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Standard Guide for Contaminated Sediment Site Risk-Based Corrective Action— Selection and Application of Analytical Methods and Test Procedures¹

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1. Scope

1.1 This is a guide for the selection and application of a range of analytical methods and testing protocols that may be used during sediment corrective action programs; these include physical properties testing, chemical analytical methods, passive sampling procedures, bioassays and toxicity testing, environmental forensics methods and procedures, and laboratory method development procedures for sediment corrective action programs.

1.1.1 There are numerous technical decisions that must be made in the selection and application of analytical methods and testing protocols used during sediment corrective action programs. It is not the intent of this guide to define the appropriate technical decisions, but rather to provide technical guidance within existing decision frameworks. The user of this guide should review existing information and data available for a sediment corrective action program to determine the most appropriate entry point into (and use of) this guide.

1.1.2 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 corrective action program. This guide recognizes the complexity and diversity of sediment corrective action programs and project objectives and provides appendixes to support a range of project applications.

1.2 Sediment corrective action 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 corrective action programs.

¹ 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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1.2.1 This guide may be used at any time during a sediment corrective action program, including site characterization, risk assessment, remedy selection, remedial design, remedial implementation, remedial operation and maintenance, baseline and post-remedy monitoring (Guide E3164), remedy optimization, and corrective action (Guide E3240).

1.3 Sediment corrective actions are performed under various regulatory programs, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Although many of the references cited in this guide are CERCLA-oriented, the guide is applicable to corrective actions performed under local, state, tribal, federal, and international corrective action programs. This guide describes the selection and application of analytical methods and test procedures, but it does not provide a detailed description of the regulatory requirements or existing guidance for each jurisdiction.

1.3.1 This guide is intended to inform, complement, and support (but not supersede) the requirements and guidelines established by local, state, tribal, federal, and international regulatory agencies. The user should consult applicable regulatory agency requirements and guidelines 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 corrective action programs.

1.4 This guide highlights key considerations for designing sediment corrective action program data acquisition plans, including applicability and use limitations of analytical methods and test procedures, as well as 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 corrective action programs.

1.5 Test methods, procedures, and guidelines published by ASTM International (ASTM), the U.S. Environmental Protection Agency (USEPA), and other U.S. and international agencies are used for sediment corrective action 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 corrective action programs. This guide describes widely accepted considerations and best practices used in the selection and application of analytical procedures used during sediment corrective action programs. This guide supports and complements existing regulations and technical guidance.

1.6 Units—The values stated in SI or CGS units are to be regarded as the standard. Units in the appendices are provided in Imperial units when commonly associated with standard materials.

1.7 *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.*

1.8 *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:²

- D854** Test Methods for Specific Gravity of Soil Solids by the Water Displacement Method
- D1586/D1586M** 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
- 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
- D3213** Practices for Handling, Storing, and Preparing Soft Intact Marine Soil
- 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
- D4823** Guide for Core Sampling Submerged, Unconsolidated Sediments
- 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
- D5856** Test Method for Measurement of Hydraulic Conduc-

- tivity of Porous Material Using a Rigid-Wall, Compaction-Mold Permeameter (Withdrawn 2024)³
- D6913/D6913M** Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis
- D7263** Test Methods for Laboratory Determination of Density and 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
- D7968** Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
- D7979** Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
- 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
- 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
- E2122** Guide for Conducting In-situ Field Bioassays With Caged Bivalves
- E3164** Guide for Contaminated Sediment Site Risk-Based Corrective Action – Baseline, Remedy Implementation and Post-Remedy Monitoring Programs
- E3240** Guide for Risk-Based Corrective Action for Contaminated Sediment Sites
- E3242** Guide for Developing Representative Background Concentrations at Sediment Sites—Data Evaluation and Development Methodologies
- E3248** Guide for NAPL Mobility and Migration in Sediment – Conceptual Models for Emplacement and Advection
- E3282** Guide for NAPL Mobility and Migration in Sediments – Evaluation Metrics
- E3300** Guide for NAPL Mobility and Migration in Sediment—Evaluating Ebullition and Associated NAPL/Contaminant Transport
- E3302** Guide for PFAS Analytical Methods Selection

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

E3344 Guide for Developing Representative Sediment Background Concentrations at Sediment Sites—Selection of Background Reference Areas

E3382 Guide for Developing Representative Background Concentrations at Sediment Sites—Framework Overview, Including Conceptual Site Model Considerations

2.2 *USEPA Analytical Test Methods and Extraction/Extract Cleanup/Digestion Methods*:⁴

USEPA Method 160.3 Residue, Total (gravimetric, Dried at 103-105°C), EPA/600/4-79/020

USEPA Method 608 Organochlorine Pesticides and PCBs by GC/HSD, EPA 821-R-16-009

USEPA Method 680 Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry, 905R85112

USEPA Method 1613 Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, EPA 821-B-94-005

USEPA Method 1630 Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

USEPA Method 1631 Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA-821-R-02-019

USEPA Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, EPA 821-R-24-001

USEPA Method 1664 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, EPA-821-R-10-001

USEPA Method 1668 Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGS/HRMS, EPA-820-R-10-005

USEPA Method 1699 Pesticides in Water, Soil, Sediment, Biosolids, and Tissues by HRGC/HRMS, EPA-821-R-08-001

USEPA Method 3050 Acid Digestion of Sediments, Sludges and Solids, SW-846 Compendium

USEPA Method 3051 Microwave Assisted Digestion of Sediments, Sludges, Soils and Oils, SW-846 Compendium

USEPA Method 3060 Alkaline Digestion for Hexavalent Chromium, SW-846 Compendium

USEPA Method 3540 Soxhlet Extraction, SW-846 Compendium

USEPA Method 3541 Automated Soxhlet Extraction, SW-846 Compendium

USEPA Method 3545 Pressurized Fluid Extraction (PFE), SW-846 Compendium

USEPA Method 3546 Microwave Extraction, SW-846 Compendium

USEPA Method 3550 Ultrasonic Extraction, SW-846 Compendium

USEPA Method 3610 Alumina Cleanup, SW-846 Compendium

USEPA Method 3620 Florisil Cleanup, SW-846 Compendium

USEPA Method 3630 Silica Gel Cleanup, SW-846 Compendium

USEPA Method 3640 Gel-Permeation Cleanup, SW-846 Compendium

USEPA Method 3665 Sulfuric Acid/Permanganate Cleanup, SW-846 Compendium

USEPA Method 5030 Purge-and-Trap for Aqueous Samples, SW-846 Compendium

USEPA Method 5035 Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, SW-846 Compendium

USEPA Method 6010 Inductively Coupled Plasma – Optical Emission Spectrometry, SW-846 Compendium

USEPA Method 6020 Inductively Coupled Plasma – Mass Spectrometry, SW-846 Compendium

USEPA Method 7471 Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique), SW-846 Compendium

USEPA Method 7473 Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, SW-846 Compendium

USEPA Method 7474 Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry, SW-846 Compendium

USEPA Method 8015 Nonhalogenated Organics Using GC/FID, SW-846 Compendium

USEPA Method 8081 Organochlorine Pesticides by Gas Chromatography, SW-846 Compendium

USEPA Method 8082 Polychlorinated Biphenyls (PCBs) by GC, SW-846 Compendium

USEPA Method 8260 Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Compendium

USEPA Method 8270 Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Compendium

USEPA Method 8272 Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water by Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode, SW-846 Compendium

USEPA Method 8290 Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDF) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), SW-846 Compendium

USEPA Method 9045 Soil and Waste pH, SW-846 Compendium

USEPA Method 9060 Total Organic Carbon, SW-846 Compendium

3. Terminology

3.1 Definitions:

3.1.1 *background* (aka “reference”), *n*—a term applied to substances, conditions, or locations that are similar to those found at a sediment site but not influenced by current or historical releases or activities from the sediment site; these are usually a combination of naturally occurring and anthropogenic sources.

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

present in the environment but not influenced by human activity) and anthropogenic (influenced by human activity but not related to specific current or historical releases or activities at the sediment site) components. **E3382**

3.1.2 *conceptual site model (CSM)*, *n*—the integrated representation of the physical and environmental context, the complete and potentially complete exposure pathways, and the potential fate and transport of potential contaminants of concern at a site. **E3242**

3.1.2.1 *Discussion*—The CSM should include both the current understanding of the site and an understanding of the potential future conditions and uses for the site. It provides a method to conduct the exposure pathway evaluation; inventory the exposure pathways evaluated; and determine the status of the exposure pathways as incomplete, potentially complete, or complete.

3.1.3 *contaminant of concern (COC)*, *n*—substances identified as posing a risk based on a tiered risk assessment and that may warrant corrective action. **E3382**

3.1.3.1 *Discussion*—Typically, all potential COCs (PCOCs) identified for a sediment site are evaluated in the risk assessment process. PCOCs that have sediment concentrations greater than risk-based thresholds identified in the risk assessment process are defined as COCs. Thus, the COCs identified for a sediment site are a subset of the PCOCs identified for that site.

3.1.4 *corrective action*, *n*—the sequence of actions that may include site assessment and investigation, risk assessment, evaluations of potential remedial action alternatives, interim remedial action, remedial action, operation and maintenance of the remedy, monitoring of progress, making “No Further Action” determinations, and completion of the remedial action. **E3240**

3.1.5 *ecological risk*, *n*—the potential for or probability of an adverse effect on a relevant ecological receptor or habitat (including populations or communities). These risks may be expressed qualitatively or quantitatively. **E3240**

3.1.6 *human health risk*, *n*—the potential for or probability of an adverse effect on a human receptor. These risks may be expressed qualitatively or quantitatively. **E3240**

3.1.7 *non-aqueous phase liquid, NAPL*, *n*—chemicals that are insoluble or only slightly soluble in water that exist as a separate liquid phase in environmental media. **E3248**

3.1.7.1 *Discussion*—NAPL may be less dense than water (light non-aqueous phase liquid [LNAPL]) or more dense than water (dense non-aqueous phase liquid [DNAPL]).

