sites. Data gathered from these sites were used to assess oil loss, oil weathering, and bioavailability of oil residues to mussel communities.

The stratified random sampling (SRS) of 64 sample locations permitted results to be generalized to the affected area of the sound. The SRS survey of the spill area shoreline was divided into four habitats which characterized over 99% of the shoreline of interest, and four oiling levels which produced information on all shoreline spill levels. The matrix of four habitats by four oiling levels, with each cell containing four replicates, constituted a reasonable compromise between project cost, the need to complete sampling within the short Alaskan summer, and the need for statistical power. The principal objective was to compare means within strata (habitat/oiling level) and not to obtain overall estimates (see Table B-1).

Specific natural variables, including wave exposure, percentage sand, percentage silt/clay, and total organic carbon (TOC) were also quantified, and served as covariates in statistical analyses of oil effects.

Precautions were taken to minimize the possibilities for petroleum hydrocarbon contamination of field samples by:

- positioning the ship's stern into the wind to prevent stack gases from blowing onto the sampling equipment during deployment, recovery, and subsampling
- cleaning equipment just prior to arriving on station
- ensuring that the sampling equipment was never deployed or recovered through oil slicks or sheens
- closing the top access doors to the sampler when it was not being deployed or cleaned
- field blanks were collected from each piece of equipment at regular intervals

- potential sources of hydrocarbon contaminants were also collected to enable their identification later

Sample documentation included station logs and chain-of-custody forms. All sediment samples were logged in on the chain-of-custody forms along with other important information (station, date, time, sampling equipment and method, subsampling method, and type of sample.) Any additional information was also noted. This form accompanied each sample during shipping to the analytical lab and each sample cooler was sealed with a custody seal which was initialed and dated by the packer.

Several analytical laboratories were needed to process and analyze the large numbers of samples collected. A laboratory standard oil was analyzed with each analytical batch to monitor analytical precision and to provide data for interlaboratory comparisons. Duplicate precision for both subtidal sediment studies and 1991 deep subtidal studies was ±30%. Other MQOs are listed in the Table B-1.

Table B-1. Measurement quality objectives for subtidal sediment studies in Prince William Sound oil spill study (Gilfillan et al. 1995).

Parameter	Subtidal Sediment Studies	1991 Deep Subtidal Studies
Units	µg/kg dry weight	µg/kg dry weight
Practical Quantification Limit (PQL)	10	1.0
Estimated Method Detection Limit (MDL)	1.0	0.1
Procedural Blank	5 x MDL	5 x MDL
Field Blank	5 x MDL	5 x MDL
Matrix Spike Recovery	40 - 120%[a]	40 - 120%[a]
Surrogate Recovery	40 - 120%[b]	40 - 120%[b]
Duplicate Precision	± 30%	± 30%
EVC Control Oil Standard Precision	± 20%	± 20%
Katalla Control Oil Standard Precision	NA	± 20%
NIST SRM 1941 Precision	NA	± 25%
NIST SRM 1291 Accuracy	NA	± 15%

[a] The average percentage recoveries for all 16 compounds must fall between 40 and 120%. Only one compound can be below its minimum percentage recovery. This allowed a deviation for a single analyte of not less than 10% for chrysene and benzo(a) pyrene and not less than 20% for the others.

[b] Surrogate recoveries must fall between 40 and 120%. The upper control limit may be exceeded by one compound.

[c] The average percentage difference for the target compounds should not exceed 20% of the mean of all previous values, and no single compound/isomer grouping should deviate by more than 30% of its mean value of all previous determinations.

[d] SRM = Standard reference material.

Example 2: Measurement Quality Objectives used in the Great Lakes Assessment and Remediation of Contaminated Sediment (ARCS) Program

Background

Although toxic discharges into the Great Lakes and elsewhere have been reduced in the last 20 years, persistent contaminants in sediments continue to pose a potential risk to human health and the environment (GLNPO 1994). Elevated concentrations of contaminants in bottom sediments and associated adverse effects have been found throughout the Great Lakes and connecting channels. The extent of sediment contamination and its associated adverse effects have been the subject of considerable concern and study in the Great Lakes community.

To address these concerns, Annex 14 of the Great Lakes Water Quality Agreement between the United States and Canada (as amended by the 1987 Protocol) stipulates that the cooperating parties will identify the nature and extent of sediment contamination in the Great Lakes, develop methods to assess impacts, and evaluate the technological capability of programs to remedy such contamination. The 1987 amendments to the Clean Water Act, authorized GLNPO to coordinate and conduct a 5-year study and demonstration projects relating to the appropriate treatment of toxic contaminants in bottom sediments. To fulfill the requirements of the Act, GLNPO initiated the Assessment and Remediation of Contaminated Sediments (ARCS) Program. ARCS is an integrated program for the development and testing of assessment techniques and remedial action alternatives for contaminated sediments. Information from ARCS Program activities will help address contaminated sediment concerns in the development of Remedial Action Plans (RAPs) for all 43 Great Lakes Areas of Concern (AOCs, as identified by the United States and Canadian governments), as well as similar concerns in the development of Lakewide Management Plans.

Program Objectives

Sediments are associated with impairment of beneficial uses at 42 of the 43 Great Lakes AOCs. Prior to addressing the potential need for remediation of those sediments, the following questions are addressed:

- Are the sediments sufficiently “contaminated” to warrant consideration for remediation? In this context, “contaminated” refers to the presence of chemicals in the sediments that have the potential to cause adverse effects in humans or ecological receptors.

- Is there evidence indicating that existing concentrations of sediment contaminants are adversely affecting ecological receptors? In other words, can it be shown that the presence of contaminants in the sediments is causing adverse effects in organisms, either organisms naturally occurring in the environment, or those exposed to sediments in controlled, laboratory toxicity tests?

- Are ecological receptors exposed to the sediments bioaccumulating chemical contaminants to the extent that the resultant body burdens are adversely affecting the organisms themselves or other organisms higher in the food chain, including humans?

- If the sediments are judged to be sufficiently contaminated to be causing such effects, what is the spatial extent (i.e., both horizontal and vertical) of the contamination, and what are the implications of the distribution of contaminants on possible remedial alternatives?

Early in the ARCS Program, it was recognized that the current state of sediment assessment methods was rapidly evolving. The sediment assessment methods currently available consider a wide variety of endpoints and effects, which differ in their suitability and sensitivity for investigating sediment contamination. Therefore, assessment methods selected in the ARCS Program, reflect site- and program-specific objectives of the study being conducted.

The ARCS Program developed several measurement quality objectives (MQOs) that it uses in the design and conduct of studies at AOCs. Table B-2 summarizes these MQOs.

Table B-2. Examples of the measurement quality objectives for inorganic and organic chemistry analyses of sediment used by the ARCS program in the Great Lakes (GLNPO, 1994).

Parameter	MDL[a] (µg/kg)	Accuracy[b]	Frequency	Precision[c]	Frequency [d]
Total organic carbon	0.03%	± 20 percent	1/batch[d]	≤ 20 percent	1/batch
Oil and grease	10,000	± 20 percent	1/batch	≤ 20 percent	1/batch
pH	N/A	± 0.1 unit	1/batch	± 0.1 unit	1/batch
Acid-volatile sulfides	1,000	N/A	N/A	≤ 20 percent	1/batch
Organohalogens[e]	0.03	± 20 percent	1/batch	≤ 20 percent	1/batch
Total sulfur	10,000	± 20 percent	1/batch	≤ 20 percent	1/batch
Total solids	1,000	N/A	N/A	≤ 20 percent	1/batch
Volatile solids	2,000	N/A	N/A	≤ 20 percent	1/batch
Particle size[f]	1,000	windows	1/batch	≤ 20 percent	1/batch
Solvent extractable residue	1,000	± 20 percent	1/batch	≤ 20 percent	1/batch
Moisture content	1,000	N/A	N/A	≤ 20 percent	1/batch
PAHs	200	± 20 percent	1/batch	≤ 20 percent	1/batch
Pesticides	10	± 20 percent	1/batch	≤ 20 percent	1/batch
PCB/congener	0.5	± 20 percent	1/batch	≤ 20 percent	1/batch
PCB/Aroclor®	20	± 20 percent	1/batch	≤ 20 percent	1/batch
PCDDs/PCDFs	0.002	± 20 percent	1/batch	≤ 20 percent	1/batch
Methylmercury	10	± 20 percent	1/batch	≤ 20 percent	1/batch
Tributyltin	10	± 20 percent	1/batch	≤ 20 percent	1/batch
Metals[g]	2,000	± 20 percent	1/batch	≤ 20 percent	1/batch

Table B-2 (continued). Examples of the measurement quality objectives for inorganic and organic chemistry analyses of sediment used by the ARCS program (GLNPO, 1994).

Parameter	MDL[a] (µg/kg)	Accuracy[b]	Frequency	Precision[c]	Frequency
Except:					
Arsenic	100	± 20 percent	1/batch	≤ 20 percent	1/batch
Cadmium	100	± 20 percent	1/batch	≤ 20 percent	1/batch
Mercury	100	± 20 percent	1/batch	≤ 20 percent	1/batch

Note: ARCS - Assessment and Remediation of Contaminated Sediments
MDL - method detection limit
N/A - not applicable
PAH - polynuclear aromatic hydrocarbon
PCB - polychlorinated biphenyl
PCDDs/PCDFs - polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans

[a] Units presented in the subheading are applicable to all parameters unless otherwise noted.
[b] Accuracy is determined from a certified reference material, standard reference material, or standard and is measured from the known concentration.
[c] Precision is calculated as percent relative standard deviation. Precision requirements listed here are for analytical replicates only; field duplicates are required to have a relative percent difference ≤ 30 percent.
[d] A batch is a sample group (usually 10-20 samples) that is carried through the analytical scheme simultaneously.
[e] The MDL for chlorine and bromine is 30 ng, while the MDL for iodine is 10 ng.
[f] A soil sample with acceptance windows per size fraction was provided for use as an accuracy standard.
[g] Metals include arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc. Exceptions are noted where different methodologies are used during the metals quantification.

Example 3: Sediment Toxicity, Contaminant Concentrations and Benthic Community Structure as Indicators of Sediment Quality in the St. Louis River: A Test of EMAP Concepts Applied to a Great Lakes Area of Concern

Background

The International Joint Commission (IJC) has designated 43 areas of concern (AOCs) throughout the Great Lakes as threatened by conventional pollutants, heavy metals, toxic organic compounds, habitat alterations, and introduction of undesirable species. Results of these disturbances have been biological impacts (e.g., benthic macroinvertebrate and fish community degradation), human health effects (fish consumption advisories), and beach closings. The geographic areas associated with the AOCs contain a majority of the population residing in the Great Lakes basin, and comprise approximately 50% of all Canadian citizens.

The St. Louis River AOC, which drains a watershed of 3,634 square miles in northern Minnesota and Wisconsin, forms a large freshwater estuary that represents the second largest tributary to Lake Superior. The 12,000-acre estuary is characterized by a diversity of habitat types. The AOC is unique among the Great Lakes AOCs in that the range of habitat types and contamination status is extreme: for example, the lower estuary contains two federal Superfund sites located across the river from large, undisturbed tracts of forested land currently providing excellent habitat quality for a large variety of species. The outer harbor contains actively dredged shipping channels and a number of current or former municipal and industrial effluent discharges, as well as the world's largest freshwater sand bar, which is home to numerous endangered or threatened plants and animals.

This project has a two-fold purpose: (1) determine if the EMAP intensified grid provides a sampling framework that can be used, with structural modification, to assess AOCs; and (2) develop a set of generic environmental indicators based on biological and chemical measures for long-term assessment of AOCs using the EMAP-Great Lakes and Surface Water EMAP indicators.

In order to achieve these stated purposes, the project has four goals:

1. To test the application of the Great Lakes-EMAP design features in the Harbors and Embayments resource class.

2. To identify percentage areas within the St. Louis River AOC having acceptable and subnominal quality with respect to sediment contamination, toxicity and benthic community structure, and to associate statistically certain sediment contaminants with observed ecological effects.

3. To serve as a baseline status-and-trends monitoring survey of the St. Louis River ecosystem health.

4. To determine the sampling intensity required to survey a complex Great Lakes AOC in order to apply this knowledge to other AOCs within Region V.

The project will sample 120 sites within three habitat classes in the St. Louis River AOC for sediment toxicity, chemical contaminant concentrations, and benthic community structure. The three habitat classes are: (1) ship channels and areas in the lower estuary greater than 18 ft in depth, (2) areas of the estuary less than 18 ft in depth, and (3) Thomson, Forbay and Fond du Lac reservoirs in the lower St. Louis River.

The distribution of sampling points in the three habitat classes is as follows: 30 sites in ship channels and deep water areas, 30 sites in the reservoirs, and 60 sites in the shallow-water estuarine areas. Sampling locations were selected based on the Great Lakes-EMAP grid for habitat classes 1 and 2, and a 7^5-fold enhancement for habitat class 3. These numbers were determined through consultation with EMAP statisticians at ERL-Corvallis. Each site will be sampled twice during the two-year project period in order to estimate the short-term temporal variability for all three assessment metrics. Split-sample, surface sediments will be used for toxicity, chemistry and benthic assessment.

Project Objectives

The questions to be answered by and/or objectives for this project are the following:

1. What percentage of the sediments in the St. Louis River AOC have unacceptable levels of sediment contamination, toxicity, and benthic community disturbance?

2. Make statistical associations on an AOC-wide basis between contaminant levels and sediment toxicity or sub-nominal benthic community status.

3. How many sampling sites and time points are necessary to characterize sediment quality, using the criteria determined in Objective 1, in each of the identified habitat classes (i.e., ship channels and deep holes, shallow shoal or stream areas, and upstream reservoirs)?

4. Establish a relevant integrity index for benthic community assessment for the St. Louis River using the EMAP sampling design.

