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Critical Issues for Contaminated Sediment Management

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1. EXECUTIVE SUMMARY

1.1 NAVIGATING IN UNCERTAIN WATERS: RECOMMENDATIONS AND OVERVIEW OF TECHNICAL GAPS FOR EFFECTIVE SEDIMENT MANAGEMENT

Marine sediments are the ultimate receptor of contaminants in effluent from urban, agricultural, industrial and recreational activities, both at sea and on shore. Because of past industrial and ship activities, non-point source input, etc., sediments at many sites have some level of impact from anthropogenic compounds. As marine sediment and coastal sites fall under increasing scrutiny, the number of sites for which ecological risk assessment, and potentially, management, will be deemed necessary is bound to increase. Contaminated sediment sites must be ranked and prioritized, and cost-effective management strategies must be developed. It is assumed that the management process will seek to balance two parallel goals: (a) minimizing contaminant risk to the environment and human health and (b) minimizing cost.

The Office of Naval Technology (ONR) funded a project to identify problems, remediation approaches, technology gaps and needs relative to managing contaminated sediments in an integrated, cost-effective way. The goal was to examine what aspects of contaminated sediment assessment and management were successful, and what barriers existed for streamlining contaminated sediment management. As stated above, sediment management is complex, potentially contentious and often regional in its approach. However, seven major themes emerged as essential to better sediment management:

- A need for better integration of sediment R&D and "user" (e.g., site managers, policy makers, etc.) communities

- A need for better use of site data for risk assessment, communication and negotiation in support of decision making

- A need for clear and standardized methods for separating site-specific contaminant levels from regional background and off-site levels

- A need to better evaluate the impacts of innovative in-place and ex situ management technologies

- A need to evaluate pathways of contaminant mobility and attenuation in dynamic, near-shore sediments

- A need to standardize methods for evaluating soils and groundwaters to protect downstream sediment communities

- A need to evaluate the role of sediments in the TMDL process

1.2 THE CONCEPTUAL SITE MODEL

A conceptual site model (CSM) is critical for determining the most cost effective and efficient manner of protecting human health and the environment in environmental and remediation investigations. The CSM is a three-dimensional description of a site and its environment that represents what is known (or suspected) about the contaminant source area(s), as well as, the physical, chemical, and biological processes that affect contaminant transport from the source(s) through site environmental media to potential environmental receptors. The CSM identifies assumptions used in site characterization, documents the relevant exposure pathways at the site, provides a template to conduct the exposure pathway evaluation and identifies relevant receptors and endpoints for evaluation. CSM development is an on-going, iterative process that should be initiated as early as possible in the investigative process.

The CSM should be as simple or as complex as required to meet site objective(s) but the overall site remediation strategy and risk-based considerations should guide the development of the CSM. Refinements to the CSM can drive re-optimization of remedial design and/or operation. The CSM is also an important communication tool to facilitate the decision-making processes at the site.

1.3 ECOLOGICAL ASSESSMENT TOOLS

Assessment or measurement tools are a fundamental part of the formulation of an ecological risk assessment. Contaminated sediments are particularly complex media to measure and assess. This brief chapter summarizes the currently available measurement methods and considers those tools with specific chemical considerations. The tool descriptions provided herein should provide an outline for the risk assessor in assessing the fate and effects of a particular substance in the sediment, and the potential for bioaccumulation, bioconcentration, and/or biotransformation. Tissue residue analysis and an introduction to bioaccumulation modeling are also addressed.

1.4 CHARACTERIZING THE SPATIAL EXTENT OF SEDIMENT CONTAMINATION AT IMPACTED SITES

Once sediment contamination has been discovered at a site, characterization of the full nature and spatial extent of contamination – that is, the extent of its vertical as well as lateral distribution – is often required to make appropriate and cost-effective, risk management-based decisions for the site. A logical, step-wise approach should be followed for characterizing the spatial extent of sediment contamination. This chapter briefly summarizes a step-wise and iterative approach – the Data Quality Objectives (or DQO) Process – that may be used to develop a resource-effective sampling and analysis plan for adequately characterizing the spatial extent of biologically relevant sediment contamination at an impacted site. A general example of application of the DQO process for characterizing the spatial extent of biologically relevant sediment contamination within a dynamic riverine environment is also included. Finally, the roles that site-specific information, the conceptual site model, and statistical considerations collectively play in developing a sampling and analysis plan consistent with the DQOs are also briefly discussed.

1.5 THE USE OF FIELD SCREENING OR RAPID SEDIMENT CHARACTERIZATION (RSC) TOOLS FOR SEDIMENT ASSESSMENTS

The primary goals of a sampling and analysis plan for an Ecological Risk Assessment (ERA) or a sediment site assessment are to identify potential contaminant sources and to delineate areas of contamination. However, traditional sampling and analysis approaches do not always provide all the information necessary to support the risk assessment process in a cost- and time-effective manner. Site assessments performed in the marine environment are often hindered due to the complexity and heterogeneity of marine ecosystems. One measure that can be implemented at various stages of the assessment or ERA process at sediment sites is the use of field screening or rapid sediment characterization (RSC) technologies. These are field transportable screening tools that provide measurements of chemical, biological or physical parameters on a real-time or near real-time basis. When used appropriately, these tools can streamline many aspects of the assessment process. The tools can be used to delineate areas of concern, to fill in information gaps and to assure that expensive, certified analyses have the greatest possible impact.

This paper provides information about several of the rapid sediment characterization technologies that can be used at marine sediment sites. Potential applications of RSC tools are described to illustrate the use of applying rapid sediment characterization tools to different stages of the ERA process. Finally,

important considerations are described for the evaluation, selection and application of RSC tools for the assessment process.

1.6 EVALUATING REFERENCE AREA CONDITIONS IN SEDIMENT ASSESSMENTS

Reference areas can be used to make comparisons among biological, chemical or physical sediment data that might be collected from an area under study. Lack of appropriate criteria for selecting the reference area may result in an inappropriate location being selected, and inappropriate sediment remedial actions being taken. Identification of the reference site may depend on the remedial goals and options, historical and existing conditions at the site, as well as the critical physical, chemical and biological parameters that are being evaluated. A proper approach to assessing and selecting a reference area is a key element of the overall sediment assessment process. Currently, there is no definitive approach to selecting a reference area; however, criteria can be established that would permit a more systematic process for making this selection.   Important considerations for selecting reference areas are discussed as well as where these areas may find application in sediment assessments.

1.7 APPLICATION OF SEDIMENT TOXICITY TESTING IN SITE REMEDIATION ACTIVITIES

Sediment toxicity tests have become an integral component of environmental assessments. Toxicity testing is a feature of many regulatory programs in the U.S. (e.g., CWA, FIFRA, TSCA, CERCLA/SARA, RCRA, MPRSA). Numerous sediment bioassays have been developed for a variety of purposes. Most of these bioassays have been designed to assess the toxicity of sediments to make regulatory-based decisions (e.g., identifying acceptable disposal alternatives for dredged material; determining cleanup levels; or evaluating the effectiveness of the cleanup remedy). Since sediments serve as the ultimate repository for many environmental contaminants, the use of sediment bioassay as a tool in site assessment and site remediation/management activities logically follows.   However, sediment toxicity tests should not be applied without proper consideration of the strengths and weaknesses of the individual procedures. This chapter provides an overview of the general types sediment toxicity testing procedures currently available. A discussion of the strengths and weaknesses of individual procedures in context of the potential application to site assessment, remediation/management, and post-remediation/management monitoring is also included. While testing procedures exist for evaluating the potential for exposure and/or uptake of contaminants (e.g., biomarker and bioaccumulation tests), the scope of this review is limited solely to toxicity testing procedures.

