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## Standard Guide for Selection and Application of Analytical Methods and Procedures Used during Sediment Corrective Action<sup>1</sup>

This standard is issued under the fixed designation E3163; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### INTRODUCTION

This guide discusses the selection and application of analytical methods and test procedures used during sediment programs. This guide provides a flexible, defensible framework for selection and application of analytical methods and testing protocols used in wide range of sediment programs. This guide is structured as a tool kit to support a tiered approach with procedures of increasing complexity as the user proceeds through the process. This guide provides information on key decision criteria and best practices to support the user in achieving intended sediment program objectives.

There are numerous technical decisions that must be made in the selection and application of analytical methods and testing protocols used during a sediment programs. It is not the intent of this guide to define appropriate technical decisions, but rather to provide technical support within existing decision frameworks. This guide is not intended to replace existing regulatory requirements or guidance, but rather to complement these programs. This guide encourages user-led collaboration with stakeholders, including analytical laboratories and testing service providers, in the selection and application of analytical methods and testing protocols used to support project-specific decision criteria for a particular sediment program. This guide recognizes the complexity and diversity of sediment programs and project objectives and provides appendixes to support a range of project applications. The appendixes are provided for additional information and are not mandatory for the use of this guide. ASTM standard guides are not regulations; they are consensus based standard guides that may be followed voluntarily.

### 1. Scope

1.1 This is a guide for the selection and application of a range of analytical methods and testing procedures that may be used during sediment programs, including physical properties testing, chemical analytical methods, passive sampling procedures, bioassays and toxicity testing, environmental forensics methods and procedures, and methods development procedures for sediment programs.

1.2 Sediment programs vary greatly in terms of environmental complexity, physical, chemical and biological characteristics, human health and ecological risk concerns, and geographic and regulatory context. This guide provides information for the selection and application of analytical methods and testing protocols applicable to a wide range of sediment programs.

<sup>1</sup> This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee E50.04 on Corrective Action.

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1.3 This guide describes widely accepted considerations and best practices used in the selection and application of analytical procedures used during sediment programs. This guide supports and complements existing regulations and technical guidance.

1.4 This guide is designed for general application to a wide range of sediment programs performed under international, federal, state and local environmental programs. This guide describes the selection and application of analytical methods and test procedures, not the requirements for specific regulatory jurisdictions. This guide compliments but does not replace regulatory agency requirements.

1.5 This guide may be used for a wide range of sediment programs, including programs with overlapping regulatory jurisdictions, programs without a clearly established regulatory framework, voluntary programs, Brownfield programs, and international programs. The users of this guide should be aware of the appropriate regulatory requirements that apply to sediment programs. The user should consult applicable regulatory agency requirements to identify appropriate technical decision criteria and seek regulatory approvals, as necessary, prior to

selection and application of analytical methods and test procedures to sediment programs.

1.6 This guide supports the collaboration of stakeholders, including project sponsors, regulators, laboratory service providers, and others, on the selection and application of analytical procedures to sediment programs. This guide highlights key considerations for designing sediment program data acquisition plans, including applicability and use limitations of analytical methods and test procedures, and data usability considerations. This guide recognizes the challenges inherent in selection and application of analytical methods and test procedures for sediment systems, as well as the challenges inherent in generating analytical data of sufficient sensitivity to meet regulatory criteria applied to sediment programs.

1.7 ASTM standard guides are not regulations; they are consensus standard guides that may be followed voluntarily to support applicable regulatory requirements.

1.8 Test methods, procedures, and guidelines published by ASTM, USEPA, and other U.S. and international agencies are used for sediment programs, many of which are referenced by this guide. However, these documents do not provide guidance on the selection and application of analytical methods and test procedures for sediment programs. This guide was developed for that purpose.

1.9 This guide may be used in conjunction with other ASTM guides developed for sediment programs.

1.10 The user of this guide should review existing information and data available for a sediment project to determine the most appropriate entry point into and use of this guide.

#### 1.11 *Table of Contents:*

	Section
Introduction	1
Scope	1
Referenced Documents	2
Terminology	3
Significance and Use	4
Physical Property Test Methods	5
Chemistry Analytical Methods	6
Passive Sampling Methods	7
Biological Test Methods	8
Environmental Forensics Analytical Methods	9
Analytical Method Development	10
Key Differences in Physical Properties of Sediment and Soil	Appendix X1
Guidelines for Collection of Sediment Samples for Physical Properties Testing	Appendix X2
Key Concepts in Sediment Stratigraphy for Physical Properties Testing	Appendix X3
Quick Reference Guide for Sediment Chemistry Analytical Method Selection	Appendix X4
Sampling Reference Guide for Sediment Chemistry Analytical Methods	Appendix X5
Critical Success Factors for Sediment Chemistry Analytical Programs	Appendix X6
Quick Reference Guide for Passive Sampling Method Selection	Appendix X7
Advantages and Limitations of Passive Sampler Types for Organic Compounds	Appendix X8
Methodologies and Equations for Determining Aqueous Chemical Concentrations from Passive Sampler Results	Appendix X9
Pros and Cons Evaluation of Biological Test Methods	Appendix X10
Decision Tree for Biological Testing Selection	Appendix X11
Species List for Biological Testing	Appendix X12

Section  
**Appendix X13**

Daubert Criteria to Guide the Selection and Application of Analytical Test Methods Used for Environmental Sediment Forensics  
References  
Bibliography

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.13 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D854 Test Methods for Specific Gravity of Soil Solids by Water Pycnometer
- D1498 Test Method for Oxidation-Reduction Potential of Water
- D1586 Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils
- D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
- D2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants
- D2487 Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)
- D2488 Practice for Description and Identification of Soils (Visual-Manual Procedures)
- D2937 Test Method for Density of Soil in Place by the Drive-Cylinder Method
- D2974 Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils
- D3213 Practices for Handling, Storing, and Preparing Soft Intact Marine Soil
- D4220/D4220M Practices for Preserving and Transporting Soil Samples
- D4318 Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils
- D4464 Test Method for Particle Size Distribution of Catalytic Materials by Laser Light Scattering
- D4643 Test Method for Determination of Water Content of Soil and Rock by Microwave Oven Heating
- D5084 Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter
- D5739 Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- D6169/D6169M** Guide for Selection of Soil and Rock Sampling Devices Used With Drill Rigs for Environmental Investigations
- D6913/D6913M** Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis
- D7263** Test Methods for Laboratory Determination of Density (Unit Weight) of Soil Specimens
- D7363** Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode
- D7928** Test Method for Particle-Size Distribution (Gradation) of Fine-Grained Soils Using the Sedimentation (Hydrometer) Analysis
- E1367** Test Method for Measuring the Toxicity of Sediment-Associated Contaminants with Estuarine and Marine Invertebrates
- E1391** Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing and for Selection of Samplers Used to Collect Benthic Invertebrates
- E1525** Guide for Designing Biological Tests with Sediments
- E1611** Guide for Conducting Sediment Toxicity Tests with Polychaetous Annelids
- E1688** Guide for Determination of the Bioaccumulation of Sediment-Associated Contaminants by Benthic Invertebrates
- E1689** Guide for Developing Conceptual Site Models for Contaminated Sites
- E1706** Test Method for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates
- E1850** Guide for Selection of Resident Species as Test Organisms for Aquatic and Sediment Toxicity Tests
- E2081** Guide for Risk-Based Corrective Action
- E2122** Guide for Conducting In-situ Field Bioassays With Caged Bivalves
- E2205/E2205M** Guide for Risk-Based Corrective Action for Protection of Ecological Resources
- 2.2 API Document.**<sup>3</sup>
- API RP40** Recommended Practices for Core Analysis, 1998
- 2.3 EPA Documents.**<sup>4</sup>
- USEPA Method 608** Organochlorine Pesticides and PCBs, SW-846 Compendium, 1984
- USEPA Method 680** Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS, SW846 Compendium, 1985
- USEPA Method 1613 Revision B** Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, SW-846 Compendium, 1994
- USEPA Method 1664 Revision B** n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, SW-846 Compendium, 2010
- USEPA Method 1668 Revision A** Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGS/HRMS, SW-846 Compendium, 2003
- USEPA Method 1668 Revision B** Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGS/HRMS, SW-846 Compendium, 2008
- USEPA Method 8082 Revision A** Polychlorinated Biphenyls (PCBs) by GC, SW-846 Compendium, 2007
- USEPA Method 8260 Revision B** Volatile Organic Compounds by GC/MS, SW-846 Compendium, 1996
- USEPA Method 8270 Revision C** Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Compendium, 1996
- USEPA Method 8290 Revision A** Polychlorinated Dibenzop-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDF) by HRGC/HRMS, SW-846 Compendium, 2007

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 The reader should review the definitions presented below prior to proceeding with use of the guide. This guide assumes a basic working knowledge of analytical procedures and test methods applicable to sediment programs. Where possible and applicable, the terms included in this guide have meanings consistent with published regulatory definitions widely used within existing international, federal, state, and local programs. The following terms are being defined to reflect their specific use in this guide. These definitions do not replace existing regulatory definitions.