The requirements for precision, accuracy, completeness, representativeness and comparability of the data in order to attain the project objectives are described in Table B-3. Objective #1 has the least strict data quality requirements for toxicity and chemistry because the large number of samples was designed to provide an excessively-thorough site characterization. This was done in order to increase the likelihood of obtaining a wide variety of sediment types with which to carry out Objectives #2 and #3. In other words, the number of sites and sampling points is most likely overly abundant to address Objective 1. However, because this project is intended as a pilot to actually establish the requisite number of samples on an areal basis for each habitat type, an overestimate was required in the sample design. Thus, fewer sites should be required to answer Objective #1 than to satisfy Objectives 2 and 3; therefore, the required data attributes for Objective #1 are slightly less strict than for the other objectives. Objective #4 does not require data for toxicity and chemistry.

Table B-3. Summary of measurement quality objectives for the St. Louis River area of concern sediment quality assessment by sampling goal

Objective-Metric	Precision	Accuracy	Completeness	Representativeness
Goal 1	40% RPD[a]	N/A	80%	80%
#1-Toxicity	40% RPD[a]	N/A	80%	80%
Benthos	30% RPD	N/A	80%	80%
Chemistry	50% RPD	50-125%	90%	90%
Goal 2	30% RPD	N/A	90%	90%
#2-Toxicity	30% RPD	N/A	90%	90%
Benthos	30% RPD	N/A	90%	90%
Chemistry	40% RPD	70-125%	90%	90%
Goal 3	30% RPD	N/A	90%	90%
#3-Toxicity	30% RPD	N/A	90%	90%
Benthos	30% RPD	N/A	90%	90%
Chemistry	40% RPD	70-120%	90%	90%
Goal 4	N/A	N/A	N/A	N/A
#4-Toxicity	N/A	N/A	N/A	N/A
Benthos	30%	N/A	90%	90%
Chemistry	N/A	N/A	N/A	N/A

[a] Relative percent difference

Example 4: Ecological Effects of Sediment-Associated Contaminants in Inner Burlington Harbor, Lake Champlain

Background

Inner Burlington Harbor of Lake Champlain has received numerous toxicants from point and nonpoint sources in its watershed. Previous sediment sampling and analyses (Watzin et al., 1997) demonstrated relatively high concentrations of silver, lead, and PAHs in the harbor, especially in the southern end, compared to sites outside the breakwater. Much of this area corresponds to an old sewage outfall and oil dolphins but could also represent migration of inputs from the old rail yard and nonpoint sources in and around Burlington. Because the surficial sediment (top 2-3 cm) at most sites had lower pollutant concentrations than sediments at greater depths, inputs of pollutants in recent history (past 30 years) may be declining. However, these studies also indicated substantial temporal and spatial heterogeneity with respect to sediment contaminant concentrations and toxicity (Watzin et al., 1997).

Biological assessments, using benthic macroinvertebrates, were used in conjunction with other field and laboratory analyses to help determine the effects of sediment contamination and other stressors on the biota of Burlington Harbor.

Project Objectives

The overall objective of this project was to assess the hazard resulting from toxic contaminants in the sediments of Inner Burlington Harbor using a sediment quality triad approach. Because certain potentially toxic contaminants are known to occur in Burlington Harbor, the objective of this project was divided into three major component questions.

- Have toxic sediments altered benthic communities of Burlington Harbor?
- Could such changes affect other ecological components of Lake Champlain?
- Do the toxic contaminants in Burlington Harbor sediments accumulate up the food chain and cause risks to higher terrestrial and aquatic trophic levels and human health?

Sampling Design

Sampling locations in the present study were identified by reanalyzing the 1993-94 data from the harbor with a spatial statistical model known as kriging (Myers, 1988) to estimate contaminant concentrations and uncertainties throughout the harbor. Kriging is a geostatistical estimation method which incorporates a model of the spatial variability of data directly. For each chemical, a variogram was calculated using USEPA's software Geo-EAS (version 1.2.1) and fitted by a non-linear least-squared procedure.

The sampling sites selected for the present study were those with the greatest uncertainty (using existing data), and the highest likelihood of contamination. Ten sites were sampled in the harbor and 10 replicate samples from two different sites (reference sites) with relatively low contaminant concentrations and/or toxicity were sampled to help assess sediment quality in the harbor, particularly with respect to biological and toxicological measures. Five replicate samples were collected from one site inside the harbor and 5 reference samples were collected from one site. The five replicate samples collected at each reference site were tested separately for all toxicity and biological analyses, yielding five individual measures for toxicity and macroinvertebrate community structure at these two sites. Subsamples from each of the five samples collected at both sites were composited into one sample from each site for physicochemical analyses. Two other sites were

replicated once as well to obtain a measure of the variability surrounding chemical measures obtained in this study. A total of eight sites were sampled both in this study and in previous work.

Sediment Sampling and Analyses

Sites were identified using differential global positioning and checked frequently during sampling to ensure proper sampling location. Each site was sampled using five-seven petite Ponar grabs, depending on the amount of sediment collected in each grab sample. Contents of the Ponar samples from the site were composited and homogenized in the field using Teflon or high density plastic equipment to obtain a representative sample from each site for chemical, toxicological, and biological analyses.

Table B-4 summarizes the analyses performed in this study and the measurement quality objectives used. Sediment chemical analyses included PAHs, simultaneously extracted metals (SEM), total organic carbon (% TOC), acid volatile sulfides (AVS), total organic nitrogen (TON), ammonia, particle size, and pH. Five metals (those previously showing the highest levels: silver, nickel, copper, lead, and zinc) were measured. Zebra mussels (*Dreissena polymorpha*) were collected from several sites and analyzed for tissue PAHs and percent lipid content on a composite sample of organisms collected at each site. A portion of the sample from three inner harbor sites were sieved (stainless steel) to isolate the fine fraction less than 63µ and also analyzed for PAHs, total organic carbon, and organic nitrogen.

Table B-4. Summary of measurement quality objectives for precision, accuracy, and completeness of biological, toxicological, sediment, organism tissue, and field chemistry analyses conducted in Burlington Harbor (Diamond et al., 1999). RPD = relative percent difference; C.V. = coefficient of variation.

Measurement Parameter	Accuracy (% Recovery)	Precision	Completeness (%)
Benthic macroinvertebrates			
• Metric values	N/A*	• RPD≤ 20%	100
• Metric scores	N/A	• RPD≤ 5%	100
• Bioassessment scores	N/A	• RPD≤ 5%	100
Field Water Quality Measurements			85
• Conductivity	N/A	± 1% of range	
• Temperature	N/A	± 0.15° C	
• Dissolved Oxygen	N/A	± 0.2 mg/L	
• pH	N/A	± 0.2 units	
Laboratory Sediment Analyses			85
• PAH	± 25	RPD ≤ 40%	
• Ammonia	± 30	RPD ≤ 40%	
• Total organic nitrogen	± 20	RPD ≤ 40%	
• Total organic carbon	± 30	RPD ≤ 40%	
• AVS/SEM	± 30	RPD ≤ 40%	
• Particle size	N/A	RPD ≤ 20%	
Sediment Toxicity Analyses			85
• *Hyalella* 10-day acute	N/A	C.V. ≤ 30%	
• *Hyalella* 28-day chronic	N/A	C.V. ≤ 40%	
• *Pimephales* 7-day chronic	N/A	C.V. ≤ 30%	
• *Lumbriculus* 28-day bioaccumulation	N/A	C.V. ≤ 40%	
Organism Tissue Analyses			85
• PAH	± 30	RPD ≤ 40%	
• Lead	± 30	RPD ≤ 40%	
Protein Expression Analyses	N/A	RPD ≤ 20%	85

* Not applicable except through use of routine standards and calibration.

Example 5: Washington Department of Ecology Sampling and Analysis Plan Guidance

Background

The Washington Department of Ecology (WDE) provides technical guidance for developing sampling and analysis plans for sediment investigations to be conducted under the Washington Sediment Management Standards (SMS) program (WDE, 1995). Technical guidance on various aspects of sediment sampling and analysis procedures that need to be considered in the design and implementation of sediment investigations is made available through the Puget Sound Estuary Program [PSEP] protocols.

1. **Sediment Source Control Program** – Methods are described for controlling the effects of point and nonpoint source discharges through the National Pollutant Discharge Elimination System (NPDES) permit program, state water quality permit programs, issuance of administrative orders, or other mans determined appropriate by WDE; and

2. **Sediment Cleanup Program** – Administrative procedures and criteria are established to identify, screen, rank, and prioritize, and clean up contaminated surface sediment sites.

Project Objectives: Sediment Investigations Conducted under the Sediment Source Control Program

Adverse effects of contaminated sediments on biological resources and threats to human health generally will only occur when there is a pathway to ecological or human receptors. In most cases, such a pathway will only exist when surface sediments (defined by the SMS as those within the biologically active zone) are contaminated. Contaminated sediments existing at depths below the biologically active zone are unlikely to result in such effects unless the overlying sediments are removed by natural (e.g., erosion, scouring) or anthropogenic (e.g., dredging, propeller scour) means, or there are other mechanisms for the release of sediment contaminants such that exposure may occur. Additionally, the surface sediment will be most likely to exhibit impacts from recent discharges of contaminants. Hence, the focus of sediment sampling in the sediment source control process is generally on the sediments within the biologically active zone.

Table B-5 summarizes sediment management standards for biological effects criteria used by Washington Department of Ecology for Puget Sound marine sediments (WDE, 1995). These standards are, in effect, decision rules in a Data Quality Objectives context (Step 5, Figure 2-2, this Manual); cases where these standards are not met represent locations that are impaired and in need of some type of management action (e.g., remediation, follow-up sampling). WDE also has standards for many chemical contaminants (WDE, 1995) as does the Puget Sound Dredged Disposal Analysis Program (WDE, 1995).

Table B-5. Sediment Management Standards Biological Effects Criteria for Puget Sound Marine Sediments

Biological Test	Sediment Quality Standards[a]	Sediment Impact Zone Maximum Levels, Cleanup Screening Levels, or Minimum Cleanup Levels[b]
Amphipod	The test sediment has a significantly higher (t-test, $P \leq 0.05$) mean mortality than the reference sediment, and the test sediment mean mortality exceeds 25 percent on an absolute basis	The test sediment has a significantly higher (t-test, $P \leq 0.05$) mean mortality than the reference sediment, and the test sediment mean mortality is more than 30 percent greater, on an absolute basis, than the reference sediment mean mortality
Larval	The test sediment has a mean survivorship of normal larvae that is significantly less (t-test, $P \leq 0.05$) than the mean normal survivorship in the reference sediment, and the combined abnormality and mortality in the test sediment is more than 15 percent greater, on an absolute basis, than the reference sediment	The test sediment has a mean survivorship of normal larvae that is significantly less (t-test, $P \leq 0.05$) than the mean normal survivorship in the reference sediment, and the combined abnormality and mortality in the test sediment is more than 30 percent greater, on an absolute basis, than that in the reference sediment
Benthic infauna	The test sediment has less than 50 percent of the reference area sediment's mean abundance of any one of the following major taxa: Crustacea, Mollusca, or Polychaeta, and the test sediment abundance is significantly different (t-test, $P \leq 0.05$) from the reference sediment abundance	The test sediment has less than 50 percent of the reference area sediment's mean abundance of any two of the following major taxa: Crustacea, Mollusca, or Polychaeta, and the test sediment abundance is significantly different (t-test, $P \leq 0.05$) from the reference sediment abundances
Juvenile polychaete	The mean biomass of polychaetes in the test sediment is less than 70 percent of the mean biomass of the polychaetes in the reference sediment, and the test sediment biomass is significantly different (t-test, $P \leq 0.05$) from the reference sediment biomass	The mean biomass of polychaetes in the test sediment is less than 50 percent of the mean biomass of the polychaetes in the reference sediment, and the test sediment biomass is significantly different (t-test, $P \leq 0.05$) from the reference sediment biomass
Microtox®	The mean light output of the highest concentration of the test sediment is less than 80 percent of the mean light output of the reference sediment, and the two means are significantly different (t-test, $P \leq 0.05$)	Not applicable

Source: WDE (1995).

[a] The sediment quality standards are exceeded if one test fails the listed criteria [WAC 173-204-320(3)].
[b] The sediment impact zone maximum level, cleanup screening level, or minimum cleanup level is exceeded if one test fails the listed sediment impact zone maximum level, cleanup screening level, or minimum cleanup level criteria [WAC 173-204-520(3)] or if two tests fail the sediment quality standards criteria [WAC 173-204-320(3)].

WDE describes four general types of sediment monitoring (all of which are the responsibility of the discharger) that may be conducted in support of the sediment source control process:

(a) **Baseline monitoring—**Used to confirm the screening evaluation for determining potential of a discharge to cause sediment impacts conducted prior to authorization of a sediment impact zone (SIZ) to collect information that will be used in determining whether such an authorization is likely to be necessary, and to establish the baseline conditions with which future conditions can be compared

(b) **SIZ application monitoring—**Conducted to collect information to support application of the SIZ models

(c) **SIZ maintenance monitoring**—Conducted during the term of a permit that includes an authorized SIZ, with the intent to determine whether the SIZ should be renewed, reduced, or eliminated; whether areas of special importance have been adversely impacted by the discharge; and the conditions for SIZ reauthorization

(d) **SIZ closure monitoring—**Conducted following closure of an SIZ to demonstrate successful restoration of sediment quality.

The monitoring objectives vary with the type of monitoring being conducted, and the design of the monitoring program varies with both discharge- and site-specific characteristics.

Project Objectives: Sediment Investigations Conducted under the Sediment Cleanup

The Sediment Cleanup Standards set forth a decision process for identifying contaminated sediment areas and determining appropriate cleanup responses (WDE, 1995). The sediment cleanup decision process includes procedures for screening and ranking contaminated areas of sufficient concern to warrant active cleanup, as well as procedures for selecting an appropriate cleanup alternative on a site-specific basis.

Because cleanup of contaminated sediments may require their removal, sediment sampling and analyses, conducted in support of sediment cleanup studies, need to assess the total spatial extent (including both lateral and vertical) of the sediment contamination. In this respect, these sediment investigations differ from those previously described under the sediment source control process, where the focus there is generally only on sediments within the biologically active zone.