1.8 BIOAVAILABILITY OF CONTAMINANTS IN SOIL AND SEDIMENT SYSTEMS

The bioavailability of a contaminant defines the relationship between the absolute concentration of a chemical in a specific environmental matrix and the level of chemical that actually enters the receptor, potentially causing harm. The quantity of chemical that actually negatively impacts the health of the receptor, or concentration of contaminant that reaches the site of toxic action in an organism, is specific to the receptor, the route of entry and the time of exposure. Bioavailability considerations play a significant role in the management of soil and sediments systems, as the toxicity of chemicals in aqueous or gaseous phase is often changed once the chemicals come in contact with soil or sediments.

Assessment of bioavailability addresses the fundamental issue of exposure of the contaminant to a receptor. Exposure is not the result of the total concentration of a chemical in which the potential receptor is found, but only that portion which is biologically available. Exposure occurs once a chemical is released from a soil/sediment particle and then transported to receptor.   Exposure of soil/sediment-borne contaminants is impacted by physico-chemical properties of the chemicals and environmental parameters including solubility, sorption, chemical form (speciation), and compartmentalization within

the environment. These physico-chemical processes often result in environmental sequestration of the contaminant; exposure is then the result of the availability of any non-sequestered fraction. Exposure is further affected by the interaction of the non-sequestered fraction of the contaminant with an organism through its life history, which takes into account route and duration of exposure. Ultimately, bioavailability is species-specific, because the dose that reaches an organism's target organs or tissues, and results in a biological response, may differ between receptors.

1.9 IN SITU BIOACCUMULATION TESTS

This chapter presents a brief description and evaluation of in situ techniques that have been used to evaluate bioavailability of sediment-associated contaminants, specifically caged biota studies and semi-permeable membrane devices (SPMDs). In general, these techniques are intended to provide a relatively short-term, reproducible indicator of contaminant bioavailability. These techniques combine the advantages of experimental control offered by lab studies with the environmental realism provided by field studies. They are often used to gauge effectiveness of sediment remediation through performance of pre- and post-remediation studies. A brief description of these techniques is provided below, followed by a discussion of their advantages and disadvantages.

1.10 NATURAL PROCESSES DETERMINING CONTAMINANT AND SEDIMENT FATE

Natural fate and transport processes normally control the recovery of unremediated contaminated sediments, the effectiveness of in situ remedial processes, and the amount and fate of any residual contamination after disturbance of the sediment. Ultimately, it is the portion of the chemical (or constituent or contaminant) of concern (COC) that moves via natural processes into the water or food chain that is the source of exposure and potential risk to human and ecological receptors. Some of the processes that must be considered include,

- In-bed fate processes, including irreversible adsorption and chemical or biological reactions

- In-bed transport processes, including diffusion and advection as influenced by reversible sorption/desorption and colloidal transport

- Interfacial transport processes, including sediment deposition and resuspension, bioturbation, and water-side mass transfer

The purpose of this chapter is to describe the basic characteristics of these processes and their roles in determining contaminant and sediment fate. The range and significance of natural processes are influenced heavily by site-specific characteristics that must be adequately assessed prior to the selection, design and optimization of any management options for contaminated sediments. Any attempt to summarize and compare management options must recognize the different environments in which contaminated sediments are found. The relative importance of release, transport and fate processes differ significantly between lacustrine, riverine, estuarine, and coastal environments.

1.11 ASSESSMENT OF MONITORED NATURAL RECOVERY OF SEDIMENTS

Monitored Natural Recovery (MNR) of sediments as a remedial option relies upon natural environmental processes to permanently reduce risk and requires careful assessment, modeling, and monitoring. Pertinent natural processes include sediment deposition (burial), dispersion, irreversible adsorption, and chemical and biological reactions. MNR differs from "No Further Action" in that the assessment, modeling, and long-term monitoring are required to verify remediation is taking place.

Given that a site possesses appropriate conditions, benefits of MNR include reduction or elimination of secondary impact on habitats caused by construction, lower risk to workers, avoidance of possible resuspension, avoidance of disposal requirements, and lower potential cost than more invasive remedies.

This chapter provides a table of assessment tools for evaluating MNR, broken into three categories: 1) Sedimentation/burial by clean sediments, 2) Contaminant weathering, bio-transformation/ degradation, and 3) Ecological recovery. The paper also discusses the role of modeling. A reliable site conceptual model is needed, which is a qualitative or quantitative statement and diagram of how the various physical, chemical, and biological processes affect risk. For more complex sites, there are many available mathematical models, including hydraulic, sediment transport, physical and chemical transport, and biological/ecological. They are generally applied in sequence, the outputs of the more basic models becoming the inputs to the more advanced.

When assessing a site for MNR, it is also important to identify parameters that are counter-indicative for MNR. These include ongoing sources, immediate and significant harm, insufficient clean deposition, ongoing or potential high energy resuspension, low sediment sorptive capacity, microbial processes that enhance bio-availability, and instances where active remediation can achieve risk-based objectives much more rapidly.

MNR should never be assessed by itself, but rather in comparison with other remedial alternatives, and the assessment should encompass "cradle to grave" risks.

1.12 MONITORING REMEDIAL EFFECTIVENESS

Selection, design and optimization of remedial technologies for contaminated sediments requires an understanding of the following factors:

1. Ultimate effectiveness of the technology with contaminated sediments

2. Potential risks associated with application of the technology or resulting from the residual contamination left by the technology

3. How to measure and evaluate the performance of the technology when applied to contaminated sediments

4. Economics of the technology when applied to contaminated sediments, including the effects of scale and the balance between capital and operating costs

5. Uncertainties in application of the technology or in evaluating its potential risks and benefits

Unfortunately, many of these factors are not well understood. More importantly, however, the lack of standardization in how to measure and evaluate the performance of a remedial technology and the lack of adequate monitoring during implementation of these technologies suggests that our ability to select, design and optimize is not improving. The goal of this chapter is to identify these inadequacies and push for improved monitoring of remedial actions both during implementation and afterward in order to enhance our ability to define appropriate management approaches for contaminated sediments. A three-pronged program of monitoring is recommended: 1) long term monitoring of resource driving the remediation, 2) short-term monitoring of interim measures of remedial success, and 3) short-term monitoring of implementation of the remedial or management technology.

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2.1 BACKGROUND

Marine sediments are the ultimate receptor of contaminants in effluent from urban, agricultural, industrial and recreational activities, both at sea and on shore. Because of past industrial and ship activities, non-point source input, etc., sediments at many sites have some level of impact from anthropogenic compounds. It can be difficult to determine the magnitude, nationally, of sediment problems, for a number of reasons. Sediment sites are often not separated from other sites in organizational environmental databases, though this is rapidly changing. Key-word searches for sediment data often fail to be sufficiently specific, since the term "sediment" has many definitions, depending upon the user (e.g., sludge, soil, aquifer material, bottom sediments). Sediment environmental data are often kept in different places, depending upon the funding source, regulatory structure, potentially responsible party (PRP) and site definition (e.g., construction, dredging, hotspot, NPL, etc.). Often, due to the large volumes of sediment on coasts and in waterways, data may be limited. Unless a problem is encountered, sites are often not "on the map". In spite of these difficulties, a recent United States Environmental Protection Agency (USEPA) report (1997) identified 96 watersheds in the United States as having areas of probable concern for sediment contamination. As marine sediment and coastal sites fall under increasing scrutiny, the number of sites for which ecological risk assessment, and potentially, management, will be deemed necessary is bound to increase. Contaminated sediment sites must be ranked and prioritized, and cost-effective management strategies must be developed. It is assumed that the management process will seek to balance two parallel goals: (a) minimizing contaminant risk to the environment and human health and (b) minimizing cost (NRC 1997).

Marine sediments have a number of features that make them less straightforward to manage than are soils. Sediments in coastal areas are often integrators of contaminant input from multiple point or non-point sources within a watershed. This creates difficulties in tracking sources of contamination, and also can result in ubiquitous, regional "background" levels of anthropogenic contaminants that are difficult to separate from site-specific sources. For the same reason, sediments, much more often than soils, are impacted by multiple contaminants (or chemicals or constituents) of concern (COCs), making risk and management decisions complex. The hydrodynamics and geochemistry of sediment systems are also quite different than those of soil systems. While soils and groundwaters are often geographically removed from the receptors to be protected, sediments are in direct contact with the benthic community, near the base of the food chain that requires protection. Thus, sensitive biota can be directly impacted by remedial strategies, and cleanup targets can be orders of magnitude lower than those in most soil sites, pushing the limits of assessment and cleanup technologies and increasing costs.