3.1.2 *sediment, n*—a matrix of pore water and particles including gravel, sand, silt, clay and other natural and anthropogenic substances that have settled at the bottom of a tidal or non-tidal body of water.

### 4. Significance and Use

4.1 This guide should be used to support existing decision frameworks for the selection and application of analytical procedures to sediment programs.

4.2 Activities described in this guide should be conducted by persons familiar with current sediment site characterization and remediation techniques, sediment remediation science and technology, toxicology concepts, risk and exposure assessment methodologies, and ecological evaluation protocols.

4.3 This guide may be used by various parties involved in sediment programs, including regulatory agencies, project sponsors, environmental consultants, toxicologists, risk assessors, site remediation professionals, environmental contractors, analytical testing laboratories, data validators, data reviewers and users, and other stakeholders, which may include, but are not limited to, owners, buyers, developers, lenders, insurers, government agencies, and community members and groups.

4.4 This guide is not intended to replace or supersede federal, state, local or international regulatory requirements. Instead this guide may be used to complement and support such requirements.

<sup>3</sup> Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, <http://www.api.org>.

<sup>4</sup> Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

4.5 This guide provides a decision framework based on over-arching features and elements that should be customized by the user based on site-specific conditions, regulatory context, and sediment program objectives for a particular site. This guide should not be used alone as a prescriptive checklist.

4.6 The selection and application of analytical methods and test procedures for sediment programs is an evolving science. This guide provides a systematic but flexible decision framework to accommodate variations in approaches by regulatory agency and by user based on project objectives, site complexity, unique site features, programmatic and regulatory requirements, newly developed guidance, newly published scientific research, use of alternative scientifically-based methods and procedures, changes in regulatory criteria, advances in scientific knowledge and technical capability, multiple lines of evidence approach, and unforeseen circumstances.

4.7 The user of this guide should review the overall structure and components of this guide before proceeding with use, including: Section 1 - Scope; Section 2 - References; Section 3 - Terminology; Section 4 - Significance and Use. The remainder of this guide is organized as a tool kit to support the selection and application of a range of test methods and procedures that may be used at various stages of a sediment program, including: Section 5 - Physical Property Test Methods; Section 6 - Chemistry Analytical Methods; Section 7 - Passive Sampling Methods; Section 8 - Biological Test Methods; Section 9 - Environmental Forensics Analytical Methods; and Section 10 - Analytical Methods Development. Nonmandatory Appendix X1 – Appendix X13 provide users of this guide with additional information. A list of References and a Bibliography are provided at the end of this guide.

4.8 *Project Scoping and Planning*—This guide supports that systematic planning process for selection and application of analytical procedures used for sediment programs. The use of this guide compliments applicable existing guidance used to develop a Quality Assurance Project Plan (QAPP) and to establish data quality objectives (DQO) necessary to meet project goals and to fully understand data quality. This process encourages planners to identify and focus on the key issues that must be addressed and resolved for successful, cost-effective, and defensible project outcomes.

4.9 The use of this guide also supports the development and refinement of a Conceptual Site Model (CSM) as part of the planning process for site activities that involve gathering environmental data.

4.10 Implementation of the guide is site-specific. The user of this guide may choose to customize the implementation of the guide for particular types and/or phases of sediment programs.

4.11 This guide may be initiated at any time during a sediment program, including: site characterization, assessment, remedy selection, remedial design, remedial implementation, remedial operation and maintenance, baseline and long-term monitoring, remedy optimization, and corrective action.

4.12 Use of this guide supports the use of systematic project planning, dynamic work strategies, use of innovative sampling

and analytical technologies, and application of best management practices and guiding principles as applied to contaminated sediment programs.

4.13 Use of this guide supports a multiple lines of evidence approach, including a weight of evidence approach, for assessment, remediation, and monitoring of contaminated sediments.

4.14 Use of this guide is consistent with the Sediment-RBCA process which guides the user to acquire and evaluate additional data, obtain the appropriate data and refine goals, objectives, receptors, exposure pathways, and the site conceptual model. As the Sediment-RBCA process proceeds, data and conclusions reached at each tier help focus subsequent tiered evaluation. This integrative process results in efficient, cost-effective decision-making and timely, appropriate response actions for contaminated sediment programs.

4.15 *Planning Framework*—When applying this guide, the user should undertake a systematic project planning and scoping process to collect information to assist in making site-specific, user-defined decisions for a particular project. Planning activities should include the following factors: (a) Assemble an experienced team of project professionals; (b) Engage stakeholders early and often in the planning process; (c) Define, agree on, and document clearly stated project objectives and intended outcomes; (d) Recognize that sediment programs are complex, uncertainty is high, that an appropriate projectspecific approach may be developed with the investment of time and effort, and that compromise and uncertainty are inherent in the process; (e) Identify the applicable regulatory program(s); (f) Compile existing site data; and (g) Establish a plan for documenting and reporting key decisions and results. These project planning and scoping activities should be carried forward as the project progresses.

4.16 *Experience and Expertise*—The users of this guide should consider assembling a team of experienced project professionals with appropriate expertise to scope, plan and execute a sediment data acquisition program. The team may include: regulatory agencies, project sponsors, environmental consultants, toxicologists, risk assessors, site remediation professionals, environmental contractors, analytical testing laboratories, and data reviewers, data validators, data users, and other stakeholders.

4.17 *Stakeholders*—The users of this guide are encouraged to engage key stakeholders early and often in the project planning and scoping process, especially regulators, project sponsors, and service providers including analytical testing laboratories. A concerted ongoing effort should be made by the guide user to continuously engage stakeholders as the project progresses in order to gain insight, technical support and input for resolving technical issues and challenges that may arise during project implementation.

4.18 *Documentation*—The users of this guide should establish a plan for documenting and reporting the results of the project planning process, including: key challenges, options considered, decisions taken, data acquisition approach, data results, and project outcomes relative to project objectives.

Project documentation may include: Project Work Plans, Sampling and Analysis Plans (SAP), Quality Assurance Project Plans (QAPP), Technical Memos, and Project Reports. The user must ensure that the test methods used meet the analytical rigor required by the regulatory agency or agencies having oversight authority for the project.

4.19 The users of this guide are encouraged to continuously update and refine the project Conceptual Site Model (CSM), Work Plans and Reports used to describe the physical properties, chemical composition and occurrence, biologic features, and environmental conditions of the sediment project.

4.20 *Key Considerations*—This guide supports users in the identification of key considerations for designing and implementing sediment program data acquisition plans, including discussion of applicability and use limitations of analytical methods and testing procedures.

4.21 *Challenges*—This guide is designed to assist the user in more fully understanding and navigating the challenges inherent in the selection and application of analytical methods and test procedures for use in sediment programs, specifically challenges in generating analytical data of sufficient sensitivity to support the stringent regulatory screening levels applied to sediment programs. USEPA (2005a) (1)<sup>5</sup> has long recognized the challenges associated with sediment programs, as summarized below:

4.21.1 Sources may be various, large, ongoing, and/or difficult to control,

4.21.2 Impacts may be diffuse, large, and diverse,

4.21.3 Environment may be dynamic, increasing the difficulty in understanding effects of natural forces and man-made events on sediment movement and stability and contaminant fate and transport,

4.21.4 Cleanup work often involves engineering challenges and higher costs than for other media,

4.21.5 Mixed land uses and numerous property owners and communities with differing views, opinions, and impacts often complicate cleanup efforts, and

4.21.6 Ecologically valuable resources and/or legislatively protected species or habitats may be present.

## 5. Physical Property Test Methods

5.1 This section of the guide discusses the selection and application of physical property test methods to characterize sediment sites for the evaluation of risk. This section of the guide contains a general discussion of tools and common methods separated via stratigraphic and internal scale of analysis.

5.2 The guide is intended to provide technical direction with respect to the fundamental physical properties to enable an independent and comprehensive description of the sediment to support general environmental investigations. Physical property measurements provide quantitative understanding of the size, composition, and consolidation of the particles composing the sediment and the capacity for water to move through the

sediment. Although the chemical composition and chemistry of the porewater may influence these fundamental properties to a degree, these are generally minor influences and do not affect the selection and use of physical property tests.

5.3 Sediment physical properties have significant impacts on how sediment functions in the environment and are therefore important components of the conceptual site model. Knowledge of physical properties has many uses during every phase of sediment programs, from initial assessment through corrective actions and finally closure. For example, measurements of sediment physical properties provide information on sediment behaviors such as deposition, erosion, and re-suspension, habitat types for plants and animals, groundwater to surface water seepage, and assessment of gas generation and ebullition facilitated NAPL transport. The physical properties, such as density, water, hydraulic conductivity, and plasticity, also provide useful information for remedial purposes including the ability of the sediments to be dredged, dewatered, and handled once removed from the water, and the ability of the sediments to support caps.