3.1.8 *potential contaminant of concern (PCOC)*, *n*—a contaminant whose sediment concentrations at the site may exceed applicable screening levels; this includes chemicals of potential environmental concern (COPECs) and chemicals of potential concern (COPCs). **E3242**

3.1.9 *remedial action objectives (RAO)*, *n*—stated objectives that describe what the remedial action for a site is expected to accomplish, based on the CSM and the exposure pathways that may pose an unacceptable risk as determined in a risk

assessment. RAOs are specific and achievable goals for reducing risk to human health and the environment. **E3240**

3.1.10 *representative background data set*, *n*—a background data set obtained by evaluating candidate background data using the steps described in Guide **E3242**. **E3382**

3.1.10.1 *Discussion*—The evaluation determines if there are any data points in the candidate background data set that are not representative of sediment site background conditions. These data points are then removed from the candidate background data set (using technically justifiable rationale) to obtain a representative background data set, which is then used to develop representative background concentrations for the sediment site using methodologies described in Guide **E3242**.

3.1.11 *risk assessment*, *n*—an analysis of the potential for adverse effects on relevant human or ecological receptors caused by a COC from a site. The risk assessment results support a decision on whether interim remedial actions, remedial action or a combination of actions are required, and form the primary basis for the development of RAOs. **E3240**

3.1.12 *risk management*, *n*—the consideration of scientific factors, economic factors, legal decisions, social factors, and technological factors to develop a response to identified risks. **E3240**

3.1.13 *sediment site*, *n*—the area(s) defined by the likely physical distribution of COC(s) from a source area and the adjacent areas required to implement the corrective action. A site could be an entire water body or a defined portion of a water body. **E3240**

3.1.14 *site assessment*, *n*—a characterization of a site through an evaluation of its physical and environmental context (for example, subsurface geology, sediment properties and structures, hydrology, and surface characteristics) to determine if a release has occurred. The characterization may identify the concentration and distribution of COCs. Information collected during the site assessment may include data on sediment, groundwater, and surface water quality; land and resource use; and potential human and ecological receptors. This information is used to develop a CSM and support risk-based decision making. **E3240**

3.1.15 *stressor*, *n*—a chemical, physical, or biological agent or condition that causes stress to an organism. **E3240**

3.2 Definitions of Terms Specific to This Standard:

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

4. Significance and Use

4.1 Intended Users:

4.1.1 This guide may be used by various parties involved in sediment corrective action 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, the following:

developers, lenders, insurers, government agencies, and community members and groups.

4.2 *Reference Materials:*

4.2.1 This guide should be used in conjunction with other ASTM guides listed in 2.1 (especially Guides E3164, E3240, E3242, E3344, and E3382), as well as the material in the References section.

4.3 *Flexible Site-Specific Implementation:*

4.3.1 This guide supports users in the identification of key considerations for designing and implementing sediment corrective action program data acquisition plans, including discussion of the applicability and use limitations of analytical methods and testing procedures.

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

4.3.1.2 This framework facilitates the selection and application of analytical methods and testing protocols used in a wide range of sediment corrective action programs. This guide provides best practices to support the user in achieving intended sediment corrective action program objectives.

4.3.2 Implementation of the guide is site-specific. The user may choose to customize the implementation of the guide for a particular sediment site, especially smaller, less complex sites.

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

4.4 *Regulatory Frameworks:*

4.4.1 This guide is intended to be applicable to a broad range of local, state, tribal, federal, or international jurisdictions, each with its own regulatory framework. As such, this guide does not provide a detailed discussion of the requirements or guidance associated with any of these regulatory frameworks, nor is it intended to supersede applicable requirements and guidance. The user of this guide will need to be aware of (and comply with) the regulatory requirements and guidance in the jurisdiction where the work is being performed.

4.4.2 This guide may be used to support existing regulatory decision frameworks for the selection and application of analytical procedures and testing protocols used in sediment corrective action programs.

4.5 *Systematic Project Planning and Scoping Process:*

4.5.1 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, including assembling an

experienced team of project professionals. These practitioners should have the appropriate expertise to scope, plan, and execute a sediment corrective action program. This team may include, but is not limited to, project sponsors, environmental consultants, toxicologists, risk assessors, site remediation professionals, environmental contractors, analytical testing laboratories, data reviewers, data validators, data users, regulatory agency personnel, and other stakeholders.

4.5.2 Use of this guide is consistent with the Risk-Based Corrective Action process for contaminated sediment sites (Sediment-RBCA) (Guide E3240) that guides the user to acquire and evaluate appropriate data and refine goals, objectives, receptors, and exposure pathways to refine the CSM. As the Sediment-RBCA process proceeds, data and conclusions reached at each tier help focus the subsequent tier of evaluation. This integrative process results in efficient, cost-effective decision-making and timely, appropriate response actions for sediment corrective action programs.

4.5.3 This guide supports the use of systematic project planning, the use of innovative sampling and analytical technologies, and application of best management practices and guiding principles as applied to sediment corrective action programs. Planning activities should include the following:

- (1) Assemble an experienced team of project professionals.
- (2) Engage regulators and other relevant stakeholders early and often in the planning process.
- (3) Define, agree on, and document clearly stated project objectives and intended outcomes.
- (4) Recognize that sediment corrective action programs are complex and that uncertainty is high and inherent in the process; however, an appropriate project-specific approach may be developed with the investment of time and effort, as well as compromise.
- (5) Identify applicable requirements and guidance.
- (6) Compile existing site data.
- (7) Establish a plan for documenting and reporting key decisions and results.

4.5.3.1 These project planning and scoping activities should be carried forward as the corrective action process progresses.

4.5.4 The use of this guide complements applicable existing guidance used to develop a quality assurance project plan (QAPP) and to establish the data quality objectives (DQOs) necessary to meet project goals and to fully understand data quality. This planning process facilitates project planners identifying and focusing on the key issues that must be addressed and resolved for successful, cost-effective, and defensible project outcomes.

4.6 *Stakeholder Engagement:*

4.6.1 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 (especially testing laboratories). A concerted, ongoing effort should be made by the user to continually engage regulators and other relevant stakeholders as the project progresses to gain insight, technical support, and input for resolving technical issues and challenges that may arise during project implementation.

4.7 Documentation:

4.7.1 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, field sampling and analysis plans (FSAPs), QAPPs, technical memoranda, and project reports. The user must ensure that the test methods used meet the analytical rigor required by the regulatory agency that has oversight authority for the project.

4.7.2 The users of this guide are encouraged to update and refine the sediment site CSM (Guide [E1689](#)) as needed, as well as updating work plans and reports used to describe the physical properties, chemical composition and occurrence, biologic features, and environmental conditions of the sediment site as new data become available.

4.8 Challenges:

4.8.1 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 corrective action programs; specifically, challenges in generating analytical data of sufficient sensitivity to support the stringent generic regulatory screening levels or risk-based screening levels typically applied during sediment corrective action programs. Ref ([1](#))⁵ has long recognized the challenges associated with sediment corrective action programs, as summarized below:

4.8.1.1 Contaminant sources may be various, large, ongoing, or difficult to control (or any combination of these).

4.8.1.2 Impacts may be diffuse, large, and diverse (or any combination of these).

4.8.1.3 The environment may be dynamic, increasing the difficulty in understanding effects of natural forces and anthropogenic events on sediment movement (or stability), as well as contaminant fate and transport.

4.8.1.4 Cleanup work at sediment sites often involves engineering challenges and higher costs than for other media (such as upland soils and groundwater).

4.8.1.5 Mixed land uses; numerous property owners; and communities with differing views, opinions, and impacts often complicate cleanup efforts at sediment sites.

4.8.1.6 Cultural and historical resources and inadvertent discoveries may be more likely at sediment sites than upland sites. This may increase a project's complexity.

4.8.1.7 Ecologically valuable resources or legislatively protected species/habitats (or both) may be present.

4.9 Other Considerations:

4.9.1 The overarching process for risk-based corrective actions at sediment sites is not covered in detail in this guide; Guide [E3240](#) contains extensive information concerning that process.

4.9.2 Developing representative background concentrations for the sediment site is not covered in detail in this guide;

Guides [E3242](#), [E3344](#), and [E3382](#) contain extensive information concerning that topic.

4.9.3 In this guide, sediment ([3.2.1](#)) is defined as a matrix being found at the bottom of a water body. Upland soils of sedimentary origin are excluded from consideration as sediment in this guide.

4.9.4 In this guide, only COC concentrations are considered. Residual background radioactivity is out of scope for this guide.

4.10 Structure and Components of This Guide:

4.10.1 Guide users should review the overall structure and components of this guide before proceeding with use, including:

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5. Physical Property Test Methods

5.1 Overview:

5.1.1 This section of the guide discusses the selection and application of physical property test methods to characterize sediment sites for sediment corrective action. This section of the guide contains a general discussion of tools and common methods.

5.1.2 This section is intended to provide technical guidance with respect to the fundamental physical properties needed 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 consistency of the

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

particles that compose the sediment and the ability for water or NAPL to move through the sediment (Guides E3248 and E3282). 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 test methods.