Effectively managing contaminated sediments is quite interdisciplinary. Chemistry, biology, ecology, hydrodynamics and engineering all must be considered and balanced. Good science alone does not yield good management - science must be linked with regulatory framework, politics, engineering, economics, public relations and policy (site owner, Federal and regional). While most soil cleanups are based on human health risk assessments, most sediment studies begin with ecological risk assessments. Furthermore, sediments are subject to a multitude of regulatory criteria, from local to national and international. According to NRC (1997), "The mechanisms of the regulatory process in a given situation depend on where the sediments are located; where they will be placed; the nature and extent of the contamination; and whether the purpose of removing or manipulating the sediment is navigation dredging, environmental cleanup, site development or waste management." As a result, multiple

regulators or stakeholders may have different goals, cleanup criteria, or contaminants of concern, which drive their part of a site management decision.

The range of sediment management options exist on a continuum – beginning with those requiring no containment or physical control, through more aggressive in situ treatment and containment technologies, and finally, ending with removal and disposal or treatment technologies. In essence, risk management for in-place sediments consists of exposure pathway interdiction while ex situ approaches represent mass removal. If contaminants are to be left in place, it is critical to evaluate potential pathways by which contaminants might pose an ecological or human health risk, and to monitor, minimize or eliminate these pathways, particularly in surface sediments, while assessing the potential of these same mechanisms to drive natural recovery of the sediments. On the other hand, if sediments are to be removed, it is essential to know more about sediment characteristics as a function of depth (to determine volumes to be removed) and of whole volumes of sediment (to determine treatability or consequences of disturbance or disposal).

Nationally, sediment management issues are highly politicized and newsworthy. Not surprisingly, given the complex environmental issues and the enormous potential costs, in some regions, the decision process can be very adversarial. On the other hand, in other regions, sediment sites are managed with few problems. In spite of this, a consistent approach is not generally being applied to sediments at different sites (with some notable exceptions). Approaches to contaminated sediments are in flux. Less that a decade ago, regulators (and most potentially responsible parties or PRPs) thought that removal and treatment of contaminated sediments would be the remedy of choice, most sediment-related research and development (R&D) pursued technologies to support such an approach. However, based upon potential volumes and projected treatment costs, estimated potential costs of the indiscriminate use of such an approach nationally are prohibitive. Thus, many (though not all) groups predict or advocate that large volumes of contaminated sediments will be managed in place. Clearly, the critical issue is how to determine what volumes of sediment actually require management, and, for those that do, what is the most cost-effective but responsible approach. There are large gaps in our knowledge of the fate of contaminants in place, and the effects of in place and ex situ remedial strategies, which must be filled if management strategies are to be compared and chosen wisely.

2.2 OVERVIEW OF TECHNICAL GAPS FOR EFFECTIVE SEDIMENT MANAGEMENT

The Office of Naval Technology (ONR) funded a project to identify problems, remediation approaches, technology gaps and needs relative to managing contaminated sediments in an integrated, cost-effective way. The goal was to examine what aspects of contaminated sediment assessment and management were successful, and what barriers existed for streamlining contaminated sediment management. This assessment began with a Navy workshop on contaminated sediment management. The goal was to obtain user community input to assure that sediment-related research, development, testing and evaluation (RDT&E) is user-driven. This workshop brought together Navy personnel who are responsible for managing contaminated sediments (for both maintenance and construction dredging and site cleanup), and the RDT&E community. More than 60 attendees, from Engineering Field Divisions, the Navy Laboratories, Naval Facilities, Navy and Marine Activities, a USEPA lab and the Army Corps of Engineers, took part in the workshop, and the resulting documents are being used as a tool for the evaluation of sediment management policy and needs by the Navy as well as the Department of Defense.

To further evaluate sediment approaches, a variety of organizations that address sediment management issues were consulted, evaluated, or their publications were reviewed. These included basic research and academic programs (e.g., the Hazardous Substances Research Center, South/Southwest, University Research Initiatives at University of Washington and Rutgers University, the ONR Harbor Processes Program and its principal investigators (PIs)); PRP groups (e.g., the Sediment Management Work Group, Navy working groups); inter-organizational expert groups (e.g., the National Research Council

Committee on Contaminated Sediments, the Remediation Technology Development Forum Sediments Group), as well as USEPA, Environment Canada, European Environmental agencies and organizations, regional sediment policy and guidance, and a number of case studies.

As stated above, sediment management is complex, potentially contentious and often regional in its approach. However, seven major themes emerged as essential to better sediment management. While most are described in more detail below, in short they were:

- A need for better integration of sediment R&D and "user" (e.g., site managers, policy makers, etc.) communities

- A need for better use of site data for risk assessment, communication and negotiation in support of decision making

- A need for clear and standardized methods for separating site-specific contaminant levels from regional background and off-site levels

- A need to better evaluate the impacts of innovative in-place and ex situ management technologies

- A need to evaluate pathways of contaminant mobility and attenuation in dynamic, near-shore sediments

- A need to standardize methods for evaluating soils and groundwaters to protect downstream sediment communities

- A need to evaluate the role of sediments in the Total Maximum Daily Load (TMDL) regulatory process. While important, this is outside the scope of this report, and will not be discussed further.

2.2.1 Integration of the R&D and user community

Given the dynamic and complex nature of contaminated sediment management, it is critical that technical, policy and user personnel are more closely linked so that they can interface extensively, nationally and within organizations. There has been a marked improvement on this front in recent years, but a number of barriers still make these interactions difficult. While it has become increasingly common for even basic researchers to be required to be "vertically integrated" with an identified "end user" who can speak for technologies before they are funded, the difference in critical time horizons for many researchers and users creates a problem. Most successful environmental technology requires at least a decade, from bench concept to acceptance and implementation. Researchers and developers must focus on the myriad of technical details, such as scaling problems, potential interferences, etc., in order to assure that the approaches are meaningful and useful. On the other hand, most technology users, such as Regional Project Managers (RPMs) and regulators, are addressing problems that require some level of resolution within 1-3 years. They are generally addressing multiple issues and sites at once, and may only be minimally involved with technical details of the projects they manage. It is critically important that scientists and technologists assure that their work is driven by the "reality" that RPMs face, but it is not entirely reasonable to expect the users alone to guide such long-horizon development. The R&D community should, to a certain extent, provide an "informed push", rather than completely relying on users to anticipate their long-term needs. In short, developers should be visionary, but willing to adapt projects, even under way, to regulatory and economic reality and change. Ultimately, the science must be guided by need, and have as its end-goal a transfer to the next level of users (e.g., basic researchers to technology developers, technology developers to users) in a form which is useable and relevant to that community. This may require the involvement of brokers who are able to bridge the gaps between the minute details relevant to the scientists and the customers' need for tangible, standardized tools. This can only work well if there is a continued attempt to link these communities via working groups, mutual information exchanges, and technical meetings.

2.2.2 Maximizing data utility for contaminated sediment management

Frequently, original site assessment data are collected without input from the eventual modelers, decision makers, and risk managers on data needs. Since sediment risk assessments are often begun with no clear idea of where along the continuum site management will end, data are often collected in an iterative manner. A minor extra investment to assure that samples and data collected will serve the needs and priorities of multiple users or stakeholders can assure broader utility of data, and help prevent multiple sampling events, thus expediting site decisions at reduced cost. Once collected, it is critical that data are summarized and communicated in a manner that can address the concerns and priorities of all stakeholders who will be part of the decision process (for examples of some approaches, see Kirtay et al., 2000, Apitz, 1998, Apitz, 1999 and Apitz et al., 1999).