In addition to initial investigations and site characterization, which are described in by WDE (1995), there are three general types of monitoring that may be conducted in support of the sediment cleanup process:

(a) **Source control monitoring—**Conducted prior to and following sediment cleanup to determine how ongoing sources at or near a site may affect the success of active cleanup and/or natural recovery

(b) **Compliance monitoring—**Long-term monitoring conducted following cleanup actions that include containment of contaminated sediments, or to assess the progress of natural recovery and/or to evaluate recontamination of the area

(c) **Closure monitoring—**Conducted following completion of removal actions or compliance monitoring to demonstrate successful cleanup of sediment contamination. Closure monitoring must be performed before a site can be considered for delisting.

The primary objectives of sediment sampling and analyses conducted as part of a preliminary investigation of a contaminated sediment site are to: (1) Identifying sediment station clusters of potential concern, and (2) Ranking identified cleanup sites.

Such sampling and analyses must be sufficient to enable a determination of whether there are exceedances of the numerical chemical criteria or biological effects criteria (Table B-5) at three or more stations within a specific area of concern. Thus, the decision rules used by WDE in these studies (Step 5 of the DQO Process, Figure 2-2, this Manual) are defined by explicit criteria and the number of the samples demonstrating exceedence of criteria. The spatial extent of such exceedances is not required to be defined as part of a preliminary investigation (WDE, 1995).

Given the decision rules above, there are clear implications for how sampling is designed, as there need to be several samples collected and analyzed from a specific area of concern and some assurance of representative coverage of the area. At smaller sites of known or suspected sediment contamination, the addition of a relatively small number of stations or samples in a preliminary investigation is suggested by WDE (1995) to allow assessment of the spatial extent of contamination, gradients toward or away from other sources, or other important details. Hence, a single study could suffice, thereby precluding the need for a second, focused investigation.

Alternatively, if there are no plans to dredge or otherwise disturb the sediments, sampling and analyses, conducted as part of a preliminary investigation, could focus only on surface sediments. After the need for cleanup has been identified, a more focused sediment sampling and analysis program would then be required by WDE to define the spatial extent of contamination (including its vertical extent) and to evaluate cleanup alternatives.

Comparison of Data Requirements: Sediment Management Standards (Sms) and the Dredged Material Management Program (DMMP)

In addition to WDE's Sediment Management Strategy (SMS), the other major framework for sediment management activities in the Dredged Material Management Program (DMMP). The SMS and DMMP programs are very similar in the suites of biological and chemical evaluations that are required, and in the evaluation criteria that are applied. While the two programs have the same goal, protection of sediment quality, the two programs have different applications and, as a result, some differences in data requirements.

Sediment sampling and analysis is conducted under the SMS to determine whether, and to what extent, surface sediments are contaminated, whether point or nonpoint source discharges have contributed or may still be contributing to such contamination, and whether contaminated sediments should be remediated. Sediment sampling and analysis is conducted under theDMMP program to determine whether the sediment matrix (volume) proposed for dredging, when dredged and discharged at unconfined, open-water disposal sites within Puget Sound, could cause or contribute to unacceptable adverse effects on the aquatic environment. Because of these different purposes, sampling gear and compositing techniques will differ. However, both theDMMP and SMS data requirements are based upon "exposure potential" and a "sediment unit" concept. In dredging situations (DMMP), the exposure potential of concern is with the entire mass of sediments released at the DMMP sites and the sediment unit of concern is the minimum dredge unit that can be effectively managed. In SMS

situations, the exposure potential and sediment unit of concern is generally the surface, specifically the "biologically active zone" (often the top 10 cm).

DMMP sampling is designed to characterize the bulk properties of the sediments to be dredged, transported, and discharged. Sediment core samples (e.g., vibracorer) are typically collected to characterize the sediment matrix to the depth of proposed dredging for disposal determinations and to assure that the quality of newly exposed surfaces do not result in degradation. Because dredging removes the material in bulk, the cores are typically segmented on a 4-foot basis and composited across that segment (rather than further subdivided) to define a "dredged material management unit." Sediment sampling under the sediment source control process of the SMS is generally designed to characterize conditions near the sediment surface. In cases where the goal is to characterize the exposure potential, such sampling may target the biologically active zone of the sediments. In other cases, where the goal is to sample only the most recently deposited sediment, such sampling may target only the uppermost 0–2 cm of sediments. Sediment sampling designed to identify contaminated sediment sites under the sediment cleanup process of the SMS is also targeted on the near-surface, biologically active zone of the sediments. After a contaminated site is identified, however, collection of sediment cores will also generally be required to assess the vertical extent of contamination and to determine the sediment quality of any new surface to be exposed after cleanup.

The process of compositing samples from a range of depth intervals below the sediment surface may dilute higher concentrations of contaminants as pointed out in Section 2.4.3 of this Manual and in USEPA/ACOE (1998). Compositing over depth provides an assessment of the condition of the overall sediment matrix, but does not provide an assessment of the sediments within the biologically active zone. Compositing of samples from a range of depth intervals is therefore appropriate for DMMP purposes, but is ordinarily not performed for SMS investigations. In addition, many more samples may be needed for SMS purposes to establish patterns or gradients of contamination, to identify contaminant sources, or to delimit the area of contamination.

Development of Sediment Sampling and Analysis Plans

Although the specific details of individual sampling and analysis plans may be very different, all such plans submitted for review by WDE contain certain basic elements. Figure B-1 provides a recommended outline for sediment sampling and analysis plans that can also serve as a checklist for those preparing or reviewing such plans.

Each sediment sampling and analysis plan, regardless of whether it is being prepared under the sediment source control process or the sediment cleanup process, should include as part of the introduction a brief summary of site background information. The following background information should be provided:

- Site history
- Regulatory framework (e.g., NPDES; Model Toxics Control Act; SMS; Comprehensive Environmental Response, Compensation, and Liability Act)
- Summary of results of previous investigations, if any, of the site
- Location and characteristics of any current and/or historical wastewater or stormwater discharge(s) at the site

- Location and characteristics of any current and/or historical wastewater or stormwater discharge(s) in the local area

- Information on onsite waste disposal practices or chemical spills in the local area, if any

- Site location, including a location map showing the surrounding area and a site map.

The second section of a sampling and analysis plan should describe the objectives of the sediment investigation in the context of the appropriate regulatory framework (e.g., sediment source control process, sediment cleanup process). WDE (1995) provides guidance on appropriate field sampling methods; sample handling procedures; laboratory analytical methods; quality assurance and quality control requirements; data analysis, record keeping, and reporting requirements; health and safety plan; schedule; and project team and responsibilities.

Sediment Sampling and Analysis Plan Outline and Checklist

(From WDE, 1995)

1. Introduction and Background Information

- ❑ Site history
- ❑ Regulatory framework (e.g., NPDES, MTCA, SMS, CERCLA)
- ❑ Summary of previous investigations, if any, of the site
- ❑ Location and characteristics of any current and/or historical wastewater or storm water discharge(s at the site
- ❑ Location and characteristics of any current and/or historical wastewater or storm water discharge(s) in the local area
- ❑ Information on on-site waste disposal practices or chemical spills in the local area, if any
- ❑ Site location map showing the surrounding area
- ❑ Site map showing site features

2. Objectives and Design of the Sediment Investigation

- ❑ Objectives of the sediment investigation
- ❑ Overall design of the sediment investigation, including related investigations, if any
- ❑ Chemical analytes (including description of their relevance to the objectives and the regulatory framework)
- ❑ Biological tests (including description of their relevance to the objectives and the regulatory framework)
- ❑ Sampling Station Locations
  - ❑ Rationale for station locations
  - ❑ Site map(s) showing sampling stations and other pertinent features (e.g., bathymetry and current regime; outfall(s)/diffuser(s); authorized mixing zone(s), if any; sites of waste disposal, spills, or other activities that may have affected the sediments, such as sandblasting, boat repair, etc.; historical dredging activities)
  - ❑ Proposed reference stations
  - ❑ Table showing the water depth at each proposed station
  - ❑ Proposed depth(s) below the sediment surface where sediments will be collected

Figure B-1. Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995).

3. Field Sampling Methods

- ❑ Station positioning methods
- ❑ Sampling equipment
- ❑ Decontamination procedures
- ❑ Sample compositing strategy and methods
- ❑ Sample containers and labels
- ❑ Field documentation procedures
- ❑ Procedures for disposal of contaminated sediments

4. Sample Handling Procedures

- ❑ Sample storage requirements (e.g., conditions, maximum holding times) for each type of sample
- ❑ Chain-of-custody procedures
- ❑ Delivery of samples to analytical laboratories

5. Laboratory Analytical Methods

- ❑ Chemical analyses and target detection limits
- ❑ Biological analyses
- ❑ Corrective actions

6. Quality Assurance and Quality Control Requirements

- ❑ QA/QC for chemical analyses
- ❑ QA/QC for biological analysis
- ❑ Data quality assurance review procedures

7. Data Analysis, Record Keeping, and Reporting Requirements

- ❑ Analysis of sediment chemistry data
- ❑ Analysis of biological test data
- ❑ Data interpretation
- ❑ Record keeping procedures
- ❑ Reporting procedures

Figure B-1 (continued). Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995) (cont.).

8. Health and Safety Plan (required for cleanup investigations)

- ❑ Description of tasks
- ❑ Key personnel and responsibilities
- ❑ Chemical and physical hazards
- ❑ Safety and health risk analysis for each task
- ❑ Air monitoring plan
- ❑ Personal protective equipment
- ❑ Work zones
- ❑ Decontamination procedures
- ❑ Disposal procedures for contaminated media and equipment
- ❑ Safe work procedures
- ❑ Standard operating procedures
- ❑ Contingency plan
- ❑ Personnel training requirements
- ❑ Medical surveillance program
- ❑ Record keeping procedures

9. Schedule

- ❑ Table or figure showing key project milestones

10. Project Team and Responsibilities

- ❑ Description of sediment sampling program personnel
- ❑ Table identifying the project team members and their responsibilities

11. References

- ❑ List of references

Figure B-1 (continued). Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995).

APPENDIX C

STATISTICAL CONSIDERATIONS IN DETERMINING THE APPROPRIATE NUMBER OF REPLICATE SAMPLES NEEDED AT EACH SAMPLING STATION

For certain programs or types of studies, it is desirable (or necessary) to determine if a particular location is significantly affected as compared to known non-impacted or reference locations (e.g., presence of toxicity and/or high contaminant concentrations in sediments or interstitial waters). This type of monitoring objective is used frequently in certain regulatory programs, such as the Dredged Materials Management Program and Superfund (CERCLA), however, many non-regulatory programs also have a similar objective (see for example the Burlington Harbor example in Appendix B).

If one is interested in determining statistical differences in certain measures (e.g., toxicity to *Hyalella azteca*) among or between stations, then analysis of replicate field samples may be necessary. This entails collecting multiple samples from the same station (or other spatial unit of interest), processing each sample independently, and analyzing separately each sample. For example, if the purpose of a study is to determine whether the sediment in a specific location is toxic to the estuarine amphipod *Rhepoxynius abronius* as compared to sediment from a reference location, then it is desirable to collect multiple samples from each location and perform a *Rhepoxynius* whole sediment toxicity test (including standard replication within a test) for each sample collected. Clearly, this type of replication could entail substantial laboratory effort, as compared to compositing samples from a single location and performing a single analysis or test (see Section 2.4.3 for a discussion of compositing versus replication of samples). However, compositing does not provide any information on the true variability of a given location and is rather, a form of pseudoreplication. For some programs or studies, true field replication is necessary.

The appropriate number of replicates needed for a given study depends on the statistical power and level of confidence (i.e., measurement quality objectives; see Appendix B for examples) one needs to support or refute a given decision (see Data Quality Objectives Process, Section 1.1 and Appendix A). Power is represented as $1-\beta$ and is a measure of the Type II error rate: the probability of accepting the hypothesis that the results from two different samples or stations are similar, when in fact they are not. Confidence is represented as $1-\alpha$ and is a measure of the Type I error rate: the probability of rejecting the hypothesis that the results from two different samples or stations are different when in fact they are really the same. For examples, if the question is whether a given location should be dredged for remediation purposes, the study will need to have a certain statistical power, to determine if the sediment sample from the target location is more toxic or contaminated than the reference location sediment, with a certain degree of confidence that one is making the correct decision. Both power and confidence are dependent on the expected variability in the endpoint or parameters of interest, both within a given location and within a given test or analysis. The appropriate replication, then, is required so that one has sufficient statistical power and confidence to reliably make correct decisions about the status of a given location.

To determine the number of replicates required, the following questions should be answered (Alldredge, 1987):

1. What is being compared (i.e., toxicity endpoint, parameter value)?

2. Is the significance criterion directional (is one only interested in whether a station is more toxic than another, not less toxic as well; i.e., one-tailed test)?

3. What is the level of significance between the expected and actual value of the parameter being measured?

4. How large a difference is acceptable between the expected and actual value of the criterion being measured, and with what level of probability?

5. What variability is expected in the data?

There are a number of approaches that can be used to determine the number of replicates required to achieve a minimum detectable difference at a specific confidence level and power (see Environment Canada, 1995). While many programs specify a fixed number of replicates per station (often 3-5 replicates), in other cases, this could represent too many or too few replicates for study data quality objectives. Several factors need to be defined to establish the appropriate number of replicates (see text box). U.S. EPA (2000c) presents a concise discussion of the relationships of these statistical considerations. Traditionally, acceptable coefficients of variation vary from 10 to 35%, the power from 80 to 95%, the confidence level from 80 to 99%, and the minimum detectable relative difference from 5 to 40% (Barth and Starks, 1985).

Several books on sampling design (e.g., Keith 1993; USEPA 2000b) discuss methods to determine the appropriate number of replicates needed for a given set of objectives. Table C-1 summarizes statistical approaches for determining the appropriate number of replicate samples needed per station given different study objectives.