5.4 This guide does not provide a comprehensive discussion of the analyses that may be warranted in remedial selection or design, and it is not intended to provide guidance for geotechnical testing or analysis of sediments. However, many of the physical property analyses presented would be needed in evaluating remedial actions.

### 5.5 Overview:

5.5.1 The physical properties of sediment are utilized throughout the investigation including development of the Conceptual Site Model (CSM), site characterization, risk evaluation, and monitoring processes. Since the results of these analyses are applied throughout the environmental process, it is critical that the analyses conducted are appropriately performed. This section of the guide documents the key parameters that can describe the physical characteristics of sediments, the methods that are applied to quantify the parameters, and the sampling protocols for physical parameters testing. One of the challenges faced by practitioners working with sediments is accurately defining and interpreting physical properties of sediments

5.5.2 Many of the inferences relied upon in land-based programs, may not be appropriate to apply in sediments. Sediments may exhibit significant differences compared to soil for several key physical properties. In particular, sediments typically have higher porosities and higher moisture contents than land-based soils. As a result, sediment bulk densities are significantly lower and more variable than soils.

5.5.3 Due to the differences in variability in porosity and bulk density between land-based soils and sediments, similar values of common parameters such as concentration and saturation cannot be assumed to be consistent between these media. For example, the concentration of a chemical compound in soils and sediment is reported on a dry weight basis (that is, mg/Kg). Due to the variability and significant differences in bulk densities of sediments relative to soils, direct comparison of concentration values between soils and sediments may not be technically valid. A two to four-fold

<sup>5</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

difference may occur between the Bulk Density values between sediments and soils, which then produces a two to four-fold mass per volume difference between these media. This difference as well as many others relative to soils can affect perspectives on risk, remedial mass, and porewater volume. Hence, the recognition of the importance of measuring sediment physical properties is critical throughout the sediment evaluation, corrective action, and monitoring phases. Further information on the differences in soil and sediment is further discussed in [Appendix X1](#).

5.5.4 In the sediment environment, physical parameters may vary vertically and laterally within the sediment profile. For example, in many cases, the bulk density of the sediment increases with depth as consolidation of the sediment column occurs. This reduces porosity and the sediment moisture content. Hence, a comprehensive sampling program is needed to fully characterize the sedimentary environment.

5.5.5 Physical properties are important in numerous facets of the evaluation, remediation, and monitoring of contaminated sediments. Physical properties aid in defining such key CSM components as (1) the depositional energy of the site, (2) the rate and form of sedimentation, (3) the stratigraphy of the sediment column, (4) the nature of the sediment pore structure, and (5) the movement of fluids within the sediment.

5.5.6 Moreover, the physical properties may provide key information as to the origin and source of contamination, the form and distribution of the contamination, and the mobility of the contamination, which are critical elements in evaluating risk.

#### 5.6 *Sediment Collection:*

5.6.1 Sediment collection for physical properties testing may be performed by the general methods of grab samples, cores, and borings. Grab samples disturb the sediment structure and include sediment collected from ponar, box or similar methods. Grab samples may also include sediment from cores where hand samples are collected. Core samples refer to sediment collected within a continuous core tube driven or vibrated into the sediment. The sediment is retained within the container and, if handled and capped appropriately, provides a representative sample of the sediment column. Borings are generally used to obtain a relatively undisturbed sample, which is critical to obtaining accurate measurement values for many physical properties. Borings are drilled into the sediment using equipment similar to land borings and relatively undisturbed sediment samples are collected at discrete depth intervals.

5.6.2 Methods for collecting sediment samples for physical testing are described in several of the ASTM methods in Section 2 including Test Method [D1586](#), as well as in EPRI (2008) (2), ITRC (2014) (3), National Research Council (2007) (4), NAVFAC (2003) (5), NAVFAC/SPAWAR (2010) (6), USACE (1998, 2008) (7, 8), and USEPA (2001, 2005b, 2014) (9-11), as well as state regulatory agency documents.

5.6.3 Some of the analyses performed for sediment physical properties (including bulk density, porosity, saturation, and permeability) require an intact, relatively undisturbed sample, which can be collected from borings.

5.6.4 In finer grained sediments, vibracore, Geoprobe, or use of thin-walled tubes, or a combination thereof, in borings

may be more practicable methods to collect an intact sample. However, each drilling technique will have positive and negative attributes. In particular, the disturbance of the sediment structure by these methods will require an independent, site-specific assessment.

5.6.5 Other physical properties analyses (for example, grain size, water content, Atterberg limits) can be performed on disturbed samples, which can be collected from grab or core samples. [Appendix X2](#) discusses the collection of sediment samples for physical property analyses conducted for characterization purposes. Discussion of the collection of sediment samples for higher level geotechnical testing for engineering design applications (including hydraulic conductivity, consolidation, and shear strength) is beyond the scope of this document.

#### 5.7 *Sediment Characterization:*

5.7.1 Since sediments are deposited and are generally composed of a series of layers that have accumulated through time, scale becomes an important component in the characterization process. In particular, the sample(s) obtained from a sediment core should be representative of a select sediment interval.

5.7.2 In general, the characterization process should be conducted whereby the stratigraphic characteristics of the sediment are described first, followed by subsequent investigation of the internal structure of the sediment.

5.7.3 This may require more than one co-located core, where intact, non-disturbed samples are needed. The following analyses are discussed with respect to the scale evaluated.

#### 5.8 *Stratigraphic Physical Analyses:*

5.8.1 Upon retrieval, sediment cores utilized for descriptive observations may be handled in a similar manner as land-based cores.

5.8.2 Specifically, the sediment is extracted from the core tube and is examined visually with characteristics of color, texture, moisture, and stratification being recorded. Visual observations of the particles and their arrangement provide the basis to discern a representative sample from a defined interval. As such, a hand lens should be used to describe the size and shape of the particles considering such characteristics as roundness, sphericity, and mineralogy. The distribution of the particle sizes should also be described and the relative consolidation of the sediment. Shallow sediments, in particular, may act as a fluid due to their high water content and lack of consolidation. From these descriptions, the macroscale components of the sediment, such as stratification and the character and nature of contacts, are identified. These features ultimately define representative intervals from which samples can be collected to further refine the visual observations.

5.8.3 When appropriate, observations and measurements associated with organic or other constituents can be made. If safe conditions exist, odors should be documented and described. Organic vapor measurements can be made using Photo Ionization Detection (PID) equipment and identification of separate phase organic liquids may be identified by applying UV light.

5.8.4 By defining the elevation of the water surface and the depth of the water during the collection process, the elevation (relative to a benchmark) of the measurements and samples can be determined.

5.8.5 The collected data is then presented in a sediment core log. A comprehensive description of the sediment is the fundamental basis from which sediment profile is discerned and is the technical document to which laboratory results, both physical and chemical, are ultimately referenced.

5.8.6 The collection and description of several cores will produce an understanding of the sediment stratigraphy. The stratigraphy will document changes in sediment texture laterally and vertically and the nature of the contact between the different sediment layers.

5.8.7 These features will provide an understanding of the depositional conditions during the past. If the contamination was derived from sedimentation, then the stratigraphy will document the physical conditions that were occurring during the time period of contamination. **Appendix X3** provides further information regarding sediment stratigraphy.

### 5.9 Physical Property Analyses:

5.9.1 Characterization of the internal nature of the sediment entails measurement of numerous properties to evaluate the particle size and distribution and the fluids contained within the pore structure. In general, with depth sediments become compacted, which changes the physical properties of the sediment.

5.9.2 The following discusses the measurement of physical properties that are commonly applied to characterize sediments. The applicable Method Reference, preferred sample volume/size, preservation requirements, and holding time constraints are summarized in **Table 1**.