5.1.3 Sediment physical properties have substantial impacts on how sediment behaves in the environment, so they are important components of the CSM. Physical properties are important in numerous facets of the evaluation, remediation and monitoring of contaminated sediments. Physical properties aid in defining key CSM components such as the depositional energy of the site, the rate and form of sedimentation, the stratigraphy of the sediment column, the nature of the sediment pore structure, and the movement of fluids (that is, water and NAPL) within the sediment.

5.1.3.1 For example, measurements of sediment physical properties provide information on sediment behaviors such as deposition, erosion, and resuspension; habitat types for plants and animals; groundwater to surface water seepage; NAPL mobility and migration (Guide E3282); and assessment of gas generation and ebullition-facilitated NAPL/contaminant transport (Guide E3300). Physical properties (such as density, water content, 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 body; the ability of the sediments to support engineered caps; and the suitability of in situ treatments as remedial actions. Physical properties may provide key information about the origin and source of contamination, the form and distribution of the contamination, and the mobility of the contamination.

5.1.4 This guide does not provide a comprehensive discussion of the physical property testing 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 testing results presented would be needed in evaluating and designing remedial options.

5.2 Differences Between Sediments and Upland Soil Physical Properties:

5.2.1 The physical properties of sediment are utilized during CSM development, site characterization, risk assessment, and monitoring processes. Because the results of these analyses are applied throughout the sediment corrective action process, it is critical that the analyses conducted are performed correctly, according to the documented physical property test method or procedure. This section of the guide (and associated appendices) documents the key parameters typically used to describe the physical properties of sediments, the methods that are applied to quantify these parameters, and the sampling protocols for the physical property test method.

5.2.2 Many of the physical property inferences relied upon in land-based upland programs may not be appropriate to apply to sediments. Sediments may exhibit substantial differences compared to upland soil for several key physical properties. In particular, sediments typically have higher porosities and higher moisture contents than upland soils. As a result,

sediment bulk densities are substantially lower and more variable than for upland soils.

5.2.3 Due to the differences in variability in porosity and bulk density between upland soils and sediments, similar values of common parameters (such as concentration and saturation) cannot be assumed to be consistent between these media (refer to Appendix X1). For example, the concentration of a chemical compound in soils and sediment is reported on a dry weight basis (such as mg/kg). Due to the increased variability and substantial 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 difference may occur between the bulk density values of sediments and soils, which then produces a two- to four-fold contaminant mass per volume difference between these media—even though the concentrations on a dry weight basis have the same numerical value in both media. This difference, as well as many others relative to upland soils, can affect perspectives on risk, remedial mass, and porewater volume. Hence, the recognition of the importance of accurately measuring sediment physical properties is critical throughout all phases of the sediment corrective action process. Additional information on the differences between upland soil and sediment physical properties (and how these can effect concentration and water/NAPL saturation values) is further discussed in Appendix X1.

5.2.4 In the sediment environment, physical parameters may vary more vertically and laterally within the sediment profile when compared to upland soils. For example, in many cases, the bulk density of the sediment increases substantially with depth below the sediment–surface water interface as consolidation of the sediment column occurs, whereas the bulk density of upland soil changes much less with depth. This consolidation reduces porosity and moisture content in the sediment. Hence, a comprehensive sampling program is needed to fully characterize the sedimentary environment.

5.3 Sediment Sample Collection:

5.3.1 Sediment collection for physical properties testing may be performed using the general methods of grab samplers and coring.

5.3.1.1 Grab samplers (such as box, clam, or similar sampling devices) disturb the sediment structure when collecting samples. Grab samples may include sediment from cores where hand samples are collected.

5.3.1.2 Core sampling refers to collecting sediment samples within a continuous core tube driven, pushed or vibrated into the sediment. The sediment is retained within a core liner and, if handled and capped appropriately, provides a representative sample of the sediment column. Corings are generally used to obtain a minimally disturbed samples, which is critical to obtaining accurate measurement values for many physical properties. Cores are obtained from the sediment using equipment similar to that used for land corings, and minimally disturbed sediment samples are collected at discrete depth intervals.

5.3.2 Methods for collecting sediment samples for physical property testing are described in Test Method D1586/D1586M and Guide D4823, as well as other guidance documents.

5.3.3 Some of the analyses performed for sediment physical properties (including bulk density, porosity, saturation, and permeability) require an intact, minimally disturbed sample, which can be collected from cores.

5.3.4 In finer grained sediments, use of vibracore or direct-push drill rigs with thin-walled tubes may be applicable methods to collect an intact and minimally disturbed sample for physical property testing. However, each drilling technique will have positive and negative attributes. In particular, the degree of disturbance of the sediment structure by these methods will require an independent, site-specific assessment.

5.3.5 Other physical properties analyses (for example, grain size, water content, Atterberg limits) can be performed on disturbed samples, which can be collected from either 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 engineering design geotechnical testing (including sediment consolidation and sediment shear strength) is out of scope for this Guide.

5.4 *Sediment Characterization:*

5.4.1 Because deposited sediments are generally composed of a series of layers that have accumulated through time, scale becomes an important component in the characterization process. In particular, samples obtained from a sediment core should be representative of a select sediment interval.

5.4.2 In general, the characterization process should be conducted so the stratigraphic characteristics of the sediment are described first, followed by subsequent investigation of the internal structure of the sediment. This may require more than one collocated core, when intact, minimally disturbed samples are needed for physical testing.

5.5 *Stratigraphic Description of Core Samples:*

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

5.5.2 Specifically, the sediment is extracted from the core tube, split longitudinally, and examined visually with characteristics of color, texture, moisture, and stratification being recorded. Visual observations of the particles and their arrangement provide the basis for identifying 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 (the relative consolidation of the sediment is an important observation). Sediments near the sediment–surface water interface may act as a fluid due to their high water content and lack of consolidation. Standardized descriptions from Practice [D2487](#) or [D2488](#) should be used when logging the core.

5.5.2.1 From these descriptions, the macroscale components of the sediment, such as stratification and the character and nature of contacts between different strata, are identified. These features ultimately define representative intervals from which samples can be collected to further refine the visual observations.

5.5.2.2 A recommended practice is photographing these cores in color, using consistent lighting with the cores being

displayed on a white background (this will provide good color contrast against the more darkly colored sediment core material).

5.5.3 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 photoionization detection equipment and separate phase organic liquids may be identified by ultraviolet (UV) light photography.

5.5.4 By defining the elevation of the water surface at the time of sampling (the sampling time is critically important in tidally influenced water bodies) and the depth of the water during the sample collection process, the elevation (relative to a benchmark) of the samples and the measurements taken on those samples can be determined.

5.5.5 The collected data are then presented in a sediment core log. A comprehensive description of the sediment is the fundamental basis from which a sediment profile is developed and the core log is the graphical depiction to which laboratory testing results (both physical properties and chemical) are ultimately referenced.

5.5.6 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, as well as the nature of the contact (such as sharp or diffuse) between the different sediment layers.

5.5.7 These features will provide an understanding of the current and historical depositional conditions at the sediment site. If the sediment contamination originated from contaminated particulates settling on the sediment bed, then the stratigraphy will document the physical conditions that were occurring during the period of contamination. [Appendix X3](#) provides further discussion of sediment stratigraphy.

5.6 *Physical Property Testing:*

5.6.1 Characterization of the internal nature of the sediment entails measurement of numerous properties to evaluate the particle size distribution and the fluids contained within the pore structure. In general, sediments become more compacted with increasing depth below the sediment–surface water interface, which changes the physical properties of the sediment.

5.6.2 [Appendix X3](#) provides a Quick Reference Guide for Sediment Physical Property Test Method Selection ([Table X3.1](#)).

5.6.3 *Grain Size Distribution*—Grain size distribution is one of the most fundamental sediment characteristics. The selection of the test method used for a given sediment investigation needs to consider many factors including project DQOs, intended data uses, cost, and regulatory acceptance.

5.6.3.1 Information on sediment consisting primarily of clay to fine sand size particles is typically provided using Test Methods [D6913/D6913M](#) (sieve analysis) and [D7928](#) (hydrometer analysis). In these test methods, particles sizes larger than 75 μm are measured by sieves and particles less than 75 μm by hydrometer.

5.6.3.2 High resolution measurement of the clay through fine sand particle fractions (1 μm –300 μm particle size range) is provided using Test Method [D4464](#) (laser diffraction).

5.6.4 *Bulk Density*—Bulk density can be measured on a dry or wet basis. 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 used in the laboratory for certain analyses.

5.6.4.1 The measurement of bulk density on a dry basis is discussed in Test Method [D7263](#). The density of the sediment is expressed as the dry weight mass of the sediment divided by the volume of sediment, and is usually reported in grams per cubic centimeter (g/cm^3). Bulk density depends on mineral composition and degree of compaction. Sediment dry-bulk density values are used in mass accumulation rate calculations.

5.6.4.2 The measurement of bulk density on a wet basis is described in Test Method [D2937](#). The density of the sediment is expressed as the wet mass of sediment divided by the volume.

5.6.4.3 Dry or wet unit weights can be calculated using formulas given in soil mechanics reference manuals ([12](#)). For saturated sediment, unit weights can be calculated based on the water content, specific gravity of dry solid particles, and the density of water.

5.6.5 *Water Content*—Test Method [D2216](#) describes the measurement of water content of the sediment. 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 Method [D2216](#) is calculated as the weight of the water divided by the weight of the dry sediment times 100 %, which can sometimes result in water contents greater than 100 %.

5.6.5.1 Percent solids are used to report chemical analytical results on a dry weight basis (refer to Section [6](#)). Percent solids are calculated as the weight of the dry sediment divided by the weight of the wet sediment times 100%. 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 is discussed in Ref ([13](#)).