Table C-1. Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	**Formula**	**Reference**
To determine the sample size required to detect an effect in an impacted area versus a control area over time:		
a) resampling same sites before and after impact and testing if the mean change in the control area is the same as that in the impacted area	$n = 2(t_\alpha + t_\beta)^2 (S/\Delta)^2$	Green, 1989
b) sampling different sites before and after impact and testing if there is no interaction between area effect and time effect	$n = 4(t_\alpha + t_\beta)^2 (S/\Delta)^2$ where: n = number of samples for each of the control and impact areas S = standard deviation Δ = magnitude of change required to be a real effect with specified power $(1-\beta)$ t_α = t statistic given a Type I[1] error probability t_β = t statistic given a Type II[2] error probability	Green, 1989

Table C-1 (continued). Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	Formula	Reference
To determine if the mean value for an impacted area: a) differs significantly from a standard value (e.g., sediment guideline) b) differs significantly from the mean of a control site	 $n \geq \frac{(Z_\alpha + Z_\beta)^2}{d^2} + 0.5\, Z_\alpha^2$ $n \geq \frac{(Z_\alpha + Z_\beta)^2}{d^2} + 0.25\, Z_\alpha^2$ where: n = number of samples Z_α = Z statistic for Type I error probability (e.g., α=0.05) Z_β = Z statistic for Type II error probability (e.g., β=0.90) d = magnitude of the difference to be detected (i.e., effect level)	Alldredge, 1987
To determine the number of samples required to estimate a mean value (representative of the area) with a given statistical certainty	$y\bar{x} = t_c \frac{S_x}{(n-1)^{1/2}}$ where: y = accepted error as a proportion of the mean value(e.g., y = 0.10) $\bar{x}$ = mean value of x_i (i = 1...n) S_x = standard deviation t_c = confidence coefficient (e.g., 90% or $t_{0.95}$ n = number of samples	Håkanson, 1984
To determine the number of samples required to estimate a mean	$n = \frac{(Z_{\alpha/2})^2 \sigma^2}{d^2}$ where: n = number of samples Z = Z statistic (standard normal curve) σ^2 = variance $\alpha/2$ = probability of a 95% confidence level d = distance between the center of the lower confidence and upper confidence bound	Milton *et al*., 1986

Table C-1 (continued). Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	Formula	Reference
To determine the number of samples required for a particular power for a normal distribution (i.e., $\bar{x} > s^2$)	$n = \frac{10^4 (t^2 s^2)}{(R^2 \bar{x}^2)} K$ where: n = number of samples t = t statistic for a desired confidence level $\bar{x}$ = mean value from preliminary sampling or historical data s = standard deviation of mean R^2 = percentage coefficient of variation K = index of clumping	Kratochvil and Taylor, 1981

[1] Type I (α) error is the probability of rejecting the hypothesis being tested when it is true.
[2] Type II (β) error is the probability of not rejecting the hypothesis being tested when it is false.

Optimizing Sampling

Having estimated the variability in a given parameter or endpoint, and the number of replicate samples per station that might be necessary to address data quality objectives, one can evaluate the cost/benefit of collecting and analyzing more or less samples in terms of the overall confidence in a given decision and the information gained. This is referred to as optimizing the study design (Step 7, Figure 2-1). Ferraro *et al*. (1994, 1989) present a method for quantitatively evaluating the optimum macrobenthic sampling protocol, including the number of replicates (*n*), which has relevance to other sediment quality studies as well. Their approach helps answer fundamental questions concerning the design of sediment quality studies such as:

- How large should the sampling unit be?
- How many replicate samples should be taken?

The procedure calculates the "power-cost efficiency" (PCE), which incorporates both the number of samples (*n*), the cost (field collection effort and lab effort combined) and the expected statistical power for each alternative sampling scheme. The various sampling schemes consist of different combinations of sampling gear, gear area, and number of replicates. The method allows determining the optimum among a set of sampling schemes for detecting differences between reference and test sites when the statistical model is a t-distribution for comparing two means. The optimum scheme can be defined as the least costly one capable of reliably (e.g., $\alpha = 0.5$, $1-\beta = 0.95$) detecting a desired difference in the means of particular measure between two sites. The approach can be applied to each parameter of interest and the results aggregated to determine the optimum protocol.

There are four primary steps in assessing the PCE of a suite of alternative sampling schemes:

1. For each scheme, collect replicate samples at paired reference and test sites. The observed difference in values between the sites is operationally assumed to be the magnitude of the difference desired to be detected. Alternatively, a percentage of the median (e.g., 20%) for a given measure calculated across reference stations could be set as the magnitude of the difference to be detected. In either case, this difference, divided by the standard deviation, is the "effect size" (ES) of interest.

2. Assess the "cost" (c_i), in time or money, of each sampling scheme *i* at each station. The cost can include labor hours for sampling, analysis, and recording results.

3. Conduct statistical power analysis to determine the minimum number of replicate samples (n_i) needed to detect the ES with an acceptable probability of Type I (α) and Type II (β) error (e.g., $\alpha = \beta = 0.05$).

4. Calculate the power-cost efficiency (PCE) for each sampling scheme by:

$$PCE_i = (n \times c)_{min} / (n_i \times c_i)$$

where $(n \times c)_{min}$ = minimum value of $(n \times c)$ among the *i* sampling schemes. The reciprocal of PCE*i* is the factor by which the optimal sampling scheme is more efficient than alternative scheme *i*. When PCE is determined for multiple metrics, the overall optimal sampling protocol may be defined as that which ranks highest in PCE for most metrics in the test set.

APPENDIX D

ADVANTAGES AND DISADVANTAGES OF DIFFERENT STATION POSITIONING TECHNIQUES

Documentation of sampling station location or position is an important aspect of field operations to ensure that: (1) sampling occurs where intended and (2) someone else (or another sampling team) could re-sample the same location at a later date. This is particularly critical for trend monitoring such as that performed by NOAA's Status and Trends Program.

With current technology, a global positioning system (GPS) device is generally the positioning method of choice because it is usually very accurate, reliable, easy to use, and affordable. However, occasionally, other positioning methods may be desired or necessary. The following tables, originally developed under the Puget Sound Estuary Program, summarize most of the positioning methods that have been used in monitoring studies, including their advantages and disadvantages.

Table D-1. Positioning methods appropriate for small water bodies (small embayment, small lakes, rivers) (modified from PSEP 1997a).

Method	Accuracy	Range	Advantages	Disadvantages
GPS or Navstar	± 100 m (0.1 to 1 m for differential GPS)	no limit on the range	• Continuous position reports available worldwide • System s available comprising a range of accuracy and cost	• Site-specific problems due to military scrambling
Theodolite	10 to 30 s ≥ ± 1 m	200 m to 5 km	• Traditional method, measuring horizontal angles between known targets • High accuracy when applied successfully • Inexpensive	• Requires triangulation between two manned shore sites or targets • Requires simultaneous measurements • Requires good visibility which limits areal coverage • Requires stationary sampling platform
Electronic Distance Measurement instrument (EDMI)	1.5 to 3.0 cm	3 km without multiple prisms	• High accuracy • Compact, portable, rugged • Relatively inexpensive • Useable for other surveying projects	• Introduces error and limitations due to reflector movement and directionality as well as ground wave reflection • Requires good line-of-sight visibility unless microwave unit is available • Requires two shore sites
Total stations	5 to 7 cm	< 5 km	• Not logistically complex, requiring single onshore site • Compatible with other uses	• Introduces limitations due to reflector movement and directionality, prism costs, and line- of- sight, optical or infrared range limitations
Sextant	± 10 s ± 3 to 5 m but variable	200 m to 5 km	• High accuracy when used nearshore by experienced operator • Portable, involving handheld device • Rapid, easy to implement • Easily obtainable • No shore party necessary • Inexpensive	• Requires simultaneous measurement of two angles • Requires good target visibility • Requires location and maintenance of targets for relocation of site • Requires calm conditions for best results • Orientation of target affects accuracy • Has limitations on acceptable angles

Table D-1 (continued). Positioning methods appropriate for small water bodies (small embayment, small lakes, rivers) (modified from PSEP 1997a).

Method	Accuracy	Range	Advantages	Disadvantages
Pelorus	variable	< 5 km	• High accuracy when used nearshore • Rapid, easy to implement • Easily obtainable • No shore party necessary • Inexpensive	• Requires simultaneous measurement of two angles • Requires good target visibility • Requires location and maintenance of targets for relocation of site • Requires calm conditions for best results • Has limitations on acceptable angles
RADAR	variable	30 to 50 km	• Standard equipment on ships • Easily operated • Yields range and relative bearing to targets	• Restricts applications by not being portable • Requires a target that reflects microwave signals
Autotape	± 0.5 m	limited	• High accuracy and precision • Portable	• High cost

Table D-2. Positioning methods appropriate for large water bodies (ocean, estuaries, large lakes) (modified from PSEP 1997a).

Category	Accuracy	Range	Advantages	Disadvantages
GPS or Navstar	± 100 m (0.1 to 1 m for differential GPS)	no limit on the range	• Continuous position reports available worldwide • System s available comprising a range of accuracy and cost	• Site-specific problems due to military scrambling
Microwave navigation systems (e.g., Miniranger, Trisponder, Racal Microfi, Del Norte)	± 1 to 3 m	25 to 80 km (depends on height of transceiver units)	• No visibility restrictions • Multiple users • High accuracy • Radio line of sight • Portable, easy system to operate	• Moderately expensive system • Requires multiple onshore sites • Cost impacts due to logistics and security of the necessary shore units • Potential source of error due to signal reflective nulls • Limited range due to low-powered shore units
Shoran	± 10 m	≤ 80 km (short range)	• High accuracy	• Limited range • Requires two shore transmitters
LORAN-C	≥ ± 15m	up to 300 km (medium range)	• No visibility or range restrictions • Requires no additional personnel • Existing equipment • Relatively inexpensive	• Incurs interference in some areas • Universal coverage not available • Used only for repositioning after employing a more geodetically precise system to identify location
Decca HIFIX/6	± 1 m	up to 300 km (medium range)	• High accuracy and precision	• Requires multiple shore sites • Expensive system
Variable range	± 0.5 °	16 to 72 km	• No visibility restrictions • Requires no additional personnel • Existing equipment • Inexpensive	• Uses line-of-sight method • Relies on map accuracies of targets • Decreased accuracy with range scale
Decca Minifix	± 2 m	≥ 70 km	• High accuracy and precision • Light weight equipment	• Expensive system
Range-azimuth	0.02 ° and 0.5 m	< 5 km (optical) 30 km (elect)	• High accuracy • Single station • Circular coverage	• User-specific • Uses line-of-sight method • Potential source of error due to signal reflective nulls • Expensive system
Satellite navigation (SATNAV)	1 - 10 m	no limit on the range	• High accuracy • Single site with minimal logistics • Use possible in restricted and congested areas • No requirement for shore sites • Capability for integrating satellite fixes with other data sources to improve precision	• Continuous coverage unavailable • Introduction of error due to local and atmospheric effects • Distorted when signal path crosses polar ice caps • Requires high initial development expenditures

APPENDIX E

ADVANTAGES, DISADVANTAGES AND ILLUSTRATIONS OF GRAB AND CORE SAMPLING DEVICES USED IN SEDIMENT MONITORING STUDIES

Table E-1. Advantages and Disadvantages of Commonly Used Grab Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995).

Device	Use	Sample Depth (cm)	Sample Volume (L^3)	Advantages	Disadvantages
Orange Peel	Marine waters, deep lakes	0 to 18	10 to 20	• Comes in a range of sizes	• Need large boat, powered winch and calbe line • Blocking of jaws may cause sample losss
Smith-McIntyre	Deep lakes, rivers and estuaries	0 to 4 (in deep sand)	10 to 20	• Reasonable quantitative samples • The trigger plates provide added leverage essential to its penetration of substrate	• Heavy, need boat and power winch • Spring loaded jaws, hazardous • Inadequate for deep burrowing organisms
Birge-Ekman, small	Lakes and marine areas; soft sediments, silt and sand	0 to 10	$\leq$ 3.4	• Handles easily without winch or crane • Can be adapted for shallow water use • Good for soft sediments, sand and silt • Allows subsampling	• Restricted to low current due to light weight and messenger activation • May exceed target penetration depth • Subsampling may be restricted by size of top flaps
Birge-Ekman, large	Lakes and marine areas; soft sediments, silt and sand	0 to 30	$\leq$ 13.3	• Can be adapted for shallow water use • Good for soft sediments, sand and silt • Allows subsampling	• Restricted to low current conditions • Penetration depth can exceed desired level due to weight of sampler • Heavy; requires winch
PONAR, standard	Deep lakes, rivers and estuaries; useful on sand, silt or clay	0 to 10	7.25	• Most universal grab sampler • Adequate on most substrates • Large sample obtained intact, permitting subsampling • Good for coarse and firm bottom sediments	• May not close completely, resulting in sample loss • Metal frame may contaminate sample • Heavy; requires winch
PONAR, petite	Deep lakes, rivers and estuaries; useful on sand, silt or clay	0 to 10	1.0	• Adequate for most substrates that are not compacted	• May not penetrate sediment to desired depth, especially in consolidated sediments. • Susceptible to incomplete closure and loss of sample. • Requires more casts to obtain sufficient sample if many analyses needed.
Van Veen	Deep lakes, rivers and estuaries; useful on sand, silt or clay; effective in marine environments in deep water and strong currents	0 to 30	18 to 75	• Adequate on most substrates that are not compacted • Large sample obtained intact, permitting subsampling • Available in stainless steel	• May not close completely, resulting in sample loss • May close prematurely in rough waters • Metal frame may contaminate sample • Heavy; requires winch
Modified Van Veen (e.g., "Ted-Young grab")	Lakes and marine areas	0 to 15	$\leq$18.0	• Fluorocarbon plastic liner can help avoid metal contamination • Screened bucket cover helps reduce bow wave effects	• Requires winch • Relatively expensive

Table E-1. Advantages and Disadvantages of Commonly Used Grab Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995).