2.2.2.1 Data Management Practices for Decision Making

Countless millions are spent nationally for data on sediment sites. Often, these data are not used in the ultimate decision process or are poorly utilized. A number of "rules" about intelligent assessment, data handling and decision making became clear in a review of sediment management practices. Some seem obvious, and most are consistent with current USEPA, Navy, Corps of Engineers or other guidance. However, since there were many case studies observed where these rules were not followed, they are listed and described below.

Intelligent data handling and use involves the following approaches:

2.2.2.1.1. Data quality control (DQOs, QA/QC and statistics)

All site data collection and handling should be done in careful adherence to USEPA, organizational and other relevant regulatory DQO, QA/QC and statistical guidance.

2.2.2.1.2 Up-front negotiation of objectives, decision criteria and site conceptual models

Data are frequently collected without input or consensus from the full suite of stakeholders. A stumbling block to efficient data use has been the inability to compile and integrate or synthesize data, especially from multiple sources, in a uniform or mutually agreeable manner. Another problem at times has been a lack of openness in the process, resulting in distrust and extreme positions by some regulators, RPMs and stakeholders. Unless these issues are resolved up front, progress is unlikely at a site. One of the major observations of the National Research Council (1997) was that successful case studies resulted from openness, communication, and buy-in by all parties early in the process. This can be difficult, given that different parties may have vastly different decision drivers, but if costs are needlessly inflated by a failure to negotiate, all parties (barring, perhaps, cost-plus consultants) can lose. PRPs can spend countless millions assessing and re-assessing the sites, but, in a world of limited budgets, this can also reduce the funds available for ultimate remedial actions, possibly reducing remedial effectiveness.

Ecological risk assessment and environmental management, as described above, are complex, multivariate and uncertain processes. The goal of a well-designed RI/FS is to collect and evaluate enough information to reduce uncertainty and increase the probability that risk is properly assigned and managed. However, in most cases, "truth" is not clear-cut, and some level of uncertainty remains. For example, it is rare that a direct correlation between multiple lines of evidence (i.e., toxicity and bulk COC concentration) is observed, due to multiple confounding factors. This does not obviate the utility of each measurement, but argues for a weight-of-evidence approach. Unless, however, decision criteria are negotiated up front, preferably before data are collected, there can be a temptation by parties to exploit uncertainty in either direction to avoid "undesirable" outcomes. Clearly negotiated decision frameworks,

adherence to DQOs, and an explicitly defined Site Conceptual Model (see Chapter 3 for more details) makes it easier for all parties to have ownership of the process and to negotiate in good faith.

2.2.2.1.3 Do not generate new data where data exist

Personnel turnover (by RPMs, regulators and contractors) often results in a desire to start over, rather than "mine" existing information or honor predecessors' commitments. This can result in costly, iterative studies. Furthermore, there is a tendency by some stakeholders to fall into the "deep pocket syndrome" in which PRPs are pressured to collect data that would otherwise not be available but have no relevance to the decision process. Unless such an approach is specifically and explicitly negotiated, or it is funded by complementary R&D dollars, data collections that are not clearly in support of the remedial investigation and feasibility study (RI/FS) are not justified. Examination of case studies revealed that there were many cases in which sites were re-studied iteratively over decades. Though different regulatory and assessment frameworks were applied each time, little extra information was gained from repeated analyses that could not have been gleaned by a careful re-analysis of existing data. While there are many reasons to seek more data at a site, a critical assessment should first be carried out on currently available data. Any further sampling plans should satisfy the following criteria (which are essentially part of the DQO process): 1) Do these analyses fill existing data gaps? 2) Are these data relevant to decision criteria? 3) How will the data be used? 4) Have all stakeholders or decision makers agreed on the need for and use of these data?

2.2.2.1.4 Store data in unprocessed form for future, unanticipated use

While most site interpretation and negotiation will be based upon highly processed data (i.e., graphs, statistical summaries, contour plots, etc.), it is important to also assure that all data collected are available in a relatively unprocessed, preferably digital, form. This allows for the repeated use of data, to address questions possibly unanticipated at its collection. For instance, while total PAH (tPAH) numbers are needed to compare to potential sediment quality criteria or benchmarks, the PAH fingerprints (the relative distribution of individual PAHs) can provide a significant amount of information on source, background, weathering patterns, potential toxicity and the potential for natural attenuation. Thus, although generating tPAH numbers may the primary purpose of an initial data collection, processing and storing the more detailed distribution information allows for more detailed analysis, if necessary, at a later date.

The practice of making neutral, unprocessed data available is an important part of the data openness, which aids in good-faith negotiations. Suspicious stakeholders may be much more willing to accept data as sufficient if they are able to access and manipulate it themselves, with different approaches and assumptions. Generally, once data are mapped, contoured or plotted, they have already been highly processed, in ways that can be driven by the assumptions of the author. Simple factors such as the color choice in a contour, what benchmark values are normalized to, etc., can affect the way graphics look, and the message they convey. If all stakeholders can access data and subject them to their own benchmarks, criteria or assumptions, then communication and negotiation can be aided. In summary, critical data must be distilled for presentation to stakeholders, but still be transparent.

2.2.2.1.5 The selection of appropriate sediment benchmarks

Whenever one looks at bulk chemical concentrations in sediments, it is important to compare them to some criterion or benchmark to put the values into perspective. However, a choice of appropriate benchmarks is dependent upon a definition of the objectives of the work. If the objective is a determination of the potential risk of a contaminant of concern (COC) in the sediments, one can compare bulk chemical values to levels that are expected to be toxic in sediments (e.g., ER-L, ER-M, TEL, PEL and AETs). Such values are often termed Sediment Quality Guidelines (SQGs). If the objective is to

determine whether, for a given COC, the sediment being examined differs from other comparable sediments, one can compare bulk chemical values to background, regional or reference values. Often, a combination of the above is useful, if data may be used in more than one way.

Within a regulatory program, the SQGs to be used are often clearly laid out, or negotiated up front. If not specified by the regulatory structure, candidate SQGs could be selected and adapted to suit project objectives. Ultimately, the goal is to identify benchmark values that are relevant in regulatory and regional terms, but as technically comparable to data collected within a project as possible. While the benchmarks described above are quite useful as screening tools, it is important to remember that bulk sediment COC concentrations alone are not enough to make risk decisions. If screening concentrations are exceeded, though, more detailed examination is probably warranted.

One approach that can be applied is not to compare sediment COC concentrations to generic SQGs, but rather to generate site-specific benchmark values based upon site chemistry and bioassay results. Contaminant levels in sediments at a site can be compared with toxicity assays, bioaccumulation or flux measurements in the same sediments. If correlations are observed, "acceptable" contaminant levels can be selected for the site, based upon these values.

2.2.2.1.6 Integrating site and regional and data puts sites in perspective

Most contaminated sediment sites exist in highly populated or industrialized areas. Because of the dynamic nature of sediment systems, and the tendency of contaminants to associate with organic-rich, fine-grained sediments, entire regions may have some level of impact from anthropogenic compounds. Furthermore, contaminated sediments may have originated at a remote location, and settled at the site of concern. Sediments may have some level of a COC that originated near the site, some which came from remote sites, some at regional background levels, and some, for many chemicals, at natural background levels. Sediments with mixed contaminants may have a different mix of sources for each COC. For these and other reasons, evaluating and managing individual sediment sites in a vacuum, while not putting them in terms of other impacted and background sites in the region, can be shortsighted and misleading. Within a region, regardless of PRP or site owner, it is useful to compare data on a site of concern with data available on other sites. This allows for 1) an evaluation of potential contaminant sources, either historical or ongoing, 2) an evaluation of the relative severity of impact at multiple sites, and 3) an evaluation of site COC levels relative to regional reference or background levels.