5.6.6 *Total Porosity*—Total porosity is defined as the sediment sample pore volume as a percentage relative to the total sediment sample volume. Ref ([14](#)) describes the measurement of total porosity, which may vary in sediments depending upon depth and particle size, as well as roundness and packing of sediment particles. Porosity is an important parameter in characterizing the void space in a material. Porosity may also be calculated from specific gravity, bulk density, and moisture content results (refer to formulas in Test Method [D7263](#) and ([12](#))).

5.6.7 *Specific Gravity*—Specific gravity is the density of the sediment divided by the density of water at 4 °C. The specific gravity is used to correlate the mass and volume of a material. The measurement of specific gravity is described in Test Method [D854](#).

5.6.8 *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). The measurement of the hydraulic conductivity of water-saturated porous materials with a flexible wall permeameter is described in Test Methods [D5084](#), whereas Test Method [D5856](#) uses a fixed wall permeameter to perform the same measurement.

5.6.9 *Atterberg Limits*—Atterberg limits are a basic measure of the plasticity of a fine-grained sediment (that is, sediment composed of silt and clay). The analysis determines the moisture content where the material begins to act in a plastic state (which is defined as the plastic limit), the moisture content where the material begins to act in a liquid state (which is defined as the liquid limit), and the plasticity index. 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, semisolid, plastic, and liquid. The measurement of Atterberg limits is described in Test Method [D4318](#).

6. Chemistry Analytical Methods

6.1 Overview and Project Planning Considerations:

6.1.1 This section provides guidance to users on the selection and application of analytical test methods used for the determination of PCOC concentrations in various environmental media for sediment corrective action programs.

6.1.2 Although test methods for the determination of PCOC concentrations are available for use with sediment samples, these test methods were developed primarily for use with upland soil matrices. It is often challenging to use these methods for sediment because of the differences between upland soil and sediment matrices (such as higher water contents and more analytical interferences in sediment samples). The analytical test methods applied to upland soil matrices may not be well suited for use in sediment sample analysis. Sediment chemistry analytical programs often involve test method modifications, performance enhancements, and additional procedures to achieve project DQOs. A general project planning guide for sediment chemistry analytical programs is provided in [Table 1](#), where it is contrasted to upland soil programs.

6.2 Selection and Application of Chemical Analytical Methods:

6.2.1 *Overview*—The determination and quantitation of PCOCs is important throughout the characterization, evaluation, corrective action, and monitoring phases of a sediment corrective action program. The selection and application of chemical analytical procedures for sediment corrective action programs should include a review of available analytical chemistry approaches and best practices discussed in the following sections.

6.2.1.1 Many of the sediment chemistry analytical methods discussed in this guide are based on ASTM test methods, USEPA SW-846 test methods ([17](#)), and other USEPA test methods. Sediment chemistry analytical laboratory selection should include review of the laboratory's accreditation issued by the appropriate accreditation body (which may be a

TABLE 1 Project Planning Guide for Sediment Chemistry Analytical Programs

Considerations	Upland Soil Programs	Sediment Corrective Action Programs
Laboratory Certifications	Laboratory certification is required by regulatory entity for conventional analytical protocols (that is, published analytical reference methods).	Laboratory certifications may be required by regulatory entity for specialized extraction, extract cleanup, digestion, and instrument analysis methods, as well as approval by regulatory agencies to use nonstandard analytical protocols (such as literature references, laboratory standard operating procedures [SOPs]).
Regulatory Criteria	Standard analytical approaches are used to meet regulatory criteria for upland sites.	Specialized analytical approach may be needed to meet project-specific criteria (such as lower concentration risk-based screening levels).
Project Plans	Standardized, routine regulatory program approach is used.	Nonstandard approaches are detailed in project work plans, FSAPs, and QAPPs.
Program/Project Goals	Site characterization, delineation, risk assessment, corrective action, monitoring	Site characterization, delineation, risk assessment, corrective action, monitoring, ecological restoration
Sample Media	Soil, groundwater, soil gas, indoor air	Sediment, porewater, groundwater, surface water, biota tissue
Target Analytes	Broad screening approach typically based on Target Compound List (TCL) organics, Target Analyte List (TAL) elements, and general chemistry parameters	Focused approach typically based on parent polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, polychlorinated biphenyls (PCBs) (Aroclors, congeners, homolog groups), polychlorinated dioxins and furans (PCDD/DFs) (congeners, homolog groups), pesticides (organochlorine, organophosphorus), metals, acid volatile sulfide (AVS)/simultaneously extracted metals (SEM), total organic carbon (TOC), black carbon
Analytical Methods	Routine analytical approach with conventional method-defined reporting limits (RLs) (such as semivolatile organic compounds [SVOCs] by gas chromatography/mass spectrometry [GC/MS] in full scan mode, PCB Aroclors by gas chromatography with electron capture detector [GC/ECD], and per- and polyfluoroalkyl substances [PFAS] by liquid chromatography with tandem mass spectrometry [LC/MS/MS])	Specialized analytical approach with more involved sample extraction, extract cleanup, and trace instrumentation to achieve low-level RLs (such as alkylated PAHs by GC/MS selected ion monitoring [SIM]; PCB congeners by high-resolution gas chromatography/high-resolution mass spectrometry [HRGC/HRMS], and PFAS by LC/MS/MS)
Sample Volume	Conventional sampling approach yields suitable volume/mass for method-defined RLs.	Need to calculate sample mass/volume required for target RLs to meet project-specific criteria. Obtaining sufficient sample volumes may be a challenge for biota and porewater matrices. Limited sample volumes may increase RLs. Prioritization of analyte analyses may be required.
Sample Handling	Conventional sample handling is suitable for standard analytical approach (that is, method-defined RLs).	Customized laboratory sample handling and processing may be needed (such as centrifuging to generate porewater).
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 field implementation.
RLs	Routine analytical approach provides suitable RLs (that is, method-defined approach).	Sediment corrective action programs often require specialized analytical approach to meet project-specific criteria (such as lower risk-based screening levels).
Contaminant Concentrations	High concentrations of target and nontarget analytes (relative to instrument calibration range) may require sample dilution, which will elevate standard RLs, potentially exceeding applicable regulatory criteria.	High concentrations of target and nontarget analytes (relative to instrument calibration range and sensitivity) may require sample dilution, which will elevate low-level RLs, potentially exceeding project-specific criteria (such as human health or ecological screening levels).
Moisture Levels	Solids data are reported on a dry weight basis with results corrected for moisture content. Typically, soil moisture levels are low (that is, 10 % to 25 %). RLs are usually less than applicable regulatory criteria.	Solids data are reported on a dry weight basis with results corrected for moisture content. Elevated sediment moisture levels (that is, 30 % to >70 %) result in elevated RLs and lower extraction efficiencies. RLs may exceed the applicable regulatory criteria.
Organic Extraction	Routine extraction approach of isolate, extract, and concentrate target analytes of concern to exploit solubility difference typically offers suitable results (that is, conventional method-defined approach).	Sediment sample extraction may result in sensitivity and method performance issues, because high organic content typical of sediment and biota matrices may be extracted along with target analytes and cause analytical interferences.
Mass Extracted	Standardized approach to sample aliquot (mass) extracted (such as 5 g) then concentrated to a method-defined final extract volume (that is, the conventional method-defined approach) offers suitable results.	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 RLs and may impact data usability relative to applicable regulatory criteria.	Extraction step to concentrate target analytes will also magnify nontarget analytes and matrix interferences (which often requires dilutions) that will elevate RLs. This may impact data usability relative to project-specific criteria (such as lower risk-based screening levels).

TABLE 1 Continued

Considerations	Upland Soil Programs	Sediment Corrective Action Programs
Organic Extract Cleanups	Extract cleanups in soils are often not required due to limited matrix interferences (that is, the conventional method-defined analytical approach is suitable).	Extract cleanups (such as gel permeation chromatography, silica gel, and alumina) are typically required to support low-level analytical approach by minimizing interferences common in sediment and biota sample matrices.
Organic Extract Concentration	Standard analytical approach is suitable (that is, the conventional method-defined analytical approach).	Targeting lower final extract volumes can provide lower RLs for some (but not all) targeted analytes; alternate methods may be needed to achieve project-specific criteria.
Metals Digestion and Analysis	Standard analytical approach is suitable (that is, the conventional method-defined analytical approach).	Specialized prep and analytical approaches may be needed (such as trace metals by inductively coupled plasma mass spectrometry [ICP/MS], AVS/SEM, low-level mercury, methylmercury) to meet project-specific criteria.
Non-Detects (NDs)	ND is not detected at the RL; viewed as “inconclusive.”	ND may be viewed as inconclusive, as equal to the RL value, or as equal to half of the RL value (15, 16).

in many cases) and engagement of the laboratory in the development of the QAPP, as well as review of project DQOs and project-specific criteria (18-21).

6.2.1.2 **Appendix X4** provides Quick Reference Guides for Sediment Chemistry Analytical Method Selection and Sediment Chemistry Sample Extraction, Extract Cleanup, and Digestion Method Selection (Tables X4.1 and X4.2); note that this guide is not exhaustive or prescriptive and alternative methods may be available. **Appendix X5** provides a Sampling Reference Guide for Sediment Chemistry Analytical Methods (Table X5.1). **Appendix X6** provides a discussion of critical success factors for sediment chemistry analytical programs.

6.2.2 *Sample Media and Matrix Considerations*—Samples collected in support of sediment corrective action programs may consist of multiple media types including sediment, porewater, surface water, groundwater, and biota tissues.