Device	Use	Sample Depth (cm)	Sample Volume (L^3)	Advantages	Disadvantages
Petersen	Deep lakes, rivers and estuaries; useful on most substrates	0 to 30	9.45	• Provides large sample • Penetrates most substrates	• Shock wave from descent may disturb fine-grained sediment • Lacks lid cover to permit subsampling • May not close completely, resulting in sample loss • Metal frame may contaminate sample • Restricted to low current conditions • May exceed target penetration depth
Shipek, standard	Used primarily in marine waters and large inland lakes and reservoirs; not useful for compacted sandy clay or till substrates	0 to 10	3.0	• Sample bucket opens to permit subsampling • Retains fine-grained sediments effectively	• Metal frame may contaminate sample • Heavy; requires winch • Can result in the loss of the topmost 2-3 cm of very fine, unconsolidated sediment
Mini Shipek	Lakes, useful for most substrates that are soft	0 to 3	0.5	• Handles easily without winch or crane from most platforms	• Requires vertical penetration • Samples small volume • May lose fine-grained sediment • May close prematurely

Table E-2. Advantages and Disadvantages of Commonly Used Core Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995; USEPA/ACOE, 1998)

Device/ Dimensions	Use	Depth Sample (cm)	Volume Sample (L^3)	Advantages	Disadvantages
Fluorocarbon plastic or glass tube (3.5 to 7.5 cm inner diameter (I.D.); ≤ 120 cm long)	Shallow wadeable waters or deep waters if SCUBA available; soft or semi-consolidated deposits	0 to 10	0.096-0.44	• Preserves layering and permits historical study of sediment deposition • Minimal risk of contamination • Rapid; samples immediately ready for laboratory shipment	• Small sample size necessitates repetitive sampling
Hand corer with removable fluorocarbon plastic or glass liners (3.5 to 7.5 cm I.D.; ≤ 120 cm long	Same as above except more consolidated sediments can be obtained	0 to 10	0.96-0.44	• Same advantages as fluorocarbon plastic or glass tube • Penetrates substrate with greater ease through use of handles	• Small sample size necessitates repetitive sampling • Requires careful handling to prevent spillage • Requires removal of liners before repetitive sampling • Barrel and core cutter metal may contaminate sample
Box corer	Same as above but the depth of the uncon-solidated sediment must be at least 1 m	0 to 70	≤ 30.0	• Collects large, undisturbed sample; optimal for obtaining intact subsamples	• Difficult to handle • Relatively heavy; requiring larger vessel and power winch to deploy.
Gravity Corer, Phleger Corer (3.5 cm I.D., ≤ 50 cm long)	Deep lakes and rivers; semi-consolidated sediments	0 to 50	≤ 0.48	• Reduces risk of sample contamination • Maintains sediment integrity relatively well • Penetrates with sharp cutting edge	• Requires careful handling to avoid sediment spillage • Requires repetitive and time-consuming operation and removal of liners due to small sample size
Gravity Corer, Kajak-Brinkhurst Corer (5 cm I.D., ≤ 70 cm long)	Deep lakes and rivers; Soft fine-grained sediments	0 to 70	≤ 1.37	• Collects greater volume than the Phleger Corer.	• Same as Phleger Corer
Benthos Gravity Corer (6.6, 7.1 cm I.D. ≤ 3 m long)	Soft, fine-grained sediments	0 to 3 m	≤ 10.26	• Retains complete sample from tube because the core valve is fitted to the core liner • Fins promote vertical penetration	• Requires weights for deep penetration so the required lifting capacity is 750 to 1,000 kg • Requires vertical penetration • Compacts sediment sample
Alpine Gravity Corer (3.5 cm I.D.)	Soft, fine-grained, semi-consolidated substrates	≤ 2 m	≤ 1.92	• Allows different penetration depths due to interchangeable steel barrel	• Lacks stabilizing fins for vertical penetration • May penetrate non-vertically and incompletely • Requires a lifting capacity of 2,000 kg • Disturbs sediment stratas and integrity • Compacts sediment sample
Piston Corers	Ocean floor and large deep lakes; Most substrates	3 to 20 m	5 - 40	• Typically recovers a relatively undisturbed sediment core in deep waters	• Requires lifting capacity of >2,000 kg • Piston and piston positioning at penetration may fail • Disturbs surface (0 to 0.5m) layer

Table E-2. Advantages and Disadvantages of Commonly Used Core Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995; USEPA/ACOE, 1998)

Device/ Dimensions	Use	Depth Sample (cm)	Volume Sample (L^3)	Advantages	Disadvantages
BMH-53 Piston Corer	Waters $\leq$ 2 m deep with extension rod; soft deposits	$\leq$ 2 m	$\leq$ 2	• Piston provides for greater sample retention	• Cores must be extruded onsite to other containers • Metal barrels introduce risk of metal contamination
Boomerang Corer (6.7 cm I.D.)	Ocean floor (up to 9,000 m deep)	1 m	3.52	• Requries minimal shipboard equipment so small vessels can be used	• Only penetrates 1.2 m • Requires calm water for recovery • Loses 10 to 20% of sample
Vibracorer (5.0 to 7.5 cm I.D.)	Continental shelf of oceans, large lakes; sand, silty sand, gravelly sand substrates	3 to 6 m	5.89 to 13.25	• For deep profiles it effectively samples most substrates with minimum disturbance • Can be used in over 20 m of water depth • Portable models can be operated from small vessels (e.g. 10 m long)	• Labor intensive • Assembly and disassembly might require divers • Disturbs surface (0 to 0.5 m) layer • Special generator may be needed • Heavier models require larger boat and power winch to deploy

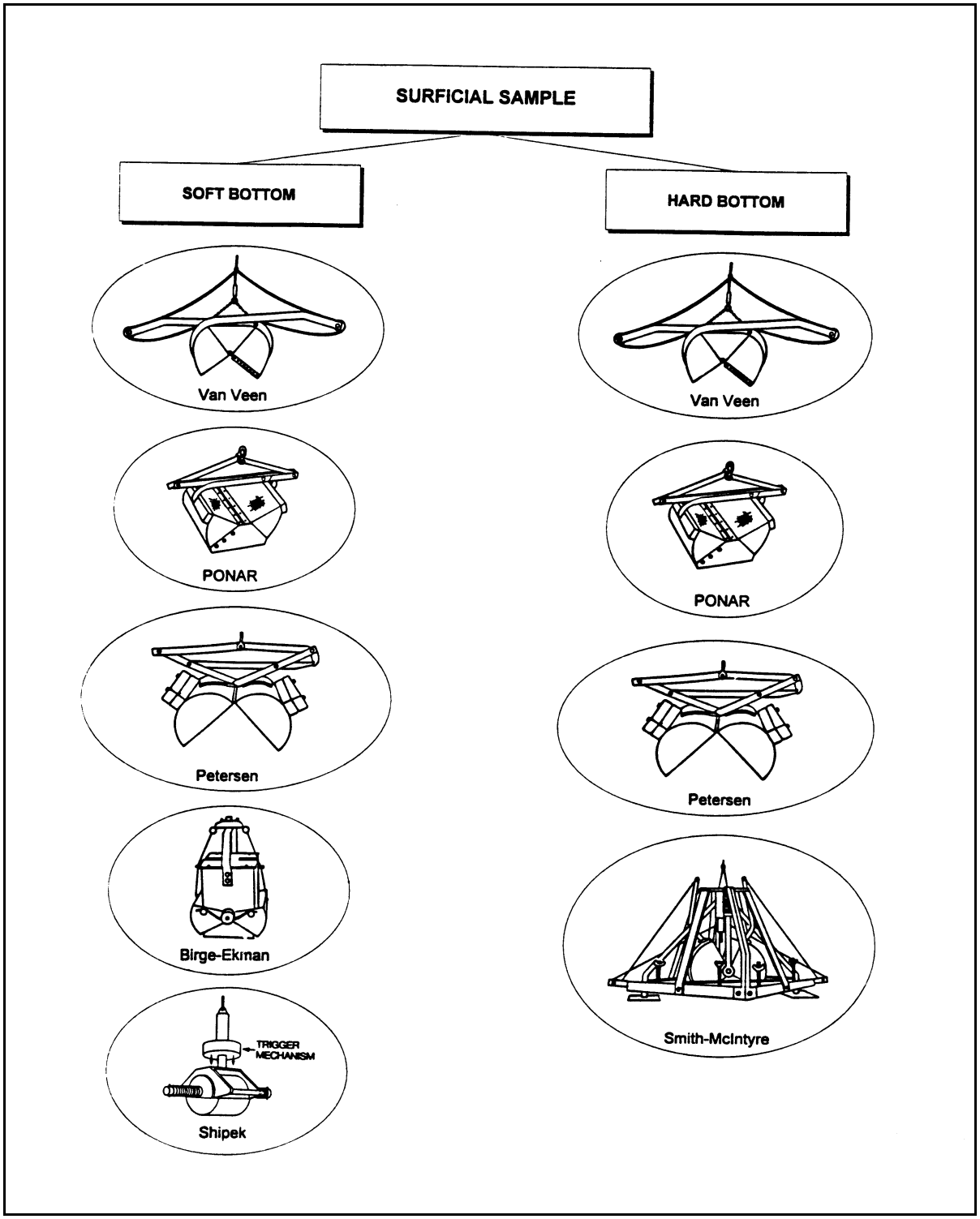

Figure E-1. Some recommended devices for collecting surficial sediments (drawings from Murdoch and Azcue 1995 and Fredette et al. 1990).

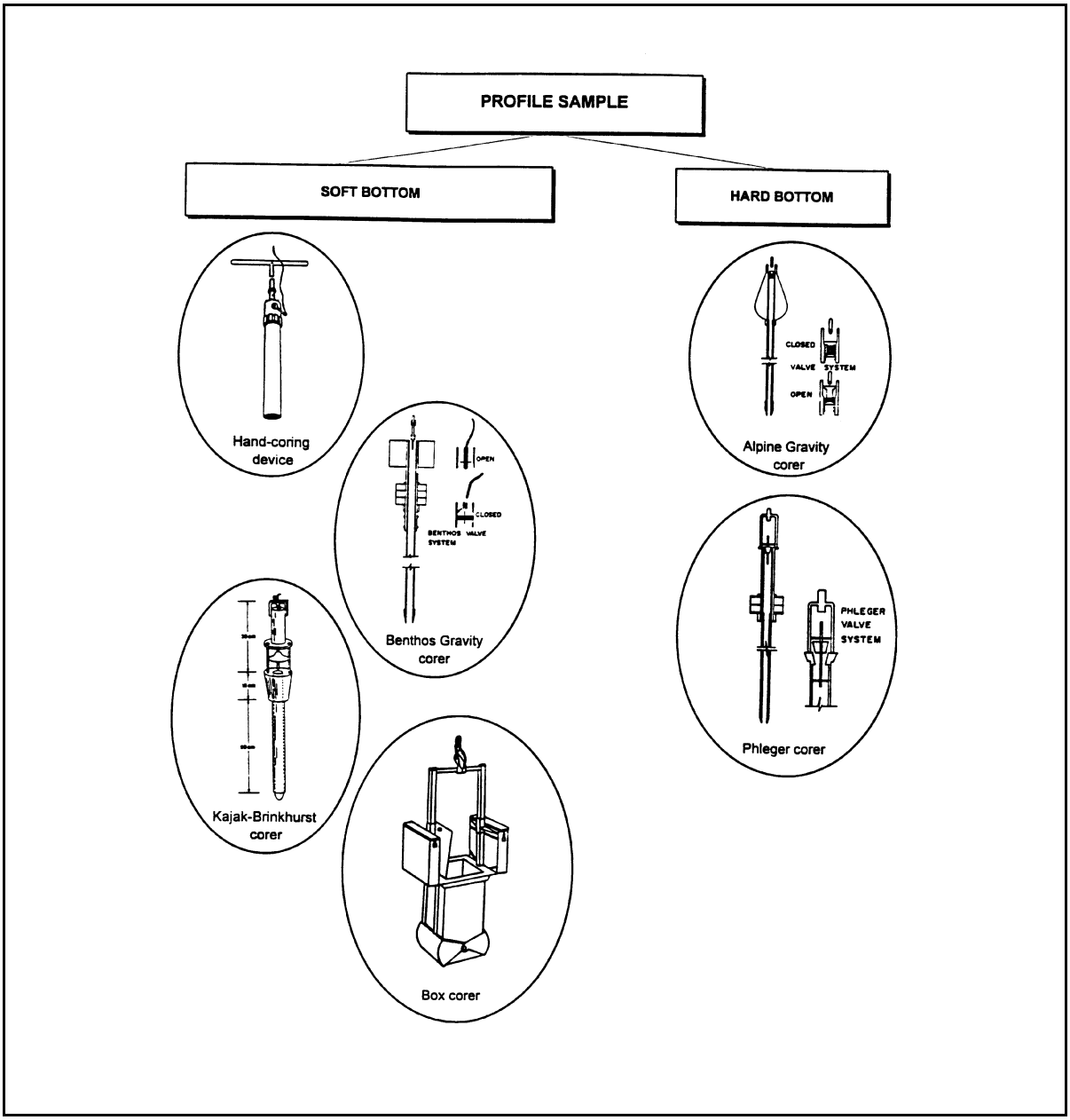

Figure E-2. Some recommended devices for obtaining sediment profiles (drawings from Murdoch and Azcue 1995 and Fredette et al. 1990).