While the fact that a site under investigation is contaminated at lower levels than other sites in the region does not remove PRP responsibility to manage the site (if risk is established), information on the relative risks of sites in a region may help avoid a number of undesirable outcomes including 1) improper allocation of limited resources by cleaning up sites based upon a schedule rather than relative risk (for a PRP with multiple sites in a region), 2) re-contamination of a cleaned site by adjacent sites left in place, or managed later in a manner which allows for dispersion, or 3) cleanup of sites which are not impacted at levels above regional background concentrations.

To achieve this goal, however, all sites, including reference sites, must be evaluated in the same manner as sites of concern. If site data are to be plotted together to examine regional trends, care should be taken to ensure equivalent data sets. Thus, all sites must be evaluated relative to the same set of benchmarks, and with comparable analytical methods. To achieve the latter, it is important to assure that laboratories that carried out analyses collected, analyzed, processed and reported data in a comparable manner. A few examples of potential pitfalls to this are:

2.2.2.1.6.1 Metals

Metals can be analyzed in a number of ways (total, acid leachable, AVS/SEM, XRF, etc.) Results from these different approaches are not directly comparable, and cannot be contoured together in a meaningful

way. Attempts to do so for regional comparisons can result in "false hotspots". For instance, if Cr is contoured in a region, with most sites reporting acid leachable Cr, and one site reporting Cr measured by total digestion, the latter site may have Cr which appears significantly higher than the other sites, but which actually comes from the natural mineral matrices, and is thus not ecologically relevant. If sites are targeted or prioritized based upon such inappropriate comparisons, evaluations of relative risk, as well as site prioritization and identification of COCs will be unsuccessful.

Many data reports compare the data to Effects Range-Low (ER-L, lower 10th percentile of the effects data), Effects Range- Median (ER-M, the 50th percentile of the effects data; values calculated in Long et al., 1995) and regional ambient values. These values are used as sediment quality criteria to aid in regulatory decisions. The data for the ER-L and ER-M calculations were taken from the biological effects database (BEDS), which is a compilation of data from around the continental United States. When these values are used, care must be taken to determine what the background concentrations for these contaminants are. In particular, caution should be exercised when sediment Cr and Ni levels are compared to ER-L and ER-M levels. ER-L concentrations for Cr and Ni are 36% and 62% lower, respectively, than values for these two metals in average crustal rock (Wedepohl, 1995) and comparable with or lower than levels in mean marine sediment (Salomons & Förstner, 1984). In other words, many typical marine sediments will contain natural levels of Cr and Ni that exceed ER-L. In many ecological studies, metals are measured after a partial sediment digestion (which is appropriate for sorbed anthropogenic metals but not for bulk metals which might be part of the sediment matrix; (Sinex et al., 1980). ER-Ls, which are a compilation of many studies, may be overly conservative for these elements (J. Trefrey, pers. comm.).

2.2.2.1.6.2 Organics

While metals in general are compared on an individual basis with candidate benchmarks, organic contaminants are broken into classes, which are then consolidated into summations. For instance, PAH can be sub-categorized into "parent" compounds (compounds with 2 or more benzene rings but no alkyl or other rings attached – e.g. naphthalene, phenanthrene, benz(a)anthracene) or substituted compounds (polycyclic aromatic compounds with 1 or more alkyl or other substitutions on the rings - e.g. methyl naphthalene, diethyl phenanthrene, 1,3,7-trimethyl pyrene…). For PCBs, the story is even more complex, since PCBs can be reported at Aroclor equivalents, as individual congeners, or as sums of various subsets of the possible congeners. Clearly, the possible permutations are endless. However, only some subset of these (those with available standards, established analytical methods, known toxicity and/or ubiquity or abundance in the environment) are commonly regulated or monitored. Depending on the goals of a study or analytical resources available, different subsets of PAHs, PCBs or pesticides are analyzed, but often all these are reported as total PAHs (tPAH), etc. For site-to-site or site-to-benchmark comparisons, it is important that the same sets or subsets of compounds are included in summations, where possible.

In order to be protective, most environmental non-detect data are not reported as zero, but as ½ the detection level. Marine sediments generally have cleanup criteria and contaminant levels significantly below those of regulated soils. If standard methods appropriate for soils are used, detection limits can be at or near many sediment benchmark criteria, and thus samples with non-detects reported as half such a relatively high detection limit can appear to be contaminated. This issue is magnified when sums of organic analytes such as total PAHs, total PCBs or total DDTs are reported, since the sums of many non-detects reported as ½ the detection limit can result in large numbers, making clean sites appear contaminated. This can make it particularly difficult to compare or contour organics data from different sources.

2.2.2.1.7 Contaminated Sediment Management: Data "Triage"

Generally, once some data are available, sediments of potential concern fall into three basic categories (if decision criteria have been clearly laid out and negotiated): 1) COCs are present, but at such low levels that there is no risk (or, COCs not present). If this is the case, detailed studies are not necessary, and a site can most likely be set aside, 2) At least one COC is clearly at high levels and poses an unacceptable risk. These sediments should not be subject to detailed risk analysis, but should be moved into the risk management arena. Further data collection should focus on more tightly delineating the 2- or 3-dimensional (depending on remedial options) COC and toxicity distribution of the site, and information relevant to F/S, and 3) "Grey area" sediments, where risk or extent are uncertain. At times, detailed studies of toxicity, availability, mobility, etc. are justified to determine degree and geographic extent of risk. These sorts of studies should be carried out in a focused manner, in order to get sites placed in one of the previous two categories. This is the main arena of the innovative and advanced sediment characterization tools, which may look at COC distribution, bioavailability, mobility, or form in greater detail. Because there is a tendency at many sites to "brand" sites as toxic if benchmarks are ever exceeded, or if any toxicity "hits" are observed, there can be great resistance and suspicion if Category 3 sites are eventually moved to Category 1. For this reason, it is important that the decision criteria are clear, negotiated and transparent.

2.2.2.1.8 Summary of Data Issues

It is a regulatory requirement that presumptive remedies or assumed endpoints or cleanup levels do not drive Ecological Risk Assessment (ERA). However, if data are not collected in such a way that the decision makers, regulators and managers can frame their decisions, unnecessary expense and delays occur. Before any but the most preliminary site assessment data are collected, all interested parties, including regulators, managers, etc., should bring their priorities, decision criteria, concerns and limitations to the table. Assessments should be designed to provide a stand-alone Ecological Risk Assessment, but also to provide data to address concerns and guide decisions. No studies or measurements should be carried out within the RI/FS structure unless it is clear what role data will have in the decision and regulatory process. It should be pointed out, however, that sediment RI/FS studies are excellent opportunities on which to "bootleg" peripheral work, funded by other projects, in order to carry out the R&D which will allow for better sediment management, or the demonstration of innovative assessment or management tools. Such work can expand the scope of or add to site information, but even if results from such a peripheral study is not going to affect the decisions at the specific site, results and demonstrated methodologies may be useful for future sites.

2.2.3 Separating site and background contaminant levels

Because of past industrial activities, ship activity, non-point source input, etc., sediments at numerous sites have some level of impact from anthropogenic compounds. Potentially responsible parties (PRPs) such as the DoD must assess and manage contaminated sediments to conduct dredging, transfer properties, or to clean up contaminated "hot spots." While it is critical to address those sites that pose a demonstrable and immediate ecological or human health risk, effective and equitable management decisions will be dependent upon a determination of where contaminants come from. It is Navy policy (Dave Olson, CNO) that the Navy will not do extensive work in contaminated sediments unless they know that they are responsible for the contamination. Due to the complexity of sediment management, and the enormous potential costs nationally, such a policy is being adopted by many organizations. This is important to a PRP from a liability/responsibility viewpoint, but more importantly, it is important because unless contaminant sources are identified, they cannot with confidence be effectively controlled. First, no sediment cleanup or management should begin until sources are controlled, since unless all potential sources are identified and controlled, recontamination may occur. Second, if contaminants in a given unit of sediments do not reflect a unique local source, but rather reflect an accumulation of

regionally contaminated "background" sediments, local remedial efforts will effect little or no ecological improvement. Bulk sediment contaminant concentrations and bioassay results, as currently examined and reported, are not effective at addressing these issues.