6.2.2.1 Sample media and matrix complexities can present unique analytical chemistry challenges (such as elevated sediment moisture levels, which directly impact analytical RLs and analyte extraction efficiencies). Also, sediments may contain elevated concentrations of target or nontarget compounds (or both) and other matrix interferences, necessitating a customized analytical approach to improve data quality and usability outcomes.

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

6.3 Trace Organic Compound Analysis:

6.3.1 *Overview*—Trace organic compound analytical methods consist of three separate stages: (1) the preparative stage to isolate (extract) and concentrate the target analytes of interest, (2) the extract cleanup stage to remove potential matrix interferences, and (3) the determinative stage, where the sample extract is analyzed for target analytes of interest by specific analytical instrumentation. The objective of the sample preparation and sample extract cleanup steps is to maximize the amount of analyte of interest extracted and minimize potential interferences; this will enhance the level of sensitivity (that is, lower the RL) for the analytes. The analytical method dictates the specific instrumentation used for a given analytical parameter and the level of sensitivity that can be achieved. 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 corrective action programs.

6.3.2 *PCB Aroclors, Homologs, and Congeners*—PCBs are a class of 209 compounds called congeners that contain from one to ten chlorine atoms substituted in different arrangements on a biphenyl molecule; groups of congeners containing the same number of chlorine atoms are called homolog groups. 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 from the late 1920s until 1977 in the United States (22) and used in a plethora of products.

6.3.2.1 Screening level investigations often begin with PCB Aroclor analysis by USEPA Method 8082 using GC/ECD instrumentation. PCB Aroclor analysis is less definitive in nature because chromatographic patterns and peak ratios are subject to change in the environment due to “weathering.” PCB Aroclors may be reported as ND due to a lack of pattern recognition, even though PCB congeners may be detectable. Determination of total PCB concentrations using the PCB Aroclor approach presents challenges because individual Aroclors represent mixtures of PCB congeners, so there is a possibility to “double count” PCBs. Additional discussion of PCB analysis is provided in Section 9.

6.3.2.2 Sediment corrective action programs often use USEPA Method 1668 based on HRGC/HRMS to determine low-level PCB congeners and homolog group concentrations to eliminate uncertainties associated with the PCB Aroclor analysis approach. USEPA Method 1668 is extremely sensitive, so it is used for surface water quality studies, forensic PCB investigations, and sediment and tissue programs. This procedure can determine all 209 PCB congeners, or a subset of congeners (that is, World Health Organization, National Oceanic and Atmospheric Administration, or a custom list), and homolog groups. USEPA Method 8270-SIM-modified gas chromatography/low-resolution mass spectrometry (GC/LRMS) for PCB congener and homolog analysis provides an option for determination of all 209 PCB congeners with less sensitivity (that is, a higher RL). Additional information on PCB analysis is provided in Section 9.

6.3.3 SVOCs, PAHs, Alkylated PAH Homologs—Analysis of acid and base-neutral extractable compounds, also known as SVOCs, for the full list of target analytes that may be quantitated by USEPA Method 8270 may not be amenable to extract cleanup techniques like other trace organic methods. For sediment samples, laboratories typically use USEPA Method 8270 in SIM modes to maximize sensitivity for analytes on a list of 70 SVOC analytes, including 17 parent PAHs, and 34 alkylated PAHs. USEPA Method 8272 or Test Method **D7363** is used for determination of parent and alkylated PAHs in sediment porewater using solid phase microextraction (SPME) and GC/MS in SIM mode. Additional information on PAH analysis is provided in Section 9.

6.3.3.1 Parent PAHs are two or more fused aromatic rings with no attached alkyl groups (that is, only hydrogen atoms are attached to the aromatic ring structure). Alkylated PAHs are the parent PAH molecules 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 alkylated 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 9 for additional information on PAH analysis.

6.3.4 Organochlorine Pesticides—Analysis of organochlorine pesticides for sediment corrective action programs typically uses USEPA Method 8081 with GC/ECD instrumentation. However, the presence of high concentrations of PCBs in samples can potentially cause false positive pesticide detections with this analytical approach.

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

6.3.5 Hydrocarbons—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 corrective action programs.

6.3.5.1 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 gasoline-range organics (GRO) by a purge and trap sample introduction approach, diesel-range organics (DRO) by an extraction approach, and oil-range organics (ORO) by an extraction approach.

6.3.5.2 Laboratory protocols based on USEPA Method 8015 vary for sample extraction, GC column types, temperature increase rates, chromatographic run times, and instrument sensitivity. Differences occur between a high-resolution output (with a longer sample run time) generated by a laboratory that specializes in hydrocarbon analysis and a low-resolution result (with a shorter sample run time) that relies on matching to known reference materials. Additional hydrocarbon analysis information is provided in Section 9.

6.3.5.3 Another analytical approach is based on separation of aliphatic and aromatic fractions, then quantitation of specific hydrocarbon ranges by each fraction using regulatory agency

defined analytical methods. Analytical protocols vary for fractionated extractable hydrocarbon analysis.

6.3.6 Polychlorinated Dioxins and Furans—Dioxins and furans are common names for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Collectively, these are referred to as PCDD/DFs.

6.3.6.1 Analysis of PCDD/DFs for sediment corrective action programs is typically based on USEPA Method 8290 or 1613 using gas chromatography/high-resolution mass spectrometry (GC/HRMS) to determine seven PCDD and ten PCDF homolog groups.

6.3.6.2 PCDD/DFs sample analytical results are reported, along with toxic equivalency factors (TEFs) relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin, using the World Health Organization internationally accepted framework (or other TEFs) as defined by the applicable regulatory program.

6.3.7 PFAS—PFAS can be categorized as polymeric or nonpolymeric, collectively amounting to more than 4,700 Chemical Abstracts Service (CAS)-registered substances. Environmental concerns pertaining to PFAS are centered primarily on the perfluoroalkyl acids (PFAA), a subclass of PFAS, which display extreme persistence, chain-length-dependent bioaccumulation, and adverse effects in biota. The published analytical methods performed by commercial laboratories are limited to determination of a small subset of the CAS-registered PFAS (Guide **E3302**).

6.3.7.1 Test Methods **D7968** and **D7979** are used for determination of 31 target analytes in soil and sediment sample matrices, respectively.

6.3.7.2 USEPA Method 1633 is used for analysis of 41 target analytes in soil, sediment, and tissue sample matrices, as well as various water matrices (such as groundwater, porewater, and surface water).

6.3.8 Volatile Organic Compounds (VOCs)—Determination of VOCs for sediment corrective action programs typically uses USEPA Method 8260 with purge and trap sample introduction and GC/MS instrumentation.

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

6.3.9 Other Organics Analyses—Other organic tests associated with a specific historic use of a chemical at a sediment site may be needed. For example, laboratory analysis of butyl tins (an antifouling agent used in boat paint) may require development of specialized analytical protocols based on a scientific literature review. Additional information on method development is provided in Section 10 of this guide.

6.4 Trace Metals, Inorganic, and Other Analysis:

6.4.1 Overview—Trace metals and inorganic compound analytical methods consist of two separate stages: (1) the preparative stage to digest (isolate) and concentrate target analytes of interest, followed by (2) the determinative stage during which the digested sample is analyzed for target analytes of interest by specific analytical methods.

objective of the sample preparation step is to maximize the mass of the analyte of interest isolated and minimize potential interferences; this will enhance the level of sensitivity (that is, lower the RL) for the analytes. The analytical method determines the specific instrumentation used for an analytical parameter and the level of sensitivity that can be achieved. 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 for sediment corrective action programs.

6.4.2 Sample Preparation—Sample preparation methods are selected based on analyte of interest and sample media/matrix type. 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.

6.4.2.1 Determining trace metals concentrations in water sample matrices with higher levels of salinity (such as sea water) presents special challenges, due to the 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 RLs elevated accordingly. Specialized sample preparatory protocols (such as chelation extraction) or instrumentation (such as hydride generation and collision/reaction cell technology) may need to be used to mitigate saline sample matrix effects while still providing the level of sensitivity needed to support sediment corrective action programs.

6.4.3 Metals Instrument Analysis—Trace metals analyses for sediment applications may specify USEPA Method 6020 using ICP/MS with collision/reaction cell technology. Certain analytes have “same mass” interferences; standard ICP/MS without the collision/reaction cell may result in false positives results for trace metals analysis. Metals analysis can also be supported by USEPA Method 6010 using inductively coupled plasma/optical emission spectroscopy (ICP/OES) for applications requiring less sensitivity.

6.4.4 Mercury Analysis—Mercury analysis for sediment corrective action programs is typically based on the cold vapor atomic absorption (CVAA) approach used by USEPA Method 7471 with target sensitivity in the 3 µg/kg–30 µg/kg range. If more sensitivity is required, USEPA Methods 7474 and 1631 (both based on atomic fluorescence [AF]) modified for sediment and biota can support target sensitivities in the 1 µg/kg–2 µg/kg range. USEPA Method 7473 (based on atomic absorption [AA]) is also used for biota tissue analysis for target sensitivity in the 20 µg/kg range.

6.4.5 Methylmercury—Methylmercury is determined by USEPA Method 1630 (based on AF) with modified sample preparation procedures for sediment and biota tissue matrices for targeted level of sensitivity of 0.1 µg/kg.

6.4.6 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 select metals simultaneously extracted during the AVS procedure. SEM typically includes 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.

6.4.6.1 Toxicity is evaluated by calculating the sum of the SEM (µmol/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, whereas a ratio greater than 1 would indicate that the metals may be bioavailable.

6.4.6.2 Method guidance (23, 24) requires maintaining anoxic conditions to sustain metal sulfide concentrations in the sediment samples submitted for AVS/SEM analysis. Exposure of sediment samples to oxygen during sample collection and analysis may result in false positive assertions of metal bioavailability. The methods presented in Refs (23, 24) are 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.