APPENDIX F

EXAMPLES OF FIELD FORMS USED TO DOCUMENT STATION AND SAMPLE CHARACTERISTICS AND SAMPLE TRACKING

NOAA - Chesapeake Bay and Adjacent Tribs. Sediment Toxicity Study - Field Form

Strata	Site Number	Alternate		
Date		Time (local)		
ANALYSIS				
Metals	Organics	AVS	Chem-Grain Size	P450/microtox
Amphipod	Porewater	Benthos-comp.	Benthos-Biomass	Grain Sz&TOC
STATION LOCATION				
STATION COORDINATES				
GPS				
Latitude:	N			
Longitude:	W			
SEDIMENT DESCRIPTION				
Color:				
Texture:				
Odor/sheens:				
Benthic Organisms:				
WATER QUALITY				
Top			Bottom	
Temperature	Celsius		Temperature	Celsius
Salinity	ppt		Salinity	ppt
Dissolved Oxygen	mg/l		Dissolved Oxygen	mg/l
Conductivity	umhos		Conductivity	umhos
Water Depth	m or ft		Secchi Depth	m or ft
Sample Team				
OTHER COMMENTS				

Example of field form used by the Great Lakes National Program Office:

Field Sampling Log Sheet

Location and Core Information

Station Number:			**Water Surface Elevation**
Date			**Water Depth**
Time			**Core tube Length**
Primary GPS	**Latitude**		**Depth of Penetration**
	Longitude		**Length of Retrieved Core**
Secondary GPS	**Latitude**		**Loggers Initials**
	Longitude		**Samplers Initials**

Sample Intervals

Sample Number	Sample Interval	Physical Descritpion of Sample

Example of field form used for site remediation sampling at Naval bases:

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____ Sample ID No.: _____
Project No.: _____ Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date: / Time: / Method: / Monitor Reading (ppm):	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)

COMPOSITE SAMPLE DATA:

Date: / Method: / Monitor Readings (Range in ppm):	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

APPENDIX G

PHYSICO-CHEMICAL SEDIMENT CHARACTERIZATION

1. General Information

It is often necessary or desirable to determine certain physico-chemical characteristics of sediments in the laboratory, in conjunction with toxicity testing or chemical analysis for inorganic or organic contaminants. This characterization should include measurement of certain parameters known to mediate the availability of contaminants in sediment (ASTM, 2000f). Bulk chemical concentrations alone should not be used to evaluate bioavailability (USEPA, 1998). The following parameters are generally measured:

- pH (pore water)
- ammonia (pore water)
- total organic carbon
- particle size distribution (e.g., percent sand, silt and clay)
- percent water content
- salinity and hardness of pore water
- conductivity of pore water

Depending on the experimental design and/or study objectives, more extensive characterization may be necessary. Several additional characteristics which may assist in study implementation, data interpretation or QA/QC (i.e., assessing sediment integrity, artifact production, optimal extraction and test procedures) include: sediment biochemical oxygen demand (BOD), sediment chemical oxygen demand (COD), sediment oxygen demand (SOD), cation exchange capacity (CEC), Redox (Eh) or oxidation-reduction potential (ORP), total inorganic carbon, total volatile solids, acid volatile sulfides (AVS), simultaneously extracted metals (SEM), metals, synthetic organic compounds (pesticides, PCBs, PAHs, and TCDD-dioxin), oil and grease, petroleum hydrocarbons, dissolved organic carbon (DOC) in the pore water. Measurements of many sediment physicochemical characteristics use analytical techniques originally developed for soils and waters, and the literature should be consulted for details regarding recommended methodology (Black, 1965; USGS, 1969; Plumb, 1981; Page et al., 1982). The following sections provide rationale for making each type of sediment physicochemical measurement, along with brief descriptions of measurement techniques, and references for further information and specific procedures.

2. pH

Sediment pH is often one of the single most important factors controlling speciation and equilibria for many chemicals including sulfides, ammonia, cyanide, and metals, all of which ionize under the influence of pH. The USEPA ammonia water-quality criterion, for example, is dependent in part on pH because ammonia toxicity is largely governed by the unionized ammonia fraction which is pH-dependent (USEPA, 1999). Metal (Cd, Cu, Ni, Pb, and Zn) speciation and bioavailability are also known to be affected by pH (Schubauer-Berigan and Ankley, et al., 1991; Ho et al. 1999).

Generally, pH is measured using a pH meter consisting of a potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are submersed. General purpose process pH electrodes are available in a wide variety of configurations for in-line and submersion applications. Generally, electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers.

Plumb (1981) and Gonzalez (1995) described a method for measuring pH in sediment using a pH probe and meter. The probe was inserted into the sediment and pH directly measured after at least a 5 minute equibration time. Electrodes have also been used for direct measurements of pH in sediment pore water, or in a 1 to 1 mixture of sediment to water (Jackson, 1958). Direct measurement of sediment pH is also possible using electrodes with "spear tip" designs allowing for greater penetration into the sample (Burgess, personal communication). Detailed methods for measuring pH in water and sediment are also described by USEPA (1983;1986b;1987), in USEPA (1979), and in USEPA (1987), respectively.

3. Ammonia in Pore Water

Nitrogen, a nutrient associated with over-enrichment of aquatic environments, exists in several forms, including ammonia. Ammonia is highly soluble in water where it is found in an un-ionized form (NH_3) and in an ionized form as NH_4^+. The extent of ionization is dependent on pH temperature, and salinity (in seawater). Ammonia in sediments and pore water is generally the result of microbial degradation of nitrogenous organic material such as amino acids (Ankely et al., 1990). Pore water concentrations of ammonia as high as 50 mg/L have been measured in otherwise uncontaminated sediments (Murray et al., 1978; Kristensen and Blackburn, 1987), while ammonia in pore waters from contaminated sediments can range from 50 to more than 200 mg/L (Ankley et al., 1990; Schubauer-Berigan and Ankley, 1991).

The toxic effects of ammonia are generally considered to be associated with the un-ionized fraction (NH_3) rather than the ionic components (NH_4^+ and $NH_4SO_4^-$), which co-exist in equilibria. This equilibrium is highly dependent on pH, temperature, pressure, salinity, and ionic concentrations of ammonia. The toxic un-ionized ammonia fraction can be calculated using known total ammonia values and measurements of pH, pressure, salinity, and temperature as described by Whitfield (1978) and Thurston et al (1981).

USEPA (1983), and APHA (1995) describe five methods available to measure ammonia in the pore water:

- the titrimetric method
- the ammonia-selective electrode method
- the ammonia-selective electrode method using known addition
- the phenate method
- the automated phenate method.

A preliminary distillation step may be required if interferences are present (APHA, 1995). Interferences, e.g., sample constituents that interact with procedural reagents, are described in detail in the APHA (1995) and ASTM (2000g) methods. Once distilled, the sample can be analyzed using any of the methods listed above.

The distillation and titration methods are frequently used when ammonia concentrations are greater than 5.0 mg/L. The ammonia-selective electrode method is appropriate when concentrations range between 0.03 and 1400 mg NH_3-N/L. Ammonia readings are calibrated against ammonia standards. To verify meter readings, confirmatory subsamples can be preserved and analyzed for ammonia using the standard Nessler technique described in APHA (1995). For the phenate method, APHA (1995) recommends distillation with sulfuric acid when interferences are present (Bower and Holm-Hansen, 1980). The automated phenate method is suitable for pore waters with ammonia concentrations in the range of 0.02 and 2.0 mg NH_3-N/L.

Hach Company, Inc. (Loveland, CO) describes the USEPA approved Nessler/distillation method adapted from APHA (1995). This is a photometric procedure and has been modified for use with Hach photometers.

4. Total Organic Carbon Content (TOC)

The total organic carbon (TOC) content of sediment is a measure of the total amount of oxidizable organic material. TOC is the sum of dissolved organic carbon (DOC), particulate organic carbon (POC) or suspended organic carbon (SOC), and colloids. TOC is an important parameter to measure in sediments because it is a major determinant of nonionic organic chemical bioavailability (DiToro et al., 1991). Metal bioavailability is also affected by the amount of TOC present in sediments. TOC is usually expressed as a percentage of the bulk sediment and is used to normalize the dry-weight sediment concentration of a chemical to the organic carbon content of the sediment. USEPA Equilibrium Partitioning Guidelines estimate bioavailability as a function of contaminant concentration sorbed to sediment organic carbon and contaminant concentration in the pore water under equilibrium conditions (USEPA, 1998). Recently, the presence of soot carbon from the combustion of organic carbon (e.g., fossil fuels) has been recognized as a fraction of the TOC in sediment. Soot carbon may alter the geochemistry and bioavailability of some organic contaminants (Gustuffson et al., 1997).

The organic carbon content of sediments has been measured using several methods including: wet oxidation titration, modified titration, and combustion after removal of carbonate by the addition of HCl and subsequent drying. USEPA methods(1986b; 1987), including SW-846 and 430/9-86-004, are often used to measure TOC. Plumb (1981) recommends one of two methods to separate organic from inorganic carbon before analyzing for TOC: (a) ignition and using HCl as the acid for pre-treating sediment, or (b) differential combustion, which uses thermal combustion to separate the two forms of carbon.

EPA/ACOE guidance (1998) recommends that TOC analyses be based on high-temperature combustion rather than on chemical oxidation, because some classes of organic compounds are not fully degraded by combined chemical and ultraviolet oxidation techniques. Inorganic carbon (e.g., carbonates and bicarbonates) can be a significant proportion of the total carbon in some sediments. Therefore, samples should be treated with acid to remove the inorganic carbon prior to TOC analysis. The procedure described by the Puget Sound Estuary Program (PSEP, 1997a) is recommended for TOC analysis because this method uses high-temperature combustion using an induction furnace. USEPA recommends a similar method using catalytic combustion and non-dispersive infrared detection (Leonard, 1991) for quantifying TOC.

U.S. EPA acknowledges that several methods for measuring the total organic carbon (TOC) content of sediments exist (See Nelson and Sommers 1996 for a review). However, acceptable methods must at a minimum include the following steps:

Sample Collection

- Sediment samples are collected and stored in non-organic containers

Sample Preparation

- Each sediment sample must have macroscopic pieces of shells (e.g., > 1 mm) removed and then be pulverized and homogenized

- Each sediment sample must be treated by direct addition with a strong non-oxidizing acid (e.g., HCL) for ~18 hours to remove inorganic carbon; sample pH should be ≤2 after acidification (Yamamuro and Kayanne, 1995)

- Each sediment sample must be oven dried following acid treatment (60 - 70° C) (Weliky et al., 1983; Yamamuro and Kayanne, 1995)

- Each sediment sample must be stored in a desiccator until analysis

- As noted, desiccation is highly recommended, however if not possible a pre- and post-acidification sample weight should be performed to correct for water uptake (Hedges and Stern, 1984).

Sample Analysis

- Each post-acidification sediment sample must be analyzed using acceptable instrumentation

- Instrumentation should have a detection limit of approximately 100 mg/Kg

- Quantification of organic carbon should be based on a sample's weight, measured before acidification.

Sample QA

A rigorous QA program should be in place to insure acceptable data quality, this may include:

- Performance of duplicate analysis on a subset of samples with the relative percent difference (RPD) between replicates below 30%

- Performance of analyses on certified standard reference materials (SRM) (e.g., NIST)

5. Particle Size Distribution (Percent Sand, Silt, and Clay)

Particle size is used to characterize the physical characteristics of sediments. Because particle size influences both chemical and biological characteristics, it can be used to normalize chemical concentrations and account for some of the variability found in biological assemblages (USEPA 1998) or in laboratory toxicity testing (USEPA, 2000d; Hoss et al., 1999). Particle size can be characterized in varying detail. The broadest divisions that generally are considered useful for characterizing particle size distributions are percentages of gravel, sand, silt, and clay. However, each of these size fractions can be subdivided further so that additional characteristics of the size distribution are determined (PSEP, 1996).

Particle size determinations can either include or exclude organic material. If organic material is removed prior to analysis, the "true" (i.e., primarily inorganic) particle size distribution is determined. If organic material is included in the analysis, the "apparent" (i.e., organic plus inorganic) particle size distribution is determined. Because true and apparent distributions may differ, detailed comparisons between samples analyzed by these different methods are questionable. Therefore, if comparisons among samples between studies is desired, sediment particle size should be measured using consistent methods (PSEP, 1996).

Sediment particle size can be measured by a number of different methods (Allen, 1975; Plumb,1981; PSEP, 1996; ASTM, 2000a). The best method will depend on the particle properties of the sample (Singer et al., 1988). Particle size distribution is often determined by either wet sieving the sample (USEPA, 1979; Plumb, 1981; PSEP, 1996; Singer et al., 1988), the hydrometer method (Day, 1965; Patrick, 1958), the pipet method (USGS, 1969; Rukavina and Duncan, 1970), settling techniques (Sandford and Swift, 1971), and X-ray absorption (Duncan and Lattaie, 1979; Rukavina and Duncan, 1970). The pipet method may be superior to the hydrometer method (Sternberg and Creager, 1961). Combinations of multiple methods may provide refined measurements of particle size distribution. Gee and Bauder (1986) used sieving and pipetting after soluble salts were removed. Gonzalez (1995) used a combination of sieve and hydrometer methods. Folk (1968) and Buchanan (1984) discuss additional methods to measure particle size.

Recommended methods for measuring sediment particle size distribution are those of PSEP (1996) and USEPA (1995). Percent gravel, sand, silt, and clay are determined as apparent distribution using a minimum sediment sample size of 100 g taken from a homogenized sediment sample (see Section 4.4). Organic matter should be removed prior to analysis by oxidation using hydrogen peroxide. Wet-sieving followed by dry sieving (mechanical shaking) separates the two coarse particle size groups. The silt-clay fraction is subdivided using a pipet technique that depends upon the differential settling rates of the two different particle size fractions. All fractions are dried to a constant weight. Cooled samples are stored in a desiccator and weighed.

To obtain an accurate determination of particle sizes for the fine fraction, the Coulter (particle size) counter method may be employed (McCave and Jarvis, 1973; Vanderpleog, 1981). This method gives the fraction of particles with an apparent spherical diameter. In a review of the available methods, Swift et al. (1972) found the Coulter counter method to be the most versatile method overall; however, it does not provide settling information. Another potential method for determining the particle size distribution of a very fine fraction is through the use of electron microscopy (Leppard et al., 1988). Collection techniques for very fine material can result in aggregation of larger colloidal structures (Leppard, 1986; Leppard et al., 1988). In general, particle settling methods are preferred to sediment sizing methods.

6. Percent Water or Moisture Content

Water content is a measurement of sediment moisture usually expressed as a percentage of the whole sediment weight. It is known to influence toxicity and is used to aid in the interpretation of sediment quality investigations. Sediment moisture content is measured as the difference between wet weight of the sediment and dry weight following oven drying at 50 to 105°C to a constant weight. Percent water is used to convert sediment concentrations of substances from wet-weight to a dry-weight. Methods for determining moisture content are described by Plumb (1981) and Vecchi (1999). Additional methods are provided in USEPA (1987).