5.9.3 *Grain Size*—Grain size is one of the most fundamental sediment characteristics. Test Methods **D6913/D6913M** Sieve analysis, Test Method **D4464** Laser Diffraction analysis, and Test Method **D7928** Hydrometer analysis provide information on sediment consisting primarily of clay to sand size particles. In these analyses, particles sizes larger than 75 microns ( $\mu\text{m}$ ) are measured by sieves and particles less than 75  $\mu\text{m}$  by hydrometer. In addition to these methods, Test Method **D4464** Laser Diffraction also provides high resolution measurement of

**TABLE 1 Summary of Typical Sample Volume, Preservation and Holding Time Requirements**

Test Description	Method Reference	Typical Sample Volume/Size <sup>A</sup>	Preservation	Holding Time <sup>B</sup>
<b>GRAIN SIZE<sup>C</sup></b>				
Grain Size Analysis: Dry Sieve Only	Test Methods <b>D6913/D6913M</b>	200-500 g; core, bag or jar	<i>D</i>	—
Grain Size Analysis: Laser Diffraction	Test Method <b>D4464</b>	50-100 g; core, bag or jar	<i>D</i>	—
Particle Size Analysis - Water: Laser Diffraction	Test Method <b>D4464</b>	1-2 L of water	<i>D,E</i>	<i>F</i>
Grain Size Analysis: Dry Sieve + Laser Diffraction "Combined analysis"	Test Methods <b>D6913/D6913M-17</b>	200-500 g; core, bag or jar	<i>D</i>	—
Grain Size Analysis: Dry Sieve + Hydrometer Particle-Size Distribution (Gradation) of Fine-Grained Soils using the Sedimentation (Hydrometer) Analysis	Test Methods <b>D6913/D6913M-17</b> Test Method <b>D7928-16</b>	200-500 g; core, bag or jar 200-500 g; core, bag or jar	<i>D</i> <i>D</i>	—
<b>BULK DENSITY</b>				
Bulk Density (dry unit weight)	Test Method <b>D2937</b> / Test Methods <b>D7263</b> or API RP40	2.5 in. diam. × 6 in. long sleeve core	<i>D,G,H</i>	—
<b>WATER CONTENT</b>				
Water Content	Test Methods <b>D2216</b>	50-100 g; core, bag or jar	<i>D,G</i>	—
<b>POROSITY</b>				
Porosity: Total	Test Methods <b>D854—14</b> / API RP40	2.5 in. diam. × 6 in. long sleeve core	<i>D,G,H</i>	—
Porosity: Air or Water-Filled	Test Methods <b>D854-14</b> / API RP40	2.5 in. diam. × 6 in. long sleeve core	<i>D,G,H</i>	—
<b>HYDRAULIC CONDUCTIVITY</b>				
Hydraulic Conductivity: Saturated; flexible wall triaxial	API RP40, EPA9100, Test Methods <b>D5084</b>	2.5 in. diam. × 6 in. long sleeve core	<i>D,G,H</i>	—
<b>ATTERBERG LIMITS AND CLASSIFICATION</b>				
Atterberg Limits; Plastic & Liquid Limits	Test Methods <b>D4318</b>	100-500 g; core, bag or jar	<i>D,G</i>	—
Classification: Engineering USCS	Practice <b>D2487</b>	Requires Grain Size + Atterberg	<i>D,G</i>	—
Classification: Visual / Manual	Practice <b>D2488</b>	100-500 g; core, bag or jar	<i>D,G</i>	—
<b>MINERALOGY</b>				
Bulk and Clay Mineralogy	USGS Open-File Report	200-500 g	<i>D</i>	—

<sup>A</sup> Typical sample size is the volume or core type needed to obtain undisturbed or minimally disturbed material for testing in laboratory instruments or apparatus, or both. The requested core sample size is a 2.5 in. diameter. × 6 in. long brass sleeved core or similar volume. Core types suitable for submittal are brass or stainless steel rings/sleeves, acetate sleeved core (from direct-push or continuous coring methods) Shelby tubes, PVC sleeves, etc.

<sup>B</sup> There are no recognized holding times for many conventional physical properties analyses or core analysis tests. Indefinite holding times may be appropriate if it can be demonstrated that the test results are not adversely affected from preservation or storage. Selection of core size/containers, preservation techniques and applicable holding times should be based on the stated project-specific data quality objectives. Samples should be analyzed as soon as possible to provide data measured at as-received conditions.

<sup>C</sup> Reported volumes are provided as a general guide. The sample volume depends on particle size of the sediment. When particles are up to 75 mm in size, sample volumes up to 5 kilograms may be required.

<sup>D</sup> Keep sealed.

<sup>E</sup> Keep cool, chilled at 4 °C is required.

<sup>F</sup> Water samples should be analyzed within 7 days of sample receipt.

<sup>G</sup> Keep cool, chilled at 4 °C is recommended.

<sup>H</sup> Minimally disturbed samples recommended.

the sand through fine clay particle fractions (2 mm to submicron range). This analysis may be needed for very fine grained sediments. Additional methods for the measurement of fine grain sediments that have been utilized include the Puget Sound Estuary Protocols (PSEP) (USEPA, 1986, 1997, 2015a) (12, 13), which utilizes a pipette approach, and the Coulter counter, which utilizes electric currents in electrolyte solutions. The selection of the test method employed for a given sediment investigation needs to consider many factors including project data quality objectives, intended data uses, cost, and technical acceptance.

**5.9.4 Bulk Density**—Bulk Density can be measured on a dry or wet basis. In Test Methods D7263 discusses the measurement of bulk density on a dry basis. The density of the sediment is expressed as the mass of the sediment divided by the volume of sediment, and is usually reported in grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ). This is based on dry unit weight. Bulk density depends on mineral composition and degree of compaction. Sediment dry-bulk density values are used in mass accumulation rate calculations.

NOTE 1—Shallow sediments, in particular, may act as a fluid due to the high water content and lack of compaction; special sample preparation methods such as freezing subsamples may need to be employed in the laboratory for certain analyses. In Test Method D2937 the measurement of bulk density on a wet basis is described. The density of the sediment is expressed as the wet mass of sediment divided by the volume and is reported in pounds per cubic foot.

**5.9.4.1 Dry or wet unit weights** can be calculated using formulas given in soil mechanics references such as Design Manual 7.1, Soil Mechanics (NAVFAC, 1986) (14). For saturated sediment, unit weights can be calculated based on the water content, specific gravity of dry solid particles and the density of water.

**5.9.5 Water Content**—In Test Methods D2216 the measurement of water content of the sediment is described. The geotechnical method for calculating moisture content on a dry-weight basis is not comparable to the chemical method for calculating percent solids or total solids on a total-weight basis or percent water (refer to Section 6). Water content determined by Test Methods D2216 is calculated as a percent of the weight of the water divided by the weight of the dry sediment, which can result in moisture contents greater than 100 %.

**5.9.5.1 Percent solids** are used to report chemical analytical results on a dry weight basis (refer to Section 6). Percent solids analyzed using SM 2540G or USEPA Method 160.3 is calculated as the weight of the dry sediment divided by the weight of the wet sediment (refer to Section 6). An explanation of the different ways of reporting solids concentration and the relationship between Water Content, percent solids by weight, and dry unit weight for saturated sediment or soils is discussed in Chapter 3 of USACE (1987) (15).

**5.9.6 Total Porosity**—Total porosity is defined as the sediment pore volume as a percent relative to the total sediment volume. Method API RP40 describes the measurement of total porosity. Total porosity values may vary in sediments depending upon depth and particle size, as well as roundness and packing of particles. Porosity is an important parameter in characterizing void space in a material. Porosity may be determined by calculation from Specific Gravity, Bulk Density

and Moisture Content results (see formulas in Test Methods D7263 and NAVFAC 1986 (14)).

**5.9.7 Specific Gravity**—Specific gravity is the density of soil divided by the density of water. Specific gravity is the ratio between density of the soil or sediment particles and the density of water at 4 °C. The specific gravity is used to correlate the mass and volume of a material. Test Methods D854 describe the measurement of specific gravity.

**5.9.8 Hydraulic Conductivity (Permeability)**—Hydraulic conductivity is the rate of discharge of water under laminar flow conditions through a unit cross-sectional area of porous medium under a unit hydraulic gradient and standard temperature conditions (20 °C). Test Methods D5084 describes the measurement of hydraulic conductivity of water-saturated porous materials with a flexible wall permeameter at temperatures between 15 and 30 °C. The method describes six methods to measure the hydraulic conductivity.

**5.9.9 Atterberg Limits**—The Atterberg limits are a basic measure of the plasticity of a fine-grained (that is, silt and clay) sediment. The analysis determines the moisture content where the material begins to act in a plastic state which is defined as the plastic limit and the moisture content where the material begins to act in a liquid state which is defined as the liquid limit. The changes in behavior and consistency are characterized as fine grained sediment takes on increasing amounts of water. Depending on the water content of the sediment, the sediment may appear in four states: solid, semi-solid, plastic and liquid. In Test Methods D4318 the measurement of the Atterberg limits is described.