6.4.7 Organic Carbon—Organic carbon has been shown to influence contaminant bioavailability. Organic carbon methods include determination of TOC, black carbon (also called soot), particulate organic carbon, and fraction of organic carbon.

6.4.7.1 TOC analysis is conducted by USEPA Method 9060 in water, whereas the USEPA Lloyd Kahn protocol is used for sediment (25). Black carbon analysis has no published USEPA methods, so laboratories follow procedures based on the scientific literature.

6.4.7.2 Laboratories typically perform both TOC and black carbon analysis for sediment in duplicate (at a minimum) due to the inherent variability from the small sample aliquots used. Upon 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, referred to as the portion of the organic matter available to adsorb organic COCs. In general, the higher the organic carbon content, the more organic chemicals may be adsorbed to solids and less of those chemicals will be available to leach into water. Laboratories typically rely on the scientific literature for method protocols.

6.4.8 Lipids Determination—Percent lipids analysis is often requested to normalize the results of lipophilic contaminants present in biota samples. There are no published USEPA 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. An example of a lipids determination protocol used by some laboratories is documented in Ref (26).

7. Passive Sampling Methods

7.1 Overview:

7.1.1 The freely dissolved concentration (C_{free}) of chemicals in sediment porewater is the driving force for contaminant transport to the surface water column and bioaccumulation in benthic organisms. The freely dissolved chemicals in surface water control chemical uptake by 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_{free}).

7.1.2 Potential risks of adverse biological effects from chemicals are most directly related to a chemical's C_{free} , which can be measured through passive sampling methods (PSM). Passive sampling measurements can be used to better understand contaminant bioavailability and associated risk, inform design specifications of a remediation technology, and monitor the efficacy of a remedy.

7.1.2.1 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_{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 an engineered sediment cap.

7.1.3 The application of PSM is a relatively new practice compared to other sediment analytical techniques, and the state of the practice for PSM continues to evolve. It is expected additional standard methods and guidance documents will be developed, further improving and standardizing the use of PSM.

7.2 Passive Sampling Method Advantages/Disadvantages:

7.2.1 The use of PSM provides the following benefits:

7.2.1.1 Measures the C_{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 bulk sediment concentrations.

7.2.1.2 Can provide a time-averaged response.

7.2.1.3 Can reduce or eliminate the need for frequent environmental sampling through deployment over large temporal and spatial scales.

7.2.1.4 Can provide high vertical resolution.

7.2.1.5 Can provide representative measures of undisturbed site conditions, as compared to more conventional sampling methods.

7.2.1.6 Are increasingly being accepted by regulators as a reliable and accurate tool for measuring C_{free} .

7.2.2 The use of PSM has the following drawbacks:

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

7.2.2.2 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 (especially if performance reference compounds [PRCs] are used) requires additional effort, as does data analysis to interpret results.

7.2.2.3 There may be additional costs associated with the use of PRCs, especially when using deuterated and ^{13}C -labeled compounds (refer to 7.4.3).

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

7.2.2.5 Oxygen present in passive samplers prior to deployment and oxygen accumulation after retrieval may impact results, especially for redox-sensitive elements.

7.2.2.6 Surficial sediment may be disturbed during deployment of passive samplers.

7.3 Passive Sampler Material Selection:

7.3.1 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 7.4 for organic constituents and 7.5 for inorganic constituents. Appendix X7 is Quick Reference Guide for Passive Sampling Method Selection, a matrix of potential sampler types that can be used for different COCs; Appendix X8 is Designs and Implementation Considerations for Passive Samplers for Inorganic Constituents; Appendix X9 is Advantages and Limitations of Passive Sampler Types for Organic and Inorganic Compounds; and Appendix X10 is Methodologies and Equations for Determining Aqueous Chemical Concentrations (C_{free}) from Passive Sampler Results.

7.4 Organic Constituents:

7.4.1 Principles—The C_{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 measures a time-specific concentration that must be corrected to the concentration at an equilibrium condition (27, 28).

7.4.1.1 It is important to understand how rapidly the target contaminants reach equilibrium with the passive sampler, sediments, and other environmental media. This depends on factors such as exposure time, passive sampler characteristics (such as construction material, sampler dimensions [including thickness]), and the target contaminant's physicochemical properties (29, 30). Passive samplers with polymer thickness of a few micrometers are available for equilibrium sampling of most hydrophobic organic chemicals within a practical time frame.

7.4.1.2 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 allow precise measurement of their loss, follow the same kinetics as the target analyte, and do not exist in the target environment (31). The depletion rate of a PRC during sampler deployment reflects the uptake rates of a contaminant, assuming isotropic exchange kinetics occur (31). 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, so 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 7.4.3 (32–34).

7.4.2 Types of Organic Passive Sampler Materials—The three types of passive sampler polymers typically used for estimating the C_{free} of HOCs include polyoxymethylene (POM), polyethylene (PE), and polydimethylsiloxane (PDMS). Each of these passive sampler materials can be used in field and laboratory applications.

7.4.2.1 PE and POM can easily be deployed as sheets in both surface water and sediment; if chosen with a high surface area to volume ratio, sheets have the advantage of lower analytical detection limits.

7.4.2.2 PDMS typically serves as the passive sampler polymer used on solid phase microextraction (SPME) fibers. SPMEs are fiber-optic cables with an inner core of glass, which is coated with PDMS. The PDMS coating can vary in thickness (typically it is 10 μm to 100 μm thick), and the length of coated fiber is adjustable. SPMEs are more suitable for deployment in sediment, rather than surface water, due to the limited polymer mass on the fiber. SPME fibers are fragile and need to be protected during deployment in sediment. They are typically enclosed in a protective casing during their deployment to address this limitation.

7.4.2.3 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 (for example, sampler performance, cost, durability, required detection limits, polymer–water partition, sampler fouling, and material availability), as outlined in Refs (31, 35–38) and summarized in [Appendix X7](#). Although the passive sampler–water partition coefficient (K_{PS}) has not been determined for all organic compounds and for all passive sampler material, the list of K_{PS} continues to expand (31, 36–38). This information can inform a decision on selecting the appropriate passive sampler or the need for determining K_{PS} for a specific study.

7.4.2.4 Equilibrium passive samplers are increasingly well established for neutral organics, but the field of passive sampling is still in the early stages of development for neutral and ionic PFAS. Recent advancements include adaptations of existing passive sampling technologies (39–41). Because development and laboratory validation of PFAS passive samplers are still ongoing and some of the technologies have not been deployed in the sediment environments for porewater sampling, unique PFAS passive samplers are not discussed in this guide.

7.4.3 *Use of Organic Passive Samplers*—Usage is presented in three stages: pre-deployment, deployment, and retrieval.

7.4.3.1 *Pre-Deployment*—Prior to sampler exposure to the sediment (either in situ or ex situ), 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 (31). If the sampling program has decided to use PRCs to account for non-equilibrium 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 (32, 37, 42).

(1) Equilibration times are sampler and analyte dependent but typically range from 7 to 30 days. After 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 aluminum foil, placing in a sealable plastic bag, and storing frozen (-4°C) until deployment (36). A duplicate field blank sample is used to obtain an initial PRC concentration ($C_{\text{PRC},i}$) for analysis of results.

7.4.3.2 *Deployment*—Passive samplers can be deployed both in the field (in situ, surface 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 (31, 35, 37, 43, 44). 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 (such as capping and in situ treatment remedies), will require in situ measurements to accurately capture the full suite of site-specific processes, whereas other objectives (such as bench-scale comparison of treatment alternatives) can be addressed with ex situ methods (42).

(1) Benefits of ex situ methods include being less labor intensive, less expensive, and providing more ability to control environmental variables (for example, temperature, light, and addition of biocides) 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 allows polymer sheets (PE and POM) to 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 (31). A recent interlaboratory study of low-density PE and PDMS polymeric samplers indicated that agitated sediment exposures achieved equilibrium after continuous mixing in around 30 days (45). This study indicated that if polymeric samplers are used to characterize sediment porewater under agitated exposure conditions for longer than 30 days in the laboratory, PRC use may be omitted (45). 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 (31, 46), 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 sediment sites (36). 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 (less than 1 % depletion) (37).

(2) In situ methods generally result in a better characterization of actual field exposures. This approach may be preferable when it is important to capture local site processes, such as groundwater intrusion, currents, bioturbation, vertical contaminant concentration profiles in porewater, and sediment–water column gradients and fluxes (31). The success of an in situ passive sampling program depends in large part on the successful 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 (42). During in situ deployment in water and sediment, polymer sheets are typically attached to rigid metal (that is, aluminum or stainless steel) frames that are used to

is, aluminum, copper, or stainless steel) mesh that fully exposes the sampler surface to its environmental surroundings while protecting it from damage (37). 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, within a metal mesh or a copper or stainless steel sheath) to avoid loss or breakage (37). Shielded, modified push-point-type samplers with perforations are especially useful for housing SPME fibers and providing sufficient protection for insertion into sediments (47). 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.

(a) Generally, in situ samplers are left in place for at least a week and up to a month or longer. It is important to choose an equilibrium time that is a balance between using shorter times, to minimize the potential for sample disturbance or vandalism, and the time required to achieve a significant fraction of equilibrium for highly hydrophobic contaminants (37). This balance often means that chemical equilibrium is not reached for all target analytes, necessitating the use of PRCs. The use of PRCs adds the potential for additional errors that affect both the precision and accuracy of derived C_{free} values (28). 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 (31).

