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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.