**5.9.10 Particle Form and Mineralogy**—The form and type of minerals present in the sediment are an important characteristic that influences both the physical and chemical conditions of the sediment. Properties influenced by the sediment mineralogy include sorption, bulk density, porosity, hydraulic conductivity, water content, and Atterberg limits. Due to their generally sheet-like structure and electrical surface charges, clay minerals are particularly important in affecting the physical and chemical conditions within a sediment. Moreover, the composition of the clay mineral suite provides unique information regarding the upland source conditions. The USGS Open File Report 01-041 (USGS, 2001) (16) describes the application of x-ray diffraction (XRD) to determine the mineralogy of clay minerals. For larger particle sizes (that is, sand) the shape of the particles can be described. Two common characteristics have been widely investigated roundness, the shape of the corners of a particle, and sphericity, a measure of a particle shape relative to a sphere. These characteristics reflect the original source rock as well as the type and distance the particle has been transported. The roundness and sphericity will affect the consolidation and movement of fluids within the sediment. In general, platy minerals such as clays and micas will be deposited in a horizontal orientation, which enhances consolidation and lowers the permeability of the sediment relative to spherical-shaped particles that produce a more open porous sediment framework. Quantitative methods describing the shape of particles are described in Pettijohn (1975) (17) and Lewis and McConchie (1994) (18).



## 6. Chemistry Analytical Methods

6.1 This section of the guide supports users on the selection and application of analytical procedures used for chemical determination of compounds of potential concern (COPC) for sediment programs.

6.2 *Project Planning Considerations*—Chemical determination of COPCs for sediment programs presents unique challenges due to the significant differences that exist between upland and sediment programs. The project decision framework applied to upland programs may not be applicable for use in sediment programs. Sediment chemistry analytical programs typically involve method modifications, performance enhancements, and additional procedures to achieve project criteria. A general project planning guide for sediment chemistry analytical programs is provided in [Table 2](#).

6.3 *Selection and Application of Chemical Analytical Methods:*

6.3.1 *Overview*—The determination and quantitation of chemicals of potential concern is important throughout the characterization, evaluation, corrective action, and monitoring phases of a sediment program. The selection and application of chemical analytical procedures for sediment programs should include a review of available analytical chemistry approaches and best practices discussed in the sections below. Many of the sediment chemistry analytical methods discussed in this guide are based on USEPA’s Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium SW-846 (USEPA, 2017) ([20](#)). [Appendix X4](#) provides a Quick Reference Guide to Sediment Chemistry Analytical Methods. [Appendix X5](#) provides a Sediment Chemistry Sampling Reference Guide. [Appendix X6](#) provides a discussion of critical success factors for sediment chemistry analytical programs. Sediment chemistry analytical laboratory selection should include review of laboratory’s accreditation issued by the appropriate regulatory entity, as well as engagement of the laboratory in the development of the Quality Assurance Project Plan (QAPP) and review of project data quality objectives (DQOs) and project specific criteria (for guidance refer to USEPA, 2000 ([21](#)); USEPA, 2001 ([22](#)); USEPA, 2002ab ([23](#), [24](#))).

6.3.2 *Sample Media and Matrix Considerations:*

6.3.2.1 Samples collected in support of sediments programs may consist of multiple media and matrix types including: (a) sediment, (b) pore water, (c) surface water, (d) groundwater, and (e) biota.

6.3.2.2 Sample media and matrix complexities present unique analytical chemistry challenges, such as elevated sediment moisture levels which directly impact analytical reporting limits and extraction efficiencies. Also sediments may contain elevated concentrations of target and/or non-target compounds and other matrix interferences, necessitating a customized analytical approach to improve data quality and usability outcomes.

6.3.2.3 Considerations unique to sediment programs require detailed planning and coordination with the laboratory to develop customized analytical approaches to achieve project-specific objectives.

6.4 *Trace Organic Compound Analysis:*

6.4.1 *Overview*—Trace organic compound analytical methods consist of three separate stages: (a) the preparative stage to isolate (extract) and concentrate target analytes of interest, (b) the extract clean-up stage to remove potential matrix interferences, followed by (c) the determinative stage where the sample extract is analyzed for target analytes of interest by specific analytical instrumentation. The objective of the sample preparation step is to maximize the analyte of interest concentration, minimize potential interferences, and enhance the level of sensitivity (that is, Reporting Limit) required for the project. The analytical method dictates the specific instrumentation used for a given analytical parameter at the level of sensitivity which is required for the project. For projects requiring a QAPP, the analytical method reference for each of these three steps must be documented in the QAPP. A general discussion follows for the most commonly used analytical methods for sediment programs.

6.4.2 *PCB Aroclors, Homologs and Congeners:*

6.4.2.1 Polychlorinated Biphenyls (PCBs) are a class of 209 compounds called congeners with groups called homologs. PCB Aroclors are complex mixtures of congeners produced to support various commercial uses. PCB Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 identify nine commercial products produced and used from 1929 until 1979 in the United States.

6.4.2.2 Screening level investigations often begin with PCB Aroclor analysis by USEPA Method 8082 with gas chromatography with electron capture detection (GC-ECD) instrumentation. PCB Aroclor analysis is qualitative in nature due to the fact that chromatographic patterns and peak ratios are subject to change in the environment due to “weathering”. However, PCB Aroclors may be reported as not detected (ND) due to a lack of pattern recognition even though PCB congeners may be present. Determination of Total PCB concentration using the PCB Aroclor approach presents challenges as individual Aroclors represent mixtures of PCB congeners, thus there is a possibility that the “double counting” of PCBs may occur. Additional information is provided in [Section 9](#) of this guide.

6.4.2.3 Sediment programs may use USEPA Method 1668 based on high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS) to determine low level PCB congeners and homologs to eliminate uncertainties associated with the PCB Aroclor analysis approach. USEPA Method 1668 is also extremely sensitive, thus it is used for ambient water quality studies, TMDL determinations, forensic PCB investigations, and sediment and tissue programs. This procedure can determine all 209 PCB congeners, or a subset of congeners (that is, WHO, NOAA or custom list), and homolog groups. USEPA Method 8270-SIM-modified GC/LRMS for PCB congener and homolog analysis provides an option for determination of all 209 PCB congeners with less sensitivity (higher RL). Additional information is provided in [Section 9](#) of this guide.

6.4.3 *Semivolatile Compounds, Polynuclear Aromatic Hydrocarbons (PAHs), Alkylated PAH Homologs:*

6.4.3.1 Analysis of acid and base-neutral extractable compounds also known as semivolatile organic compounds (SVOCs) for the full list of target analytes that may be