7.4.3.3 *Retrieval*—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 be required for retrieval as well). After 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, because these materials can interfere with analytical procedures and data analysis (37). Once the sampler is clean, it can be processed as defined in the assessment plan (such as sectioned to evaluate depth profiles) and placed in clean glass vials (in a freezer at -4°C , in the dark) until they are analyzed (37).

(1) Processing of passive sampler devices should be performed as quickly as possible after retrieval to minimize loss of more volatile analytes (that is, naphthalene and other low molecular weight compounds) during exposure to air (37, 48). PDMS samplers have been extensively used due to their rapid uptake kinetics, but these properties also lead to faster loss of volatile analytes (48).

7.4.4 *Quality Assurance and Quality Control (QA/QC)*—Appropriate QA/QC guidelines should be followed when implementing a passive sampler monitoring program. Guidelines specific to passive samplers are described in Refs (31, 37). At a minimum, blanks (both trip blanks and field blanks) are an important measure to implement to account for residual

contamination in sampler or storage materials, as well as contamination introduced to the sampler from ambient air at the sediment site.

7.4.4.1 Proper replication of blanks will allow for reliable corrections of sampler data. Additionally, replication of deployed passive samplers at select locations can help the data user understand field-specific variability. Additional considerations for passive sampler-specific QA/QC measures (such as field solvent blanks, field control samplers, and field internal standards) are discussed in Ref (38).

7.4.4.2 Time series measurements or parallel sampling with multiple coating thicknesses can be used as an approach to confirm the attainment of equilibrium and the absence of sampling artifacts as part of the passive sampling measurement (44, 46, 49). The quality of chemical analytical methods should be quantified by using internal calibration standards (31).

7.4.5 *Data Conversions and Corrections for Field Conditions and Site-Specific Equilibrium Levels*—Results from the passive samplers typically provide two basic types of information: the concentrations of target analytes in the passive sampler (C_{PS}) and C_{free} of target analytes in the aqueous phase around the sampler (36). The C_{free} in the aqueous phase around passive samplers can be calculated based on the amount of contaminant per mass or volume of passive samplers (C_{PS}). Therefore, it is very important to measure the sampler mass and dimensions accurately. The steps to converting the C_{PS} to C_{free} will depend on whether equilibrium or non-equilibrium conditions were attained. When equilibrium has been achieved and confirmed, C_{free} can be obtained as ratio of C_{PS} and the appropriate K_{PS} value.

7.4.5.1 To correct for non-equilibrium conditions, PRCs can be used to quantify the level of equilibrium reached. Approaches to correct non-equilibrium conditions using PRCs are based on the first order exchange kinetics and Fickian diffusion (32, 50).

7.4.5.2 The methodologies and equations for calculating C_{free} in the aqueous phase based on concentrations in the sampler are provided in Appendix X10 for both equilibrium and pre-equilibrium cases.

7.5 Inorganic Constituents:

7.5.1 *Overview*—This section describes the passive samplers typically used for estimating C_{free} of inorganic constituents, including dialysis samplers, diffusive gradient in thin films (DGT), and diffusive equilibrium in thin films (DET). In addition to discussion below, Appendix X7 (the quick reference guide for PSM selection) discusses sampler types for inorganic constituents, Appendix X8 provides further details on design and implementation considerations of passive samplers for inorganic constituents, and Appendix X9 summarizes the advantages and limitations of passive sampler types for organic and inorganic compounds.

7.5.2 *Dialysis Samplers Overview*—Dialysis samplers, commonly called peepers, are one of the original passive sampling techniques that are used to obtain samples for analysis of sediment porewater concentrations (51, 52).

reservoirs of ultrapure water (that is, deoxygenated and deionized water) isolated by a membrane and rely on the equilibration of a compartmentalized sampling volume with the constituents in the surrounding water (surface water column or sediment porewater). The equilibration is achieved via diffusion of the dissolved constituents across a semipermeable dialysis membrane (53). Peepers have been found to agree well with measurements obtained using centrifugation (54, 55). The use of peepers requires consideration of a number of important factors. These include (but are not limited to) equilibration time, sample volume requirement, type of membrane used, whether redox conditions affect the constituents, and the spatial resolution between samples. In view of these considerations, the specific procedure to be followed will be design and site dependent. For example, incomplete equilibration can be addressed by adding a tracer into dialysis cell compartments. Several of these considerations are discussed briefly below, with further details provided in the cited references.

7.5.3 Use of Dialysis Samplers—Usage will be discussed in three stages: pre-deployment, deployment, and retrieval.

7.5.3.1 Dialysis Sampler Pre-Deployment and Equipment Preparation—It is imperative that peepers be properly prepared prior to deployment to prevent cross-contamination of trace metals and to remove any source of oxygen that might alter the redox state in the sediment (56-59). The peeper body and cover plate should first be cleaned with a microabrasive detergent and rinsed well with deionized water to remove any residual oil or grease that may have originated during fabrication. They should then be bathed in a nitric acid solution for at least two days to remove any trace metals. Finally, the equipment should be thoroughly rinsed with deionized water and deoxygenated by placement in a water bath through which nitrogen gas is bubbled.

(1) Peepers are often fabricated from polymethacrylate (that is, acrylic) because of its low cost, durability, and workability. However, Ref (56) has shown that these materials and other plastics may store substantial amounts of oxygen, which may alter in situ porewater concentrations that are measured in anoxic sediments. High-density polyethylene and polyvinylidene difluoride were found to be the most suitable materials for peeper fabrication, primarily due to the low solubility of oxygen in those materials (56). Regardless of material used, peeper preconditioning should include at least a 30-day immersion in deionized water that is continuously purged with nitrogen gas prior to assembly of the peeper. This should be sufficient to reduce the oxygen stored in the materials to levels that avoid problems. Finally, after final assembly (and just prior to deployment), an additional 48-hour immersion in nitrogen-purged, deionized water is recommended (56, 57).

7.5.3.2 Dialysis Sampler Deployment—Dialysis samplers can be deployed either in situ (field deployments) or ex situ (laboratory deployments) to sample the water column, sediment porewater, or both. In situ methods, when properly applied, are generally considered to provide the most direct measure of exposure to porewater constituents under field conditions. In situ measurements will also properly reflect factors that might lead to a non-equilibrium condition between the sediment and the porewater, as might occur if groundwater

seepage is ongoing at a sediment site. Ex situ laboratory measurements are often performed to characterize porewater exposure concentrations during a laboratory toxicity or bioaccumulation test. Laboratory measurements of porewater concentrations may not be representative of field concentrations, but ex situ measurements are thought to provide a more direct characterization of toxicity to benthic organisms as compared to in situ measurements.

(1) Deployment times for ex situ and in situ samplers for inorganics may range from a few days to a few weeks or longer, depending on the type of device used. Several methods have been proposed to predict the equilibration time needed during deployment and to provide a correction to adjust the results when equilibrium has not been achieved (60-62). Further discussion is provided in [Appendix X10](#).

(2) In deep water settings, a diver will be required for both the initial insertion into the sediment and for retrieval at the end of the deployment period. It should be noted that insertion of the peeper might cause some physical and chemical disturbance to the sediments, which should be minimized if possible (57). The devices should be located in areas where the potential for disturbance is minimized and, if possible, in proximity to a physical landmark. The GPS location of each sampler needs to be carefully recorded, and sampler position should be marked with a buoy or other readily locatable marker.

7.5.3.3 Dialysis Sampler Retrieval—The exact timing of retrieval is not likely to be a critical factor because estimates of equilibration time are not precise, and corrections for this can often be made using tracers to reflect the actual deployment duration. The devices should be removed from the sediment with reasonable care, using divers as required, to limit disturbance of the sediment and to ensure that the device is not damaged, particularly the exposed membranes. Once retrieved, the peeper should immediately be rinsed with deionized water to remove any sediment particles adhering to the surface. The sample water should be removed from each peeper cell using a pipette tip (or syringe) to pierce the membrane. The sample water should immediately be transferred to a previously labeled, clean plastic vial or other suitable container and capped. Exposure to the atmosphere should be minimized as much as possible. The samples should then be preserved (this will depend on the chemical analysis being performed) and stored at 4 °C until they are analyzed.

7.5.3.4 QA/QC—QA/QC guidelines that are specific for dialysis samplers typically include use of trip blanks and field blanks, with replicates, to quantify the degree of residual contamination that may be present. Replicate devices should be deployed at a subset of the sample locations to provide an indication of sampling variability. If the peeper design includes multiple cells at a fixed depth, a similar form of replication can be achieved by repeating the same analyses on subsets of samples from the same sampling horizon.

(1) If the peeper deployment duration was sufficient for equilibrium conditions to have been achieved, then concentrations measured from the peeper cell water can be used directly. If deployment times were not considered to be sufficient to achieve equilibrium conditions, then either of two approaches should be considered for making a correction to the data. First,

data with a 2-parameter kinetic equation (60) or use one or more PRCs (62). Both of these approaches are discussed in further detail in [Appendix X10](#).

7.5.4 Thin Film Samplers (*Diffusive Gradient in Thin Film [DGT] and Diffusive Equilibrium in Thin Film [DET]*):

7.5.4.1 DGT Samplers Overview—DGT passive samplers were developed as a method to measure cation flux in the near surface sediments and overlying water (63). Chemical porewater concentration in a DGT is measured based on chemical diffusion through a known uptake layer into a sampler resin with strong sorbing capacity for the chemical of interest (64, 65). The diffusion coefficient through water can be used as an approximation, or the site-specific diffusion coefficient can be found experimentally (66). DGT samplers are used to measure cations, including trace metals. Common target analytes include arsenic, cadmium, calcium, copper, lead, iron, nickel, and zinc, but these samplers have been used for dozens of cations. The DGT sampler consists of a resin gel, a diffusion gel, and a filter. The resin gel is a binding layer optimized to uptake a substantially larger amount of the target analyte than is contained in the surrounding porewater. The diffusion rate into the sampler is controlled by the diffusion gel, a porous hydrogel. The filter is typically a 0.13 mm–0.15 mm thick, 0.45 μm pore size cellulose nitrate or polyethersulfone membrane preventing binding outside of the diffusive layer and also short-circuiting of the diffusion gel layer (64). Details on porewater concentration calculation assumptions and other considerations are detailed in [Appendix X8](#).