While absolute concentrations of COCs in sediments are an important part of assessing site sediments, there are a number of reasons that this alone does not provide a full picture of what is going on at the site. Both organic and inorganic contaminants can exist in a region at background, ambient or natural levels, either because they have natural sources or because entire regions in urbanized, industrialized and other areas are exposed to ubiquitous levels of anthropogenic input. In many cases, since such contaminants have a tendency to associate with fine-grained sediments, there is a general regional tendency to have a "mixing curve" of contaminated fines, and relatively uncontaminated coarse-grained sediments. Often, either ambient contaminant levels or background natural levels or a combination of both can be separated from site-specific levels by normalizing to or plotting against sediment characteristics which tend to indicate natural metal-rich particles (*e.g.*, Fe, Al) or fine-grained particles (*e.g.*, Fe, Al, %fines, %OC). While ambient or background levels of COCs can be bioavailable, and may cause ecological impact, they are almost impossible to manage for on a site-specific basis – cost and logistics make it unlikely that an entire region will be remediated, and if specific sites are remediated to below ambient levels, those sediments are likely to be subject to re-contamination by background sediments. Thus, it is important at a given site to examine contaminant distribution relative to regional, ambient or background levels.

If sediment is determined to be of either ecological or regulatory concern, this is most likely based upon levels of COCs that exceed a regulatory, literature or site-specific toxicity threshold. However, it is not the bulk concentration of a contaminant which poses risk, but the fraction of that bulk concentration which is bioavailable. Thus, in assessing risk or a risk management approach for a specific COC, it can be very important to determine the form in which the COC resides in the sediment. If a COC exceeds a chosen benchmark, it may be useful to determine what proportion of that COC resides in a form that may be expected to be bioavailable, and what fraction resides in a less available form. If the bulk of the COC is expected to be bioavailable, the small proportion that may not be does not merit detailed investigation. On the other hand, if it appears that a significant portion of the COC in sediment may reside in a non-bioavailable, natural or unusual form, it is important to examine that portion and, perhaps, evaluate the risk (and management) of that portion of the COC individually. Size fraction distribution can be one indicator of potential differences in availability or risk. The most common association of contaminants is in the fine-grained sediment fraction, and thus, most field-related toxicity data have been generated with such sediments, and they are thus reasonably applicable to these sediments. However, if contaminants are associated with a coarser fraction, they may be either significantly less or more available than the fine-grain associated COC. In cases where this is expected to be so, this fraction merits a closer examination to determine the form a COC takes in the sediment (see, for example, Apitz et al., 1999).

Normalizing contaminant levels to or plotting against sediment characteristics which tend to indicate natural metal-rich particles (*e.g.*, Fe, Al) or fine-grained particles (*e.g.*, Fe, Al, %fines, %OC) can provide insight into whether there is a site-specific source of a given COC. However, that alone will not provide sufficient information to trace COCs to a given source, which may be necessary either to control sources, differentiate multiple sources or to allocate responsibility. More detailed examination of contaminant signatures, such as the relative distribution of individual compounds in an organic mix, the isotopic signature of metals or organic compounds, or the presence or absence of various markers can help elucidate these questions. For instance, while total PAH (tPAH) numbers are needed to compare to potential sediment quality criteria or benchmarks, the PAH fingerprint (the relative distribution of individual PAHs) can provide a significant amount of information on source, background, weathering patterns, potential toxicity and the potential for natural attenuation (e.g., Page et al., 1995). There is a rich literature in the field of environmental forensics (e.g., Morrison, 2000 and references therein). While this

field has primarily focused on terrestrial sites, some work has been carried out in marine sediments, and methodologies should be adapted and standardized for marine sediment systems.

2.2.4 Examining the impacts of in-place remedial strategies

A growing body of evidence suggests that sediment removal can at times result in more ecological damage, or, after great expense, not show measurable ecological improvement (e.g., Thibideaux et al., 1999). Because of volumes and costs involved, it seems clear that some sediment sites will be managed in place. While sediment guidance recommends an evaluation of site-specific risks and benefits of management strategies in the feasibility study process, technology-specific and site-specific data on risks or impacts of sediment remedial or management strategies (especially in-place strategies) are sparse. This forces site owners to rely on simplistic technology matrices and generic models with minimal site-specific relevance. As a result, when a risk management team chooses to implement passive, in-place or innovative management strategies at a site, convincing a skeptical regulatory community and public can be a daunting task. Many in-place management approaches and technologies are being developed and marketed, but few have been thoroughly evaluated in terms of the effects of the technologies on the bioavailability, toxicity, fate and mobility of target and non-target contaminants, nor are there data on what characteristics make a site suitable for these approaches. This is a barrier to regulatory acceptance and to site owners taking the risk of what are perceived to be relatively unproven strategies.

There is a need to validate in-place management or containment strategies, as well as in situ remediation technologies. There is also a need to validate a toolbox of analytical and modeling tools in support of the feasibility process for such in-place management, containment and remediation strategies. Without such data, it is unlikely that a wary regulator and stakeholder community will embrace in-place treatment and/or containment processes. However, the R&D community can rarely afford the multi-million dollar efforts necessary to do broad-based, multivariate studies or to test sediment remedial strategies in the field in a meaningful way. To remedy this problem, one of the questions which should be asked is: Who should bear the cost of such studies, if the benefit is for future, not current, applications, but the risk is to the current project? Those who can afford these, primarily vendors and site owners, do not have the incentive to collect the validation data necessary for PRPS and site owners to "sell" these technologies at other sites. Clearly, site owners are at risk if they look deeper into the impacts of their selected remedy than is required by regulators. Often, technology developers expect others to pay for validation data. Unfortunately, there seems to be little incentive for contractors, regulators, stakeholders or RPMs to streamline the process, since potential risks of innovation are not offset by rewards. If innovative in-place remedial strategies are to be accepted, efforts must be made to balance the risks and benefits, with collaborative consortia that bring extra assessment to site demonstrations, but with some regulatory buy-in. The EPA SITE program and the ARCS programs have filled this function well, primarily for soil and freshwater sites, but more sediment-focused efforts are called for.

2.2.5 Evaluating pathways of contaminant mobility in near-shore sediments

As stated above, given the economic, logistical, technological and ecological limitations of sediment removal and treatment technologies, it is inevitable that some contaminated sediments will be left in place, in the short or the long term, even if contaminants pose some ecological or human health risk. However, leaving sediments in place has met with regulator and public resistance at many sites due to concerns about the long-term risk to the marine environment. Decisions must be made which minimize uncertainty in a complex, multivariate system; address multiple and often conflicting priorities and agendas; minimize costs and stand up to scientific, public, legal and regulatory scrutiny. Chapters 11 and 12 address some of the factors that should be considered in these evaluations.

Many of the contaminated marine sediment sites which are currently under investigation are in shallow, coastal areas, and are much more likely than more traditionally studied offshore sediments to be impacted by advective processes such as groundwater flow, tidal pumping, wave pumping and by resuspension via ship and storm activity. While these processes are recognized in the oceanographic community as having significance to chemical fluxes, they are largely unstudied in contaminated systems, and the relative magnitudes of these processes as compared to the traditionally assessed processes such as diffusion and bioturbation have not been determined.

If impacted sediments are to be left in place, it is critical to evaluate potential pathways by which contaminants might pose an ecological or human health risk, and to monitor, minimize or eliminate these pathways. On the other hand, the relative importance of these pathways as mechanisms of sediment recovery must also be determined. Currently, there is no demonstrated, systematic process for measuring and evaluating contaminant transport pathways within sediment systems. While the attention of the EPA and others is turning towards an evaluation of the appropriateness and efficacy of in-place management strategies, as yet the understanding of the relative importance of transport pathways (e.g., diffusive vs. advective, etc.) is only qualitative and difficult to apply in a management selection or evaluation.