**TABLE 2 Project Planning Guide for Sediment Chemistry Analytical Programs**

Considerations	Upland Programs	Sediment Programs
Laboratory Certifications	Laboratory certification required by regulatory entity for conventional analytical protocols (that is, published analytical methods)	Laboratory certifications may be required by regulatory entity for specialized extraction, extract cleanup, digestion, and instrument analysis methods, as well as non-standard analytical protocols (such as literature references, laboratory SOPs, etc.)
Regulatory Criteria	Standard analytical approaches used to meet regulatory criteria for upland sites	Specialized analytical approach may be needed to meet project specific criteria (such as low level Ecological Screening Levels)
Project Plans	Standardized, routine regulatory program approach	Non-standard approaches detailed in project workplan and QAPP
Program/Project Goals	Site characterization, delineation, risk evaluation, corrective action, monitoring	Site characterization, delineation, risk assessment, corrective action, monitoring, ecological restoration
Matrices	Soil, groundwater, surface water	Sediment, pore water, surface water, biota
Target Analytes	Broad screening approach typically based on Target Compound List (TCL) Organics, Target Analyte List (TAL) Metals, and General Chemistry parameters	Focused approach typically based on Parent PAHs, Alkyl PAHs, PCB Congeners, Dioxins/Furans, Select Pesticides, Select Metals, Mercury, AVS-SEM, Total Organic Carbon (TOC), Black Carbon, Grain Size, etc.
Analytical Methods	Routine analytical approach with conventional method-defined reporting limits (that is, TCL SVOCs by GC/MS in full scan mode; PCBs aroclors by GC/ECD, etc.)	Specialized analytical approach with non-routine sample extraction, extract cleanup, and trace instrumentation to achieve low level reporting limits (that is, Alkyl PAHs by EPA GC/MS-SIM; PCB 209 congeners by HRGC/HRMS, etc.)
Sample Volume	Conventional sampling approach yields suitable volume/mass for method-defined reporting limits	Need to calculate sample mass/volume required for target RLs to meet project specific criteria; may be a challenge for biota and pore water matrices; limited volumes may increase RLs; prioritization may be required
Sample Handling	Conventional sample handling is suitable for standard analytical approach (that is, method-defined reporting limits)	Customized laboratory sample handling and processing may be needed (such as glove box to maintain anaerobic conditions; centrifuge to generate pore water; etc.)
Sample Compositing / Homogenization	Conventional sample handling approaches are suitable (that is, method-defined approach, "as is" condition)	Specialized sample handling procedures, if needed, should be well documented in project work plans and during implementation
Reporting Limits	Routine analytical approach provides suitable reporting limits (that is, method-defined approach)	Sediment programs often require specialized analytical approach to meet project specific criteria (such as ecological screening levels)
Contaminant Concentrations	High concentrations of target and/or nontarget analytes (relative to instrument calibration range) may require sample dilution which will elevate standard reporting limits potentially exceeding standard Regulatory Criteria	High concentrations of target and/or non-target analytes (relative to instrument calibration range and sensitivity) may require sample dilution which will elevate low level reporting limits potentially exceeding project specific criteria (such as ecological screening levels)
Moisture Levels	Solid data reported on a dry weight basis with results corrected for moisture content; typically low soil moisture levels (that is, 5-10 %) may not impact reporting limits relative to standard Regulatory Criteria	Solid data reported on a dry weight basis with results corrected for moisture content; elevated sediment moisture levels (that is, 30-70 + %) result in elevated reporting limits and lower extraction efficiencies
Organic Extraction	Routine extraction approach of isolate, extract, and concentrate target analytes of concern to exploit solubility difference offers suitable results (that is, conventional method-defined approach)	Sediment sample extraction may result in sensitivity and method performance issues as high organic content typical of sediment and biota matrices is extracted along with target analytes of concern (that is, "like dissolves like" plus 1000x concentration factor)
Mass Extracted	Standardized approach to sample aliquot (mass) extracted (that is, 5 grams), then concentrated to a method defined final extract volume (that is, conventional method-defined approach)	Sample mass may need to be increased and sample extract volume may need to be decreased to achieve targeted detection limits to meet project specific criteria
Interferences	Extraction step to concentrate target analytes will magnify interferences, which may require dilutions, which will elevate Reporting Limits, which may impact data usability relative to standard Regulatory Criteria	Extraction step to concentrate target analytes will also magnify non-target analytes and matrix interferences, which often requires dilutions, which will elevate Reporting Limits, which will impact data usability relative to project specific criteria (such as ecological screening levels)
Organic Extract Cleanups	Extract cleanups in soils are often not required due to limited matrix interferences (that is, conventional method-defined analytical approach is suitable)	Extract cleanups may be required to support low level analytical approach (such as gel permeation chromatography (GPC), silica gel, alumina, florisil, copper, sulfuric acid, etc.) to minimize interferences common in sediment and biota sample matrices
Organic Extract Concentration	Standard analytical approach is suitable (that is, conventional method-defined analytical approach)	Targeting lower final extract volumes can provide lower reporting limits for some but not all targeted parameters; alternate methods may be needed to achieve project specific criteria
Metals Digestion and Analysis	Standard analytical approach is suitable (that is, conventional method-defined analytical approach)	Specialized prep and analytical approaches may be needed (such as trace metals by ICP-MS, AVS-SEM, low level mercury, methylmercury, sea water prep for trace metals analysis by chelation extraction and hydride generation atomic fluorescence, etc.) to meet project specific criteria
Non-Detects	ND = not detected at Reporting Limit; viewed as "inconclusive"	ND may be viewed as inconclusive, or as = RL value, or as = 1/2 RL value (USEPA, 2015a (13); Rouhani and van Geel, 2017 (19))

determined by USEPA Method 8270 may not be amenable to extract clean up techniques like other trace organic methods. Laboratories use USEPA Method 8270 in both full scan and selected ion monitoring (SIM) modes to maximize sensitivity for the full list of 70 SVOC analytes, 17 parent PAHs, or 34 Alkyl PAHs in sediment samples. USEPA Method 8272 or Test Method **D7363** are used for determination of parent and alkylated PAHs in sediment pore water using solid phase microextraction (SPME) and GC/MS in SIM mode. Additional information is provided in Section 9 of this guide.

6.4.3.2 Parent PAHs are two or more fused conjugated rings. Alkylated PAHs are the parent PAHs with various alkyl groups attached. Alkylated PAHs are categorized by the total number of alkyl carbon atoms present. A homolog group includes all of the isomers with the same number of carbon atoms. Analysis of alkyl PAHs in combination with the parent compounds provides a more complete estimation of total PAH exposure. Thousands of alkylated forms of PAHs are unaccounted for in conventional analytical methods. Refer to Section 7 and Section 9 for additional information.

#### 6.4.4 *Organochlorine Pesticides:*

6.4.4.1 Analysis of organochlorine pesticides for sediment programs typically uses USEPA Method 8081 by gas chromatography with electron capture detection (GC-ECD) instrumentation. However, the presence of high concentrations of PCBs in samples can potentially cause false positive pesticide detections with this analytical approach.

6.4.4.2 An alternative approach for determination of organochlorine pesticides which addresses sample matrix issues is USEPA Method 1699 using an HRGC/HRMS instrument.

#### 6.4.5 *Hydrocarbons:*

6.4.5.1 The hydrocarbon category encompasses a wide range of petroleum and coal based hydrocarbon products with a variety of chemical analytical options that may be applicable to sediment programs.

6.4.5.2 A screening approach may begin with determination of total petroleum hydrocarbons (TPH) by USEPA Method 8015 modified using gas chromatography flame ionization detection (GC-FID) to determine (a) gasoline range organics (GRO) by a purge and trap sample introduction approach, and (b) diesel range organics (DRO) by an extraction approach.

6.4.5.3 Another analytical approach is based on separation of aliphatic and aromatic fractions, then quantitation of specific hydrocarbon ranges within each fraction using regulatory agency defined analytical methods. Analytical protocols vary for fractionated extractable hydrocarbon analysis.

6.4.5.4 Another analytical approach is based on a GC-FID hydrocarbon “fingerprint.” Laboratory protocols based on USEPA Method 8015 vary for sample extraction, GC column types, temperature rates, chromatographic run-times, and instrument sensitivity. Differences occur between a high resolution output generated by a laboratory that specializes in hydrocarbon analysis, and a low resolution result with a shorter run time that relies on matching to known reference materials. Additional information is provided in Section 9 of this guide.

#### 6.4.6 *Dioxins and Furans:*

6.4.6.1 Dioxins and furans are common names for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

6.4.6.2 Analysis of dioxins and furans for sediment programs is typically based on USEPA Method 8290 or 1613 using gas chromatography / high resolution mass spectrometry (GC/HRMS) to determine seven (7) polychlorinated dibenzop-dioxins and ten (10) polychlorinated dibenzofurans.

6.4.6.3 Dioxin/furan sample analytical results are reported along with toxicity equivalency factors (TEFs) relative to 2,3,7,8-TCDD using the World Health Organization (WHO) internationally accepted framework or other TEFs based on the site location or defined by the applicable regulatory program.

#### 6.4.7 *Volatile Organic Compounds (VOCs):*

6.4.7.1 Determination of VOCs for sediment programs typically uses USEPA Method 8260 with purge and trap sample introduction and GC/MS instrumentation.

6.4.7.2 Regulatory entities may require solid VOC sample collection by USEPA Method 5035. However, this approach this presents challenges for sediment programs due to sample matrix issues such as elevated moisture levels and sample collection and handling issues. The laboratory should be consulted to evaluate sediment VOC sample collection and analysis options.

6.4.8 *Other Organics Analyses*—Other organic tests associated with a specific historic use of a chemical at a sediment site may be available upon special request. For example, laboratory analysis of butyl tins, an antifouling agent used in boat paint, requires development of specialized analytical protocols based on a literature review. Additional information is provided in Section 10 of this guide.

#### 6.5 *Trace Metals, Inorganic, and Other Analysis:*

6.5.1 *Overview*—Trace metals and inorganic compound analytical methods consist of two separate stages: (a) the preparative stage to digest (isolate) and concentrate target analytes of interest, followed by (b) the determinative stage where the digested sample is analyzed for target analytes of interest by specific analytical instrumentation. The objective of the sample preparation step is to maximize the solubility of the analyte of interest, minimize potential interferences, and enhance the level of sensitivity (that is, Reporting Limit) required for the project. The analytical method determines the instrumentation used for an analytical parameter at the level of sensitivity needed to support the project. The analytical method reference for each of these steps should be documented in the QAPP. A general discussion follows for the most commonly used analytical methods to support sediment programs.

6.5.2 *Sample Preparation*—Sample preparation methods are selected based on analyte of interest and sample media and matrix types. Trace metals sample preparation by hot acid digestion is typically used for sediment and aqueous matrices. Biota matrices are subjected to a robust digestion approach to completely break down the organic matrix and solubilize the metals for instrument analysis.

6.5.3 *Specialized Preparation*—Determining trace metals concentrations in saline, brackish and sea water sample matrices presents special challenges, due to high levels of total dissolved solids present. These may interfere with trace metals

analyses yielding false positive, false negative or biased results. These interferences may be minimized by sample dilution, with reporting limits elevated accordingly. Specialized sample preparatory protocols, including chelation extraction and hydride generation, may be used to mitigate saline sample matrix effects while providing the level of sensitivity needed to support sediment programs.

**6.5.4 Metals Instrument Analysis**—Trace metals analyses for sediment applications may specify USEPA Method 6020 using inductively coupled plasma / mass spectrometry (ICP/MS) with collision / reaction cell technology. Certain analytes have ‘same mass’ interferences, which in standard ICP/MS without the collision / reaction cell may result in false positives or biased results for trace metals analysis. Metals analysis can be supported by USEPA Method 6010 using inductively coupled plasma atomic emission spectroscopy (ICP/AES) for applications requiring less sensitivity.

**6.5.5 Mercury Analysis**—Mercury analysis for sediment programs is typically based on the cold vapor atomic absorption (CVAA) approach by USEPA Method 7471 with target sensitivity in the 3-30  $\mu\text{g}/\text{kg}$  range. If lower sensitivity is required, USEPA Method 7474 or 1631 modified for sediment and biota can support target sensitivities in the 1-2  $\mu\text{g}/\text{kg}$  range. USEPA Method 7473 Direct Mercury Analyzer is also used for biota analysis for target sensitivity in the 20  $\mu\text{g}/\text{kg}$  range.

**6.5.6 Methyl Mercury**—Methyl mercury is determined by USEPA Method 1630 with modified sample preparation procedures for sediment and biota matrices for targeted level of sensitivity of 0.1  $\mu\text{g}/\text{kg}$ .

**6.5.7 Acid Volatile Sulfide / Simultaneously Extracted Metals (AVS/SEM)**—Measurements of AVS/SEM in sediments can be used to evaluate the toxicity of metals to indigenous benthic organisms. AVS is volatilized from sediments by the addition of acid. SEM are metals simultaneously extracted during the AVS procedure. Toxicity is evaluated by calculating the sum of the SEM ( $\mu\text{mol}/\text{g}$  dry weight) divided by the AVS concentration in the same units: a ratio less than or equal to 1 indicates that the sediment metals are not bioavailable while a ratio  $> 1$  would indicate that the metals may be bioavailable. SEM metals typically include cadmium, copper, lead, mercury, nickel and zinc, but it should be recognized that other binding compounds (for example, iron and manganese oxyhydroxides) can also influence bioavailability. Method guidance (USEPA, 1991, 1992) (25, 26) is predicated on maintaining anoxic conditions required to sustain metal sulfide concentrations. Exposure of sediment samples to oxygen during sample collection and analysis may result in false positive assertions of metal bioavailability. This method is written as guidance with ongoing research documenting the impacts of sample handling on the representativeness of this procedure. Sample collection and sample handling protocols should be discussed with the laboratory, as well as laboratory protocols for maximizing representativeness.

**6.5.8 Organic Carbon**—Organic carbon has been shown to influence contaminant bioavailability. Organic Carbon Methods include determination of: (a) Total Organic Carbon (TOC), (b) Black Carbon (also called Soot), (c) Particulate Organic Carbon (POC), and (c) Fraction Organic Carbon (FOC). Total

organic carbon (TOC) analysis is conducted by USEPA Method 9060 in water, while the USEPA Lloyd Kahn protocol is used for sediment (USEPA, 1988) (27). Black carbon analysis has no published USEPA methods, thus laboratories follow procedures based on the literature. Laboratories typically perform both TOC and black carbon analysis in duplicate (at a minimum) due to the inherent variability due to small sample aliquots [ $>50$  mg] utilized. On request, laboratories can perform these analyses in triplicate or quadruplicate to improve the level of certainty. There is no accepted definition of or published analytical method for fraction of organic carbon (FOC), referred to as the portion of the organic matter available to adsorb organic contaminants of concern. In general, the higher the organic carbon content, the more organic chemicals may be adsorbed to solids and the less of those chemicals will be available to leach to water. Laboratories rely on the literature for method protocol references.

**6.5.9 Lipids Determination**—Percent lipids analysis is often requested in order to normalize the results of lipophilic contaminants present in biota samples. There are no published analytical methods for lipids determination, so discussions with the laboratory to agree on suitable method references to meet project objectives should be part of the project planning process.

## 7. Passive Sampling Methods

**7.1** The freely dissolved concentration ( $C_{\text{free}}$ ) of chemicals in sediment porewater is the driving force for transport to the water column and bioaccumulation in benthic organisms. The freely dissolved chemicals in the surface water control chemical uptake by the pelagic organisms, such as phytoplankton and zooplankton, as well as higher trophic level organisms such as fish (fish uptake is controlled by both trophic transfer from prey and  $C_{\text{free}}$ ). Potential risks of adverse biological effects from chemicals are most directly related to a chemical’s  $C_{\text{free}}$ , which can be measured through passive sampling methods (PSM). Passive sampling measurements can be used for various purposes: to better understand contaminant bioavailability and associated risk; inform design specifications of a remediation technology; and to monitor the efficacy of a remedy. For example, understanding the concentration of contaminants available to benthic organisms can inform the assessment of benthic bioaccumulation and benthic toxicity, which ultimately supports improved risk assessments and the development of more accurate sediment quality evaluations. Also, measurements of the  $C_{\text{free}}$  in a sediment cap provides chemical gradient concentrations from the porewater to the surface water, which can be useful in evaluating the effectiveness of a sediment cap.

**7.2** The use of PSM provides the following benefits:

**7.2.1** Measures the  $C_{\text{free}}$  in porewater and surface water, which provides a more relevant measurement of exposure for evaluating bioaccumulation and risk as compared to traditional methods that are based on total extraction.

**7.2.2** Can provide a time-averaged response.

**7.2.3** Regulators are increasingly accepting the use of PSMs as a reliable and accurate tool for measuring  $C_{\text{free}}$ .

**7.3** The following drawbacks of PSM should be considered:

7.3.1 Trained personnel are needed for the preparation, deployment and retrieval of the samplers.

7.3.2 Obtaining results through PSM can take more time than standard sampling methods, because the passive sampler needs to be in contact with the environmental media until equilibrium or partial equilibrium conditions are achieved. Sampler preparation, if performance reference compounds (PRCs) are used, added effort is required for sampler preparation and data analysis to interpret results.

7.3.3 There may be additional costs associated with the use of PRCs, especially when using deuterated and  $^{13}\text{C}$  labelled compounds (see 7.5 and 7.5.8).

7.3.4 Proper calibration and validation of PSM are needed, including values for polymer-water partition coefficients ( $K_{\text{PS}}$ ), determination of equilibrium, and non-depletive sampling conditions.

7.4 The selection of the passive sampler material (that is, the polymer) and the selection between *in situ* and *ex situ* deployments are dependent on several site-specific goals and considerations as well as the target contaminant of interest. These key considerations and the associated sampling requirements are further discussed in 7.5 for organic constituents and 7.6 for inorganic constituents. **Appendix X7** Quick Reference Guide for Passive Sampling with a matrix of potential polymer types for different chemicals of interest; and **Appendix X8** Summary of Advantages and Limitations of Passive Sampler Types for Organics; and **Appendix X9** Methodologies and Equations for Determining  $C_{\text{free}}$  from Passive Sampler Results. A list of References and a Bibliography are provided at the end of this guide.

### 7.5 Organic Constituents:

7.5.1 The  $C_{\text{free}}$  of a hydrophobic organic constituent (HOC) can be estimated with passive samplers by two operational methods: (1) an equilibrium method, where sufficient time is allowed for the target analyte to reach equilibrium between the sampler and water or sediment, and (2) a pre-equilibrium method that targets a time-specific concentration that must be corrected to equilibrium condition (Lydy et al. 2014, Mayer et al. 2014) (28, 29).

7.5.2 It is important to understand how rapidly the target contaminant(s) reaches equilibrium with the passive sampler, sediments, and other environmental media. This kinetic state depends on exposure time, passive sampler characteristics, such as construction material, thickness, and dimensions, and the target contaminant's physicochemical properties (Vrana et al. 2005, Apell et al. 2015) (30, 31). Passive samplers with polymer thickness of a few micrometers are available for equilibrium sampling of the most hydrophobic chemicals within a practical timeframe. If equilibrium is not expected to be achieved during the sampling time span, passive samplers are "spiked" with known concentrations of PRCs prior to deployment. PRCs are analytically noninterfering chemicals that are embedded in the passive sampler before environmental exposure and (1) allow precise measurement of its loss, (2) follow the same kinetics as the target analyte, and (3) do not exist in the target environment (Ghosh et al. 2014) (32). The depletion rate of a PRC during sampler deployment reflects the uptake rates of a contaminant, assuming isotropic exchange

kinetics occur (Ghosh et al. 2014) (32). In principle, PRCs experience the same mass transfer limitations while diffusing out of the sampler as the target analytes that are diffusing into the sampler, therefore the measured losses of the PRCs can be used to infer the level of equilibrium of the target analyte, as discussed in more detail in Section 7.5.8 (Fernandez et al. 2009, Gschwend 2010, Apell and Gschwend, 2014) (33-35).