7.5.4.2 DET Sampler Overview—DET is a passive sampling technique that measures porewater concentration by coming into equilibrium with the porewater, as opposed to the flux measurement of a DGT. The DET technique relies on equilibrium between porewater or water column chemical concentrations and the DET gel. DETs have been developed to measure target chemicals including arsenic, cadmium, calcium, copper, lead, iron, mercury, nickel, strontium, and zinc. The DET sample gel comes into equilibrium with the porewater and the known partitioning coefficient for a chemical is used to calculate that concentration. These samplers do not concentrate analytes in the same way DGT does with resin layer, and they have limitations for trace metal sampling. They are more commonly used for higher concentration analytes such as arsenic, iron, and manganese and may underestimate porewater concentration if equilibrium is not achieved (67).

7.5.4.3 Use of DGT and DET Samplers—Usage will be discussed in three stages: pre-deployment, deployment, and retrieval.

(1) Pre-Deployment and Equipment Preparation—It is imperative that DGT and DET samplers be properly prepared prior to deployment to ensure that any source of oxygen that might alter the redox state in the sediment be removed.

(a) Prior to use, the DGT samplers are deoxygenated in a freshly prepared 10 mmol/L sodium nitrate solution with bubbling nitrogen gas for 12–24 hours. This step removes oxygen from the samplers that can be introduced into the

sediment when the DGT samplers are deployed. The sodium nitrate is necessary to raise the ionic strength of the diffusion gel and to increase the reproducibility of metal ion diffusion (68). DGT samplers should not be exposed to oxygen prior to deployment. If the DGT samplers need to be transported prior to deployment, the samplers should be transferred to double-bagged plastic bags in an anoxic atmosphere. The deoxygenation step should be completed as close to deployment as possible because oxygen can diffuse back into the samplers over time.

(b) DET samplers should be deoxygenated with bubbling nitrogen gas for 12–24 hours prior to deployment.

(2) Deployment—If the samplers are being deployed in water, they must be in the liquid and have the gel face exposed. In laboratory experiments, slow mixing is recommended to reduce any diffusion boundary layers at the surface of the DGT samplers. For sediment, the samplers are pushed into the sediment to desired depth. Piston samplers are placed at the surface of the sediment and can be sealed with putty to ensure that the gel face remains in contact with the porewater. After each deployment, field notes should include the time of the deployment, water temperature, depth of deployment, including reference to the sediment–water interface (mudline), GPS coordinates of the location, description of deployment location, and orientation in field notes. A buoy, lights, or both can be attached to the profilers for easier retrieval. Ideally, each location is sampled using at least three profilers to obtain a measure of the variability of measurements. If paddles are deployed in fine sediment, care must be taken to insert the profiler slowly and steadily, then stop at the desired depth without retrieving the paddle and potentially disturbing the sediment and changing its redox conditions. If the paddle is installed in a coarser sediment environment, special care must be taken to avoid ripping the profiler layers during deployment and retrieval. A casing with slide hammer can be used to protect the paddle from potential rips during the deployment, with steel cable used for protection of the profiler during deployment and to provide greater leverage for profile retrieval. If a casing is used, it should be decontaminated between deployments to avoid cross contamination.

(a) The DGT samplers are left exposed in the media for a known amount of time. In sediments, this time is typically 1–7 days, and for water samples this time is typically 1–21 days. The deployment time will vary depending on the range of concentrations that are being measured. Lower concentrations require a longer deployment to allow the samplers to accumulate a measurable amount of target analyte. Higher concentrations need deployment for less time, because the sampler can accumulate enough analyte to disrupt the linear concentration gradient across the gel, causing non-linear uptake. In addition, in mixing-limited systems, long deployment times can deplete concentrations in the vicinity of the sampler and limit sample representativeness.

(b) DET samplers are deployed in the same manner for water and sediments as DGT samplers. However, because the

DET samplers are equilibrium samplers, they should be deployed for longer times. The deployment times vary depending on the system and analyte concentrations to be measured.

(3) *Retrieval*—When the DGT and DET samplers are removed, the time should be recorded so the exact deployment period is known for each profiler. Samplers should be thoroughly rinsed with deionized water. For sediment sampling, all residual solids need to be cleaned from the exterior of the sampler in the field, because they can contaminate the gels during processing. The sampler should immediately be placed in a plastic bag and cooled with ice. Great care must be taken for trace level sampling to avoid cross contamination. The DGT and DET samplers can be extracted using similar approach. The gels are cut out from the sampler body using a tetrafluoroethylene (TFE)-fluorocarbon-coated razor blade and placed into prelabeled disposable vials. The use of TFE-fluorocarbon coating is not recommended when DGTs are used for PFAS sampling. For DGT, only resin gel is cut out from the sampler body, and the filter and diffusion gel can be discarded using disposable plastic tweezers, taking great care to ensure the resin gel is not compromised. If any solids have penetrated the filter layer and made direct contact with the resin gel, the resin should be discarded. Direct contact with the sediment will contaminate the resin gel and result in overestimation of porewater concentrations. For both DGT and DET, the resin gel is then sectioned. For DGT depth profiler samplers, the resin gel is sectioned over depth to give porewater concentrations by depth. The depth profilers are typically sectioned at 0.5 cm or 1.0 cm resolution, but sections have been taken as low as 0.1 cm. As long as there is a detectable amount of analyte in each section, the area chosen will not affect the estimated porewater concentration.

(a) For analyte elution, each resin section is analyzed using the method optimized for the chemical of interest. For example, for the analysis of total mercury in DGTs, the resin is eluted in 3 mL of concentrated trace-metal-grade hydrochloric or nitric acid for 24 hours (66). Resin gels should not be left in the acid for longer than 24 hours because the gel will break down, which can interfere with analysis. Once the acid is removed from the gel, the sample is ready for analysis. The samples should then be preserved (the method used will depend on the analysis being performed) and stored at 4 °C until they are analyzed. The samples are analyzed according to standard analytical methods, such as USEPA Method 1631.

7.5.4.4 *QA/QC*—It is important to run quality control (QC) checks during use of both DGT and DET samplers. There are several types of QC samples that should be run with every sampler batch.

(1) A laboratory blank is a check on the contamination mass contained in the resin before it is assembled into a sampler. Contamination in the resin can come from chemical contamination, especially the resin beads, glassware, or storage solutions. A laboratory blank is taken from each set of resin gels cast for a sampling event, as well as from profilers left in the lab during the sampling event.

(2) The second type of QC sample is a deoxygenation blank. The deoxygenation blank is taken after the samplers are deoxygenated, before they are taken into the field. The deoxy-

genation solution may contain a small amount of the target analyte from the ambient atmosphere and chemicals used, so the samplers may accumulate a small amount of this analyte during the deoxygenation process. The deoxygenation blank will check that this contamination is not significant compared to the analyte accumulated during sampling.

(3) Trip blanks are also taken as a QC sample. The trip blanks are samplers that are deoxygenated and then transported along with all deployed samplers. The trip blanks will measure any contamination accumulated during transportation, storage, and field use of the samplers.

7.5.4.5 *Detection Limits*—The detection limit is an important factor when considering what sampling technique to employ. For DGT, the detection limit is often controlled by the level of background analyte in the resin gels. It is not possible to clean resins prior to deployment because the chemicals required to remove the analytes from the resin also destroys the resin. The detection limit will also be a function of the physical dimensions of the sampler and deployment time for DGT samplers. Lower detection limits are possible in controlled laboratory settings where contamination from chemicals of interest are lower. Ideally, for fabricating samplers for chemicals of interest, a clean room should be designated for fabrication and this room should intentionally be kept clean of any potential cross contamination.

7.6 *Current Regulatory Perspective and Next Steps in Passive Sampling:*

7.6.1 *Utility of Passive Samplers*—Research and case studies have demonstrated PSM as an effective method for measuring C_{free} in surface water and sediment porewater. In addition, current guidance documents identify PSM as a means for further understanding contaminant migration, bioavailability, and associated risk at sediment sites (38, 69). However, there are additional improvements to PSM that would further advance the quality and confidence of data collected. Such improvements may include the following:

7.6.1.1 Development of laboratory testing procedures to verify the precision of the methods across different laboratories and technicians when prescribed field and analytical procedures are used. Recent studies demonstrated the use of standardized procedures for quantifying C_{free} in contaminated sediment porewater by multiple participating public- and private-sector analytical laboratories, which may encourage stakeholder acceptance and confidence in use of these procedures (45, 70). Ref (45) emphasizes the importance of verifying the precision of the determination of PRC-loading concentrations prior to deployment of PRC-loaded passive samplers, especially under laboratory static conditions or during in situ deployment.

7.6.1.2 Development of laboratory standard reference material to allow for method accuracy checks (31).

7.6.1.3 Development of non-equilibrium PSM for in situ deployments in order to validate PRC use in static sediment environments, and identify ways to improve the accuracy of PRC correction methods (31).

7.6.1.4 Development and validation of the PFAS passive samplers is currently ongoing.