2.2.6 Regulation of soils and groundwaters to protect sediment communities

Many agencies and industry are in the process of identifying, assessing, and remediating a large number of terrestrial hazardous waste sites. Many of these sites are located adjacent to harbors, bays, estuaries, wetlands, and other coastal environments. For example, it is estimated that approximately one-third of all Navy hazardous waste sites and many Army and Air Force landfills have coastal groundwater infiltrating the waste (Chadwick et al., 2000), and that 75% of all RCRA sites and Superfund sites are located within a half mile of a surface water body. Such water bodies can be of various types, including riparian, lacustrine, estuarine and marine. While there is a small body of work addressing such processes in freshwater systems (Hill, 1997; Stanford and Ward, 1993; Palmer, 1993), there is a growing body of evidence which indicates that groundwater-surface water interactions (GSIs) in estuarine and marine systems represent an important, complex, yet often neglected migration pathway for natural and anthropogenic constituents entering coastal waters (Lendvay et al., 1998; Paulsen et al., 2001; Millham and Howes, 1994). Because of this, there is a general requirement to determine if contaminants from these sites are migrating into marine systems at levels that could pose a threat to estuarine environments. The hyporheic zone can be defined as the region where groundwater, surface water and sediment interact. At a number of coastal sites, soil contaminant levels (e.g., TPH) are being regulated to be protective of putatively downstream sediment benthic biota. Because little is known about the behavior of contaminants moving downstream, mixing with saltwater and sediments systems, and interacting with biota, very conservative cleanup criteria are applied. As a result, soils may be regulated at unattainable cleanup levels.

Historically, the approach to these sites has been to separate the terrestrial, groundwater, surface water and sediment systems into separate "operable units." Typically these operable units have been assessed by different project managers on different timetables and with limited interaction (Duncan, 1999). This separation has also been evident in the scientific community, with significant research efforts in groundwater transport and transformations, and sediment chemistry, toxicity and ecological risk assessment, but few integrated studies to assess the relationship between groundwater-borne contaminants and estuarine ecological risk. While natural attenuation is often invoked as a rationale for ignoring surface water impacts, there are few sites where this attenuation, or the processes underlying the attenuation have been quantitatively assessed (Lee, 2000). In recognition of this issue, federal and state regulatory agencies are beginning to stress requirements to include the transition zone in site conceptual models for sites where contaminated groundwater may impinge on surface water bodies (Duncan et al., 2000), but there is almost no scientific basis with which to design an approach to such a consideration. There is a

need to develop fundamental knowledge of the processes that regulate the fate and effects of groundwater-borne contaminants in estuaries. Subsequently, there is a need to develop the technical basis to determine how to account for contaminant flow, sorption and weathering as contaminants move towards the hyporheic zone, and upon mixing with sediments, how this affects bioavailability, and, ultimately, how to predict sufficiently protective levels in upstream soils.

2.3 SUPPORTING INFORMATION

Chapters 3-13 in this document provide more detailed summaries of a number of important aspects of contaminated sediment management, which should aid in efforts to design or evaluate approaches to the sediment RI/FS process.

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3. THE CONCEPTUAL SITE MODEL

3.1 INTRODUCTION

A conceptual site model (CSM) is the site-specific conceptual framework around which a site investigation is designed. An appropriate CSM is critical for determining the most cost effective and efficient manner of protecting human health and the environment in environmental and remediation investigations. The purpose of this chapter is to provide an understanding of the purpose and application of CSMs. In addition, a general outline is presented on the development, uses and importance of the CSM in site investigations.

3.2 WHAT IS A CSM

A CSM is a three-dimensional description of a site and its environment that represents what is known (or suspected) about the contaminant source area(s), as well as, the physical, chemical, and biological processes that affect contaminant transport from the source(s) through site environmental media to potential environmental receptors. The CSM identifies the complete and potentially complete exposure pathways and provides a template to conduct the exposure pathway evaluation. It also provides a means to identify relevant ecological receptors and habitats and potential response actions. The CSM is dynamic in the sense that when available, additional data are used to refine and increase the accuracy of the CSM. Although the CSM is not a computer model; it may be the basis for a computer model should one be required.

3.3 WHY IS A CSM IMPORTANT

A CSM is invaluable in the development of a risk-based site investigation and remediation program. The CSM documents current site conditions and is supported by all available data (e.g., maps, cross-sections, site diagrams illustrating potential human and environmental exposure pathways from contaminant releases.

A CSM also is critical to the understanding of a site if significant changes occur at the site. For example, if a well suddenly shows an increasing trend in a contaminant concentration, the CSM may be used to hypothesize what is responsible for the change. Additional data may be required to verify the hypothesis or to help develop/change the hypothesis. In many cases a computer model can be very valuable in quantifying the processes described by the CSM. For example, a simple transport model may be used to suggest that attenuation is occurring because an observed plume is much smaller than would be predicted based on transport with no attenuation processes.

3.4 HOW IS A CSM DEVELOPED

The first step in the development of a CSM is a thorough literature review and evaluation of the regional geology, hydrogeology and atmospheric conditions, including maps and aerial photos describing the region and associated geomorphology and surface water bodies. This evaluation forms the basis of the CSM for contaminant fate and transport. The objective of the basic CSM is to identify pathways that could lead to potential risk to human health and the environment, while providing the necessary framework for defining and prioritizing investigation and remedial objectives. The first phase of an investigation may focus on filling in the data gaps in the basic CSM. The CSM may then be refined and risk-based decisions made on the relative priority of future investigations.

The physical processes described in the CSM should include the geology and hydrogeology of the site. The hydrogeology of the site describes movement of surface and groundwater (and associated contaminants) through the site and is a function of large-scale processes at the site (e.g., structural geology, hydrodynamics, depositional history, geomorphology, water body locations and other sinks and/or sources, atmospheric conditions, etc.). Surface water, porewater and groundwater transport are also influenced by small-scale processes or factors (e.g., matrix porosity, consolidation, grain size, angularity, degree of fracturing, groundwater surface water interaction, bioturbation, bioirrigation, wave activity, etc.).

Chemical processes and conditions also influence the environmental movement of contaminants. Chemical contaminants have characteristic properties (e.g., solubility, density, viscosity, diffusivity, vapor pressure) both individually and in combination with other chemicals. These characteristics help determine the extent and rate of a contaminant's environmental partitioning into a given media (groundwater, soil, air, sediment, porewater, surface water etc.) and transport from the source area. These characteristics, along with other physical (e.g., source size, loading rate diffusion, and dispersion) biological (e.g., biodegradation, bioirrigation and biotransformation) and chemical (e.g., hydrolysis, oxidation, reduction, volatilization, precipitation, complexation, adsorption, and ion exchange) factors determine the ultimate fate and transport of a contaminant in the environment.

A CSM can be as simple or as complex as required to meet its objective(s). A CSM should be developed as early as possible in the investigative process and should contain sufficient information to support the development of current and future exposure scenarios. One of the most important uses of the CSM is as a communication tool to facilitate the decision-making process.

Methods used to develop the CSM may, and likely will, differ from site to site. The most important aspects of CSM development are to start the development process early and to make the preliminary gathering and evaluation of existing data as comprehensive as possible. One suggested outline for the development of the CSM is presented below:

1) Assemble available information (regional, site historical, photos, etc.).

2) Identify contaminants of concern

3) Establish background concentrations

4) Characterize contaminant sources

5) Identify contaminant migration pathways
    a) groundwater/porewater pathway
    b) surface water and sediment pathway
    c) air pathway
    d) soil/sediment contact (direct contact) pathway
    e) biotic pathway

6) Identify potential environmental receptors
    a) human receptors
    b) ecological receptors

3.5 IMPORTANT CONSIDERATIONS

The overall site remediation strategy and risk-based considerations should guide the development of the CSM. The development of a CSM is a focused, goal-oriented process that should require only those data necessary to meet the goal(s) of the site strategy and objectives. The CSM should guide all subsequent investigations, but be no more complex than required to meet its objective(s).