### 7.5.3 Types of Organic Passive Samplers:

7.5.3.1 The three types of passive sampler polymers typically used for estimating the  $C_{\text{free}}$  of HOCs include polyoxymethylene (POM), polyethylene (PE), and the silicone polydimethylsiloxane (PDMS). Each of these passive samplers can be deployed in the field and laboratory. PE and POM are deployed as sheets, can easily be deployed in both surface water and sediment, and if chosen with high surface area to volume ratio, have the advantage of lower analytical detection limits. PDMS typically serves as the passive sampler polymer used on Solid Phase Micro Extraction (SPME) fibers. SPMEs are fiber-optic cables with an inner core of glass, which is insulated by PDMS. The PDMS coating can vary in thickness (typically 10 to 100  $\mu\text{m}$ ) and the length of coated fiber is adjustable. SPMEs are more suitable for sediment deployment, rather than surface water, due to limited polymer mass on the fiber. Also, the fibers are fragile, and need to be protected during deployment in sediment.

7.5.3.2 The selection of the appropriate passive sampler material should align with the overall assessment objectives, after taking into consideration pros and cons of each polymer (that is, sampler performance, cost, durability, required detection limits, polymer-water partition, sampler fouling, material availability, etc.), as outlined in Gschwend et al. 2011 (36), Ghosh et al. 2014 (32), USEPA 2012a (37), USEPA et al. 2017 (38), and summarized in **Appendix X8**. While  $K_{\text{PS}}$  have not been determined for all organic compounds and for all passive sampler material, the list of  $K_{\text{PS}}$  continues to expand (USEPA 2012a (37), USEPA 2012b (39); Ghosh et al. 2014 (32), USEPA et al. 2017 (38)). This matter can inform a decision on selecting the appropriate passive sampler or the need for determining  $K_{\text{PS}}$  for a specific study.

### 7.5.4 Pre-Deployment:

7.5.4.1 Prior to sampler exposure, it is necessary to pre-extract the passive sampler device to confirm it is free of background contamination. The selection of pre-extraction solvents varies by material type and target analytes (Ghosh et al. 2014) (32). If the sampling program has decided to use PRCs to account for nonequilibrium conditions, these compounds must be loaded into the samplers prior to deployment. This process includes soaking the sampler in a volume of water or a methanol water solution that has been "spiked" with the PRCs and allowing for adequate equilibration time (Booij et al. 2002 (40), Fernandez et al. 2009 (33), USEPA et al. 2017 (38)). Equilibration times are sampler and analyte dependent, but typically range from 7 to 30 days. Following cleaning and PRC loading (if applicable), care should be taken to avoid exposing samplers to possible sources of contamination by wrapping the samplers in clean aluminium foil, placing in a sealable plastic bag and storing frozen ( $-4\text{ }^{\circ}\text{C}$ ) until deployment (USEPA 2012a) (37). It is important to retain a subset of replicate

samplers to serve as an initial PRC concentration ( $C_{PRCi}$ ) for completing later calculations.

#### 7.5.5 Deployment:

7.5.5.1 Passive samplers can be deployed both in the field (*in situ*, water column or sediment) or used in the laboratory with field-collected samples (*ex situ*). Each deployment method has its own advantages and disadvantages as further discussed below and in other documents (USEPA 2012a (37), Ghosh et al. 2014 (32), USEPA, 2016 / Thompson et al. 2016 (41), Schmidt et al. 2017 (42), USEPA et al. 2017 (38)). Overall, the selection of *ex situ* versus *in situ* deployment depends on the objectives of the assessment weighed against logistical and financial constraints. Certain situations, such as the evaluation of the performance of in-place remedial alternatives (that is, capping and treatment remedies), will require *in situ* measurements to accurately capture the full suite of site specific processes while other objectives (that is, bench scale comparison of treatment alternatives) can be addressed with *ex situ* methods (Thompson 2016) (43).

7.5.5.2 Benefits of *ex situ* methods include being less labor intensive, less expensive, and providing more ability to control environmental variables (that is, temperature, light, addition of biocides, etc.) compared to *in situ* methods. *Ex situ* sediment exposures are performed in closed systems in a controlled environment, which typically require little or no sampler protection. *Ex situ* deployments of polymer sheets (PE and POM) can be added directly to these systems. During *ex situ* equilibration, the sediment can be agitated to enhance the exchange of chemicals between the sediment and sampler, greatly reducing the time required to reach equilibrium, while avoiding the need for PRCs (Ghosh et al 2014) (32). Equilibration times are dictated by target contaminants and polymer characteristics, such as material and surface area to volume ratio. Equilibrium can typically be achieved within 1-4 weeks (Mayer et al. 2003 (44), Ghosh et al. 2014 (32)), after which the samplers are recovered. A disadvantage of *ex situ* deployments is that *ex situ* conditions may not reflect site-specific conditions at contaminated sites (USEPA 2012a) (37). When conducting *ex situ* sediment exposures appropriate ratios of polymer mass to sediment organic carbon mass (1:100) should be used so that the relative amount of the target constituent transferred from the sediment to the sampler results in a negligible loss (<1 % depletion) (USEPA et al. 2017) (38).

7.5.5.3 *In situ* methods generally result in a better characterization of true field exposures. This approach may be preferable when it is important to capture local site processes, such as groundwater intrusion, currents, bioturbation, vertical contaminant porewater concentration profiles, and sediment-water column gradients and fluxes (Ghosh et al. 2014) (32). The success of an *in situ* passive sampling program depends in large part on the success of deployment and retrieval of the samples, which may require an experienced diver depending on the depth of the water column, the desired depth of the sampler in the sediment bed, and the required accuracy of the placement of the sampler (Thompson et al. 2016) (43). During *in situ* deployment in water and sediment, polymer sheets are typically attached to rigid, metal (that is, aluminium, stainless steel) frames or in metallic mesh (that is, aluminium, copper,

stainless steel) that is suited to fully expose the sampler surface to its environmental surroundings while protecting it from damage (USEPA et al. 2017) (38). The thinner SPME fibers are not as robust as the relatively simple passive sampling polymer sheets and are often deployed in sediment *in situ* and *ex situ* in a protected form (that is, metal mesh, copper or stainless steel sheath or tubing) to avoid loss or breakage (USEPA et al. 2017) (38). Shielded, modified push point type samplers with perforations are especially useful for housing SPME fibers and providing sufficient protection for insertion into sediments (Reible and Lotufo 2012) (45). Depending on site conditions, such as deep water settings, a diver may be required for the insertion of the sampler into the sediment and for retrieval at the end of the deployment period. The GPS location of each sampler needs to be carefully recorded and marked with a buoy or other readily located marker.

7.5.5.4 Generally, *in situ* samplers are left in place for a week up to a month or more. It is important to choose an equilibrium time that is a balance between using short times, to minimize sample disturbance or vandalism, and the time required to achieve a significant fraction of equilibrium for highly hydrophobic contaminants (USEPA et al. 2017) (38). This balance often means that chemical equilibrium is not reached for all target analytes, requiring the use of PRCs. The use of PRCs adds additional effort and potential for additional errors that affect both the precision and accuracy of derived  $C_{free}$  values (Mayer et al 2014) (29). Additionally, the use of *in situ* deployments requires adequate spatial coverage to address the extent and heterogeneity of contamination, given that these devices sample microscale environments and chemical concentrations in sediments are generally not homogeneous (Ghosh et al. 2014) (32).

#### 7.5.6 Retrieval:

7.5.6.1 After deploying the *in situ* passive samplers for an appropriate length of time, they are then removed from the environment being sampled. Recovery will require similar personnel as deployment activities (that is, if divers were needed for deployment, they will generally be required for retrieval as well). Following the retrieval of the sampler and support device, it is important to remove adhering sediment or surface growths with water or damp laboratory tissues (do not use solvents to clean), as these materials can interfere with analytical procedures and data analysis (USEPA et al. 2017) (38). Once the sampler is clean, it can be processed as defined in the assessment plan (that is, sectioned to evaluate depth profiles) and placed in clean glass vials in a freezer at  $-4^{\circ}\text{C}$ , in the dark, until they are analyzed (USEPA et al. 2017) (38).

7.5.6.2 Processing of passive sampler devices should be performed as quickly as possible following retrieval to minimize loss of more volatile analytes (that is, naphthalene and other low molecular weight compounds) during exposure to air (Thomas et al. 2014 (46), USEPA et al. 2017 (38)). PDMS samplers have been extensively used due to their rapid uptake kinetics, but these properties also lead to faster loss of volatile analytes (Thomas et al. 2014) (46).

#### 7.5.7 Quality Assurance and Quality Control (QA/QC):

7.5.7.1 Appropriate QA/QC guidelines should be followed when implementing a passive sampler monitoring program.