7. Salinity of the Pore Water (Marine Sediments)

Salinity is a measure of the mass of dissolved salt in a given mass of solution. The most reliable method to determine the true or absolute salinity is by complete chemical analysis. However, this is time consuming and costly. Therefore, indirect methods are more suitable. Indirect methods include conductivity, density, sound speed, or refractive index (APHA, 1995). Salinity is then calculated from the empirical relationship between salinity and the indirect measurement. Conductivity measurements have the greatest precision, but respond only to ionic solutes (APHA, 1995). Density measurements respond to all solutes. APHA (1995) recommends the electrical conductivity method,

because it is sensitive and easily performed. APHA (1995) also recommends the density method, using a vibrating flow densitometer. USEPA (1986) methods should also be consulted.

A salinity refractometer can be used for quick readings of salt density in solutions such as sea water. These refractometers are easy to read, non-corrosive and lightweight. They have dual scales and an adjustable focus. Temperature and non-temperature compensating refractometers are available. Most refractometers are accurate to 1 ppt and read specific gravity (1.000 to 1.070 in .001 divisions) and parts per thousand (0-100 in 1 ppt divisions).

8. Conductivity of the Pore Water (Fresh Water Sediments)

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability is dependent on the presence of ions in the solution, the concentration of the ions, their mobility and valence, and temperature. Solutions of inorganic compounds are usually good conductors while those of organic compounds are usually poor conductors. Conductivity is enhanced by calcium, potassium, sodium, and magnesium chlorides and sulfides.

Meters can be used to measure the degree to which electrical current can travel through water. The unit of measure is 1 mS/m = 1 millisiemens/meter or 1 µS/cm = 1 microsiemens/cm. The reading indicates the amount of ions in the water. While traditional chemical tests for hardness measure calcium and magnesium, they fail to provide an indication of other ions (e.g., sodium). The conductivity meter provides a much better measure of ionic strength.

9. Acid Volatile Sulfide (AVS)

Measurement of acid volatile sulfides (AVS) and simultaneously extracted divalent metal (SEM) concentrations associated with AVS extraction can provide insight into the bioavailability of metals in anaerobic (anoxic) sediments (DiToro et al., 1990; Ankley et al., 1996). AVS is the reactive solid-phase sulfide fraction that is extracted by cold hydrochloric acid. AVS appears to affect the bioavailability of most divalent metal ions as the sulfide ions have a high affinity for divalent metals. This affinity results in the formation of insoluble metal sulfides with greatly reduced bioavailability. AVS concentrations in freshwater and marine sediments can range between < 0.1 and > 50 µmol AVS/g of sediment (DiToro et al., 1990).

The bioavailability of metals in sediments has been predicted by comparing the molar concentration of AVS to the molar concentration of SEM (methods described below). If AVS is greater than SEM, the metals are bound in sulfide complexes with greatly limited bioavailability. However, if AVS < SEM, metals may or may not be toxic due to other controlling factors (e.g., TOC).

The easily extractable sulfide fraction can be measured using the acid purge and trap technique. The sample sulfide is solubilized in cold hydrochloric acid. The analytical method involves conversion of sulfides to aqueous H_2S. This may be measured with a sulfide probe or by following a wet chemistry method. In the latter method, silver sulfide is precipitated in a gas-tight assembly and flushed with nitrogen to eliminate oxidation. The precipitate is filtered, dried, and weighed. The weight is compared with the weight obtained from a non-acidified sample, and the difference is attributed to the AVS fraction (DiToro et al., 1990).

10. Simultaneously Extracted Metals

A model for predicting toxicity from divalent trace metals (DiToro et al., 1990) is based on the binding of these metals to AVS. Where the sum of the moles of the SEM, including Ag, Cd, Cu, Ni,

Pb, and Zn is exceeded by the molar concentration of AVS, the metals are insoluble and largely unavailable to biota. The extraction of AVS and metals should be achieved using a single methodology to ensure that recoveries associated with each measure are consistent. Simultaneous extraction improves the efficiency of the methodology.

SEM can be measured in filtered aliquots by atomic absorption methods (DiToro et al., 1990). Recent SEM analysis methods use inductively coupled plasma atomic emission spectrometry (ICP-AES; Berry et al., 1999). Other methods for analysis of metals are described in Section 11 below.

11. Metals

Low levels of trace metals occur naturally in the environment but highly elevated levels in sediment are generally associated with anthropogenic contaminant loads. Metals are partitioned in sediments as soluble free ions, soluble organic and inorganic complexes, easily exchangeable ions, precipitates of metal hydroxides, precipitates with colloidal ferric and manganic oxyhydroxides, insoluble organic complexes, insoluble sulfides, and residual forms (Gambrell et al., 1976).

Current instrument methods available for the analysis of trace metals include electrochemistry (e.g., differential pulse polarography), spectrophotometry (e.g., silver diethyldithiocarbamate), atomic absorption spectrophotometry, atomic emission spectrophotometry, x-ray fluorescence (XRF), and neutron activation (PSEP 1997c). The most commonly used instrumental method to analyze sediments for metals is atomic absorption spectrophotometry (PSEP, 1997c). Inductively coupled plasma mass spectrometry (ICP-MS) or ICP-AES allow for simultaneous determination of many metals at sub-ppb levels with little pretreatment (Crecelius et al., 1987; Berry et al., 1999).

The concentration of salt in marine or estuarine samples may interfere with metals analyses (USEPA/ACOE, 1998). Therefore, acid digestion and atomic absorption spectroscopy should be coupled with an appropriate technique to control for this interference. Methods in USEPA (1986b) are recommended for the analysis of mercury in sediments and EPRI (1986) methods are recommended for the analysis of selenium and arsenic. EPA methods for cadmium, hexavalent chromium, copper, lead, mercury, nickel, selenium, silver, and zinc are described by USEPA (1986b). PSEP (1997c) suggests that mercury can be extracted using vacuum distillation and analyzed by gas chromatography/mass spectrophotometry.

12. Synthetic Organic Compounds (Pesticides, PCBs, TCDD-Dioxin)

Analytical techniques for measuring organic compounds require five general steps: drying the sample, extraction, drying the extract, clean up of the extract, and analysis of the extract. PSEP (1997b) recommends centrifugation or sodium sulfate to dry the sample and a solvent extraction, with application of shaker/roller, or sonication. Sample drying with sodium sulfate is recommended for samples weighing approximately 10 grams (after overlying water is decanted). The sediment and sulfate mixture is extracted and the extract is processed (MacLeod et al., 1985).

Soxhlet® extraction (USEPA, 1986b) involves distillation with a solvent such as acetone, dichloromethane/methanol (2:1), dichloromethane/methanol (9:1), and benzene/methanol (3:2). USEPA (1983) recommends sonication with solvent mixtures and a 30-gram subsample of sediment.

Drying the extract can be accomplished through separatory funnel partitioning as needed to remove water and sodium sulfate or by using a Kuderna-Danish apparatus and rotary evaporation with purified nitrogen gas for concentration to smaller volumes (PSEP, 1997c). Using the separatory funnel partitioning method, the wet sample is mixed with methanol and centrifuged. The supernatant

is decanted and extracted later. Extraction of the sample is continued using less polar solvents and the water/methanol and solvent extracts are combined and dried.

According to PSEP (1997c) elemental sulfur can be removed from the sediment sample with vigorous mechanical agitation using a Vortex or Genie® or using activated copper. Organic interferences can be removed with gel permeation chromatography (GPC) described in USEPA (1983), bonded octadecyl columns (PSEP, 1997c), high performance liquid chromatography (HPLC) described by Metro (1981), silica gel (PSEP, 1997c), or alumina (USEPA, 1983). Instrumental analyses for volatiles and semivolatiles and pesticides/PCBs are performed using gas chromatography/mass spectrophotometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD), respectively (PSEP, 1997b; Burgess and McKinney, 1997).

13. Oil and Grease

Oil and grease tests for sediments measure material recovered that is soluble in a nonpolar solvent under acidic conditions. Oil and grease compounds are substances such as hydrocarbons, vegetable oils, animal fats, waxes, soaps, and greases. Many solvents can dissolve other substances (e.g. sulfur compounds, organic dyes, and chlorophyll). Therefore, oil and grease is operationally defined by the solvent used and the analytical method used to perform the analysis. There are two basic methods used to analyze oil and grease: the gravimetric technique and the IR (infrared spectrophotometer) technique. Both are described by PSEP (1996).

14. Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons

Petroleum hydrocarbons are oil and grease constituents which remain in solution after contact with silica gel. Petroleum distillates, also called hydrocarbons or petrochemicals, refer to a broad range of compounds which are extracted by distillation during the refining of crude oil. During the fractional distillation of petroleum, crude oil is heated to allow various compounds to turn from liquid into gas and then captured as they rise, cool, and condense. Lighter, more volatile compounds rise higher before they condense and are collected on distillation trays. Heavier, less volatile compounds such as diesel fuel and oil are collected on lower distillation trays. Waxes and asphalts are collected from the bottom after the other products have volatilized.

Petroleum distillates contain both aromatic hydrocarbons (carbon rings) and aliphatic hydrocarbons (straight carbon chains). The chemical structure of the hydrocarbon largely defines the nature and behavior of these compounds. Aromatic hydrocarbons are the most toxic compounds found in petroleum products. Most aromatic hydrocarbons are chronic toxins and known carcinogens. Aromatic compounds are found in all crude oils and most petroleum products. Many aromatic hydrocarbons have a pleasant odor and include such substances as naphthalene, xylene, toluene, and benzene. Aliphatic hydrocarbons are flammable and may be explosively flammable. Aliphatic hydrocarbons include methane, propane, and kerosene.

Aromatic and aliphatic hydrocarbons were analyzed in sediments by Page et al. (1995a, b). Sediment samples were spiked with the appropriate surrogates, mixed with equal amounts of sodium sulfate to dry the samples, and extracted with a methylene chloride acetone mixture (Method 3550, USEPA, 1986b). The concentrated extracts were partitioned on an alumina column into saturated and unsaturated hydrocarbon fractions (Method 3611, USEPA, 1986b). The fractions were concentrated using the appropriate pre-injection volume, spiked with the appropriate internal standards, and analyzed by gas chromatography with flame ionization detection (GC/FID) and gas chromatography with mass spectrometry detection (GC/MS) operating in the selected ion monitoring (SIM) mode. The method of internal standards (Method 8000, USEPA, 1986b) using the average relative response

factors generated from the linear initial calibration was used to quantify the target compounds. All data were corrected for the recovery of the appropriate surrogate compound. Their relative abundances could then be used for identification and quantification purposes.

TPH (total petroleum hydrocarbons) and PAH (polycyclic aromatic hydrocarbons) have also been analyzed by first acidifying the sample with concentrated hydrochloric acid and then extracting hydrocarbons with a mixture of methanol and hexane. The hexane extracts were then spiked with an internal standard and analyzed by GC-FID for TPH content and by GC/mass spectrometry (MS) for PAH analysis.

Kaplan et al. (1996) extracted hydrocarbons using anhydrous Na_2SO_4 with methylene chloride and sonication. The total solvent extract was then concentrated with Kuderna-Danish equipment. The concentrate was further concentrated using a gentle stream of dry nitrogen. An aliquot was then injected directly into the gas chromatography.

15. Total Sulfides

Total sulfides represent the combined amount of acid-soluble H_2S, HS^-, and S^{2-} in a sample. Sulfides are often measured because they are common in some sediments, particularly those that are anoxic, and they can be toxic to aquatic organisms. PSEP (1996) describes a method to measure total sulfides in sediments. Oxygen is removed from the sample using nitrogen gas, methyl orange and hydrochloric acid is added, and the mixture is heated. Amine solution and iron chloride are added to develop a colorimetric reaction product and sample absorbance is measured spectrophotometrically.

Methods for measuring sulfides in aqueous samples include: potentiometric methods described by ASTM (2000e) and APHA (Method 4500, 1995). Sulfide ions are measured using a sulfide ion-selective electrode in conjunction with a double-junction, sleeve type reference electrode (Phillips et al., 1997). Potentials are read using a pH meter or a specific ion meter having a direct concentration scale for the sulfide ion. Samples are treated with sulfide anti-oxidant buffer which fixes the solution pH at a high alkaline level and retards air oxidation of sulfide ion in solution. This ensures that the sulfide measured represents total sulfides as $S^=$ ion and rather than the HS^- or H_2S found at lower pH values (see pH, Section 2 in this Appendix).

APHA (Method 4500, 1995) provides qualitative as well as quantitative methods to determine aqueous sulfide concentrations. Qualitative methods include the antimony test, the silver-silver sulfide electrode test, the lead acetate paper test, and the silver foil test. Quantitative methods include the photometric method, the automated photometric methylene blue colorimetric methods, and the iodometric titration method for standardizing stock solutions.

16. Sediment Oxygen Demand (SOD)

Sediment can exhibit significant rates of oxygen uptake attributable to either: (1) a benthic ecosystem supported by soluble organic substances in the water column, (2) naturally occurring sediments derived from aquatic plants and animals, and (3) detritus discharged into the water body by natural runoff. When numerical modeling is required to predict dissolved oxygen concentrations, the rate of dissolved oxygen consumed by the benthic ecosystem is defined as the sediment (benthic) oxygen demand (SOD) in g O_2/m^2-day.

Two approaches for measuring SOD were reviewed by Truax et al. (1995) including *in-situ* respirometry and laboratory respirometry methods. Numerous techniques have been developed for each approach. Generally, in-situ methods are considered more credible than laboratory

measurements although both apply the same technique. A given amount of sediment is enclosed in a chamber with a known water volume and oxygen uptake is measured over time. The SOD rate is then calculated based on the area of the enclosed sediment, the volume of water in the chamber, and the rate of uptake.

In situ sediment oxygen demand measurement method were described by Uchrin and Ahlert (1985). A cylindrical respirometer, a dissolved oxygen probe with stirring mechanism, and a dissolved oxygen meter were used. Ambient dissolved oxygen was measured using the probe/meter as well as by using the Winkler method (APHA, 1995) in the laboratory to determine the effect of respiration on total dissolved oxygen uptake. The respirometer was deployed in a level area at the bottom of the water body. Dissolved oxygen were recorded initially and at 15-minute intervals thereafter to determine the SOD rate.