A review of the six steps outlined above demonstrates that the development of a CSM is really nothing more than a site characterization program. In fact, the development of a CSM should guide the site characterization. The CSM should be continuously evaluated and refined as data become available, and, as the level of uncertainty associated with the CSM decreases, it should help identify data gaps and target additional investigations.

The most common mistakes in the development of the basic CSM are made during the assembly and evaluation of information. Greater emphasis on the initial phases of CSM development, such as evaluating the regional geology, hydrogeology and any site-specific data, will improve the initial hypotheses and, ultimately, the CSM. Reviewing historical information on site-wide waste handling practices and locating potential contaminant source areas and quantities will aid in determining the source characteristics (i.e., physical and chemical characteristics, mass loading, distribution of the contaminant between environmental media, etc.) as well as potential migration pathways. Understanding the contaminants, their source and chemical properties is a prerequisite to estimating and determining their ultimate fate. A thorough review of existing data will help ensure that the field investigation is focused on the appropriate potential receptors, pathways, and chemical characterization.

The development of a CSM is an iterative process involving the compilation of existing information on site conditions that represent the physical, chemical, and biological processes that determine the transport of contaminants from sources to potential environmental receptors. A CSM is dynamic and evolves, as additional data become available. Refinement of the CSM can also drive re-optimization of remedial design and/or operation.

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4. ECOLOGICAL ASSESSMENT TOOLS

4.1 INTRODUCTION

   Assessment or measurement tools for an ecological risk assessment are available to measure exposure and/or direct effects and to model bioaccumulation. Exposure can be evaluated with tools to measure water, chemistry and tissue chemistry. Effects may also be inferred with the use of qualified literature values, when available. Sediment toxicity tests, benthic macroinvertebrate community analysis, and histopathology typically are used to measure effects. Biomarkers are another set of tools that are often employed for measuring exposure, but some are also used to hypothesize a direct measure of an effect. Although some of these tools measure contaminant exposure via ingestion or water contact, the source of this contamination is often partially or entirely from the sediment; the latter medium is highlighted throughout this discussion. **Table 1** summarizes some of these tools and their appropriate endpoints. The text below discusses the advantages and disadvantages of each measurement; a discussion of bioaccumulation modeling follows separately. For more detailed information on the linkage of bioaccumulation data with sediment quality, the reader is referred to the USEPA (2000A) Bioaccumulation Analysis Workgroup.

Table 1. Available Assessment Tools

Endpoints\n\nAssessment Tool	Exposure	Direct Measure of Effects	Effects from Literature
Water Chemistry	X		X
Sediment Chemistry	X		X
Tissue Chemistry	X		?
Sediment Toxicity		X	
Benthic Macroinvertebrate Community Analysis		X	
Histopathology		X	
Biomarkers	X	?	

   Exposure and effects endpoints vs. assessment tools: Uncertainty exists concerning the confidence levels which can be obtained when using tissue chemistry to predict effects found from literature sources. Similarly, predicting direct effects to organisms through the use of biomarkers is possible but not definitive.

4.2 MEASUREMENT ENDPOINTS

4.2.1 Water Chemistry

An extensive set of toxicity databases exists for water chemistry. Contaminant concentrations indicating toxicity are often linked to sediment chemistry through standard partitioning assumptions, however, spatial and temporal variability usually are high. Redox, salinity and other changes during sample preparation and analysis may affect contaminant partitioning, and equilibrium assumptions may not always correctly predict contaminant concentrations in solution. In addition, rapid mixing often results in benign water chemistry measurements, while sediments remain highly contaminated. Further, many organic chemicals of particular interest are hydrophobic and metals, even when present, may be not be bioavailable due to formation of stable trace element complexes. However, the large databases available for water chemistry toxicity make these approaches good screening tools for sediment quality.

4.2.2 Sediment Chemistry

Sediment quality guidelines include both empirical and mechanistic methods (Long et al., 1995; Smith et al., 1996; MacDonald, 2000; Swartz, 1999; USEPA, 1999A; USEPA, 1999B). Although these guidelines initially are often used to estimate exposure, these values also provide a means to predict toxicity; however, their value often lies in determining the concentrations below which a toxic response is not expected. Nevertheless, they provide a means to relate sediment chemistry to toxicity. However, reliability differs depending upon the chemical and on the available database; their use can thus result in in potential false negative and positive results. In addition, the sediment quality guidelines do not directly address bioaccumulation and trophic transfer. Spatial variability and mixtures of contaminants often are difficult to assess. As with water chemistry tests, these are good screening tools, but should be used in concert with direct measures of effects.

4.2.3 Tissue Chemistry

Tissue chemistry measurements can directly assess bioavailability and integrate exposure over time from the water, sediment and food web pathways. However, there is an uncertain relationship between tissue residues and bioeffects. Metabolism or bioregulation may result in no linkage between exposure concentrations and tissue residues. In addition, much variability often exists between species and individuals of the same species. Furthermore, it is difficult to determine exposure for mobile species. Despite these shortcomings, one can compare tissue residue values to the databases of Jarvinen and Ankley (1999) and US Army Corps of Engineers (USACE) (2000A) to predict *potential* effects. At a minimum, relative tissue chemistry between sites can help resolve issues of differing bioavailability.

4.2.4 Biomarkers

As with tissue chemistry, biomarkers can integrate exposure over time. They are a measure of sensitive biological response to contaminants and may provide a contaminant-specific response. However, they usually are best used for measuring only exposure. In addition, understanding of mechanisms of toxicity is insufficient to indicate levels of unacceptable response and responses of known biomarkers may not, in fact, be contaminant-specific. However, many biomarkers can signal exposure to certain organic compounds after the parent compound is excreted and/or metabolized. Metallothioneins are available to measure metal exposure, specifically cadmium.

4.2.5 Sediment Toxicity Tests

These commonly used tests provide location-specific information on potential toxicity. They provide a measure of response to contaminant mixtures and are rapid and relatively inexpensive to conduct. Using standardized protocols, the risk assessor can measure toxicity in bulk sediments or in pore-water, the latter conducted because contaminants often partition from the sediment. However, the physical nature and regional chemical makeup of the sediments must be known so that resulting responses can be linked to specific contaminants. Another concern is the required extrapolation from laboratory tests to field conditions along with issues concerning sensitivity of test organisms. In situ tests, mostly under development, may reduce such problems. One problem with toxicity tests is that organisms may respond to natural variables in sediments such as grain size, %OC and ammonia levels. Thus, careful use of protocols, references and controls are necessary. Successful test performance may depend upon laboratory experience.

Several bulk sediment tests are available (USEPA, 2001, 2000B and 1994; ASTM, 1999). Samples for sediment porewater tests can also be collected by homogenizing the sediment and collecting the porewater using a vacuum-operated extractor (Winger and Lasier, 1991). If one suspects that the toxicity is from site-specific physical or chemical conditions other than the chemicals of concern, then a Toxicity Identification Evaluation should be employed. These chemical manipulations of field sediments are discussed by the USEPA (1996). Due to the complexity of contaminated sediments, and the potential synergistic effects of multiple contaminants, it may not always be possible to pinpoint which contaminants are causing toxicity, however.

Of particular recent interest is the exposure and effects to organisms from persistent, bioaccumulative chemicals found in sediments. USEPA (2000A) has published a lengthy report that associates the presence and quantity of potentially bioaccumulative chemicals in sediment with uptake in the tissues of aquatic and terrestrial organisms, and with the effects of those chemicals on the organisms.

Benthic Macroinvertebrate Community Analysis: Benthic macroinvertebrate community assessments make up the third leg of the sediment quality triad introduced by Chapman (1990) along with sediment chemistry and sediment toxicity. Effects are judged when comparing the community from the site-specific sediment to a reference location. However, it may be difficult to find a suitable reference area(s). In addition, this tool may not be appropriate for