17. Sediment Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a measure of the dissolved oxygen consumed by microbial organisms while assimilating and oxidizing the organic matter in a sample (PSEP, 1996). The test is an empirical methodology in which standardized laboratory procedures are used to determine the relative oxygen uptake of environmental samples. The test measures the amount of molecular oxygen used during a specified incubation period to biochemically degrade organic material and to oxidize reduced forms of nitrogen (APHA, 1995).

Plumb (1981) described a method to analyze BOD in sediments using freshwater bacteria as a "seed" and buffered distilled water as dilution water. PSEP (1996) described an alternative procedure to analyze BOD in marine sediments using marine bacteria as the "seed" and filtered, oxygenated seawater as the dilution water. USEPA (1987) methods should also be consulted.

18. Sediment Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of organic matter content in a sample that is susceptible to oxidation by a strong chemical oxidant at elevated temperature and reduced pH. The test was devised to augment the biochemical oxygen demand test. Chemical oxygen demand can be related empirically to biochemical oxygen demand, organic carbon, or total volatile solids (PSEP, 1996).

PSEP (1996) described a method for analyzing sediment COD using a closed reflux/colorimetric method. DiChromate (Cr_2O_7) ions are used to oxidize organic matter to carbon dioxide and water and to provide oxygen. The dichromate ions remaining after the reaction are measured by titration and the amount of oxygen consumed is then calculated.

Four standards procedures for measuring COD in water are available in APHA (1995): the open reflux method, the closed reflux method, the titrimetric method, and the closed reflux/colorimetric method. USEPA (1983) methods for the colorimetric and titrimetric method are described in USEPA (1979). Semi-automated methods are described in USEPA (1993).

Hach (Loveland, CO) has modified the EPA approved dichromate reflux method and the reactor digestion method. The methods are photometric and are adapted for use with Hach photometers.

19. Cation Exchange Capacity of Sediments

Cation exchange capacity (CEC) is a parameter that provides information relevant to metal bioavailability studies (Black, 1965). Cations or positively charged elements (such as calcium, magnesium, hydrogen, and potassium), are attracted to negatively charged surfaces of clay and organic matter. There is a continuous exchange of cations between sediment and water. CEC is a measure of the sediment's ability to retain cationic elements. It is also a measure of clay activity and mineralogy, which is used to calculate mineralization rates, leaching rates, and to predict interactions with contaminants. The degree of CEC is dependent on the kind and amount of suitable surfaces such as organic matter and clay. High cation exchange capacities are associated with high clay contents and high organic matter and changes in CEC are typically associated with changes in organic carbon content and pH of the sediment. Organic matter generally supplies a greater number of exchange sites than clay particles.

Various methods have been recommended to determine bioavailable fractions of metals in sediments (Chao and Zhou, 1983; Crecelius et al., 1987; Kersten and Forstner, 1987; DiToro et al., 1990). CEC can be measured by treating samples with ammonium acetate so that all exchangeable sites are occupied by NH_4^+ ion, digesting the samples with sodium hydroxide during distillation, and titrating to determine the ammonium ion concentration. The amount of exchangeable cations are expressed as milliequivalents of ammonium ion exchanged (meq) per 100 g of dried sample. More detailed methods are provided in Bascomb (1964), Black (1965), Klute (1986), and USEPA (1986b).

20. Redox Potential (Eh) of Sediments

Redox (Eh) is a measure of the oxidation-reduction potential (ORP) of sediments. Measurements of Eh are particularly important for metal speciation and for determining the extent of sediment oxidation. Eh values below approximately -100 millivolts would indicate biologically important sulfide concentrations. Some trace metals form insoluble complexes with sulfides. These metal-sulfide complexes bind the metals in a form that is not bioavailable. Since free ionic metals are generally thought to possess the greatest toxicity potential, it is important to understand conditions which control binding dynamics, such as pH and Eh.

Potentiometric measurements of Eh using a millivolt reader can be obtained with a platinum electrode relative to a standard hydrogen electrode (Plumb, 1981). APHA (1995) does not recommend the standard hydrogen electrode as it is fragile and impractical. Instead, their method uses a silver-silver-chloride or calomel reference electrode. APHA (1995) recommends a graphite rather than platinum electrode for sediments. Once the Eh equilibrium is reached, the difference between the platinum or graphite electrode and the reference electrode is equal to the redox potential of the system. For a more detailed explanation on how to calculate the Eh potential see APHA (1995). Gonzalez (1995) also describes a detailed method that can be used to measure sediment Eh.

There are a number of problems associated with the accurate measurement and interpretation of Eh in sediments, particularly in marine sediments. Therefore, considerable attention should be paid to the use of proper equipment and techniques. Some of the problems identified by Whitfield (1969) and Mudroch and Azcue (1995) include measurement inaccuracy due to disturbance of the sediment sample during insertion of the electrode, instability and poor reproducibility of the measurements and differential responses of platinum electrodes under different environmental conditions. A comprehensive description of the limitations of sediment Eh measurement is beyond the scope of this document. Rather, it is recommended that published studies on the problems associated with measuring and interpreting sediment Eh be consulted before any attempt is made to measure these parameters in sediment samples (Berner,1963; Morris and Stumm, 1967; Whitfield, 1969; Tinsley,

1979; Bates, 1981). The recommended procedure for measuring pH and Eh in the field are described in detail in the table below**:**

Table G-1. General procedures for measurement of Eh in bottom sediments (from Murdoch and Azcue 1995).

Equipment and solutions used in the measurements: • A portable, battery-operated pH/Eh meter, batteries, and a power cord for recharging the meter. • Combination glass and platinum electrodes or other electrodes suitable for the measurements. • Plastic test-tube-shaped containers or other containers for storing the electrodes in solutions during transport in the field. • Commercially-available or laboratory-prepared pH buffer solutions (pH 4 and 7) in plastic bottles with lids. • Freshly-prepared solution for calibration of Eh electrode in a plastic bottle with a tight lid. • Freshly-prepared solution of saturated potassium chloride for storage of the electrodes. • Other solutions necessary for proper functioning of electrodes as outlined by manufacturers. • Distilled water and wash bottle for storing and rinsing the electrodes between measurements. • Several small and larger plastic beakers for holding solutions, rinsing electrodes, etc.. • Support stands, rods, clamps to secure electrodes in solutions and during measurements. • Large plastic containers for storage and transport of used buffers and Eh-calibration solutions. • Notebook and pens, soft paper tissue.
Preparation of equipment before the field trip: • Check batteries of the portable pH/Eh meter and replace/recharge them, if necessary. • Prepare calibration solutions. • Check and test the pH and Eh electrodes. • Mark the electrodes vertically at desired intervals for insertion into the sediment samples. • Store the electrodes according the manufacturers instructions. • Pack all equipment for transport to the field and take spare electrodes if available.
Measurements in the field: • Allocate a space where measurements will be carried out. Within this space, all equipment should be assembled, checked for proper functioning, and prepared for measurement of the first sample. • Place grab sampler and sediment cores with recovered sediment in such a way that they will remain steady without disturbing the sediment samples during the measurements. • Insert electrodes carefully into the undisturbed sediment samples to avoid any air. contamination, particularly around the Eh electrode. Care must be taken not to generate any open space between the electrode and the sediment. Proper insertion of the electrode without disturbing the sediment is the most important step in measuring the Eh. • Insert electrodes into the sediment to the depth marked. Switch the pH/Eh meter to the pH scale and the value recorded within 1 minute after inserting the electrode into the sample. Switch the meter to the mV scale for recording the Eh value. The potential usually drifts considerably over the first 10 to 15 minutes, and then stabilizes. After stabilization, record the mV value. In measuring Eh of sediments from waters with low ionic strength, such as most freshwater bodies, it is recommended to “acclimatize” the electrodes in the water prior to measurement, particularly the electrodes that were stored in saturated potassium chloride solution. This will reduce the drifting of the potential after inserting the electrode into the sediment. • Remove both electrodes, wash them with distilled water to remove all adhering sediment particles, and dry them gently with a soft paper tissue. • Calibrate the electrodes after each five measurements. The electrodes may need less frequent calibration if pH and Eh are being measured in a sediment core.

21. Total Inorganic Carbon

Inorganic carbon has been measured as a complement to microbial activity (Bregnard et al., 1996), to determine the fate of an organic contaminant in biodegradation studies (West and Gonsior, 1996), and to determine the % carbon unaccounted for in fate transport predictions of hydrophobic contaminants (Tye, et al., 1996). Often the total inorganic carbon (TIC) fraction in samples is many times greater than the TOC fraction and presents an interference in the measurement of TOC. There are several options to eliminate TIC interferences when trying to measure TOC. One option is to compensate for the IC interference by measuring total carbon (TC) and total inorganic carbon (see Section 4 in this Appendix). The difference between the two is the TOC.

TIC is determined by acidifying the sample to convert the inorganic carbon (i.e., carbonates, bicarbonates, and dissolved CO_2) to carbon dioxide. Carbon dioxide is purged from the sample and then detected by a non-dispersive infrared detector (NDIR) calibrated to directly display the mass of carbon dioxide measured. This mass is proportional to the mass of TIC. Other instrumentation for the analysis of TIC is described in West and Gonsior (1996) and Tye et al. (1996).

22. Total Volatile Solids (TVS)

Total volatile solids represent the fraction of total solids that are lost on ignition at a higher temperature than that used to determine total solids. Total volatile solids are used as a crude estimate of the amount of organic matter in total solids (PSEP, 1996). In this regard, total volatile solids are often measured instead of, or in addition to, organic carbon content.

Total volatile solids are operationally defined by ignition temperature. Total volatile solids content does not always represent the organic content of a sample because some organic material may be lost at the drying temperature and some inorganic material (e.g, carbonates, chlorides) may be lost at the ignition temperature. Because of the temperature dependence of total volatile solids, valid interstudy comparisons require the use of standardized drying and ignition temperatures (PSEP, 1996).

Total volatile solids measurements are generally made by igniting the sediments at 550 ± 10°C until a constant weight is achieved and reporting the percent ash-free dry weight (McLeese et al., 1980; APHA, 1995; Keilty et al., 1988a). Plumb (1981) and PSEP (1996) describe standard methods for determining the total volatile solid content of sediments. Additional methods are provided in USEPA (1987).

23. Dissolved Organic Carbon in Pore Water

Dissolved organic carbon (DOC) often consists of humic substances and is the fraction of the organic carbon pool that is dissolved in water and passed through a 0.45 µm glass fiber filter. DOC is an indicator of the chemically reactive organic fraction and accurately measures the dissolved organic load. Sediment pore waters can be rich in humic acids. Fifty to 90% of the pore water DOC can be colloidal which is a significant factor because organic chemicals will preferentially partition to pore water DOC (Resendes et al., 1992; Burgess et al., 1996).

Hermann (1996) and Gilek et al. (1996) measured DOC using a TOC apparatus and infrared detection of CO_2. Borga et al. (1996) measured DOC using atomic emission spectrometry (ECP-AES). The APHA (Method 5310, 1995) methods for total organic carbon which can be applied to the measurement of DOC are (a) the combustion-infrared method; (b) the persulfate-ultraviolet oxidation method; and (c) the wet-oxidation method. Adjustments for inorganic carbon interference may be required (see Section 21 in this Appendix).

24. Alkalinity and Hardness of the Pore Water (Fresh Water Sediments)

Alkalinity is defined as the acid-neutralizing (i.e., proton-accepting) capacity of water. It is the sum of all the titratable bases and a measure of the quality and quantity of constituents in the pore water that result in a shift in the pH toward the alkaline side of neutrality. The measured value may vary significantly with the pH end-point used. Studies have shown that effects of certain contaminants such as metals are influenced by alkalinity as it alters speciation and bioavailability.

APHA (1995) recommends a color-change titration method to measure alkalinity which is also described by ASTM (2000h). The sample is titrated with standard alkali or acid to a designated pH

and the endpoint is determined electrometrically or by the color change of an internal standard. In addition, ASTM (2000h) describes two additional methods: (1) a titration curve is developed to identify inflection points, a standard acid of alkali is added to the sample by small increments and pH is recorded after each addition, and the total volume of acid or alkali is plotted against the observed pH values; and (2) pH is determined, standard acid is added to lower the pH to 4.0 or less, the solution is boiled with hydrogen peroxide, and titrated while hot to the phenolphthalein endpoint or when cooled electrometrically with standard alkali to pH 8.2, the desired endpoint. The color-change titration method is most commonly used. Hach (Method 8202) has developed a portable water chemistry kit based on the APHA (1995) color-change titration method and an additional method using sulfuric acid with a digital titrator (Hach, Method 8203).

Hardness is the concentration of metallic cations, with the exception of alkali metals, present in water samples. Generally, hardness is a measure of the concentration of calcium and magnesium ions in water. Hardness is usually expressed as a calcium carbonate equivalent in mg/L. Like alkalinity, hardness alters speciation and bioavailability of certain contaminants particularly many metals.

AHPA (Method 2340, 1995) describes two methods to measure hardness: (1) the calculation method and (2) the EDTA titrimetric method. ASTM (2000i) describes the APHA (1995) EDTA titrimetric method. Calcium and magnesium ions in water are sequestered by the addition of EDTA. The endpoint of the reaction is measured by means of Chrome Black T[3], which is red in the presence of calcium and magnesium and blue when both are sequestered. APHA recommends the calculation method because it is more accurate. The method uses direct determinations of calcium and magnesium to determine hardness. Hach has developed portable water chemistry kits (Methods 8222, 8204, 8030, 8226, 8213, 8338, 8329) for a variety of hardness determinations using a spectrophotometer or titration methods with a decision tree for selecting the appropriate procedure. Three of the Hach methods (1992) were adapted from APHA (Method 2340, 1995): the buret and 0.020 N titrant method (8222); the ManVer 2 buret and 0.020 N titrant method (8226); and the buret titration method (8338). The APHA EDTA titration method is most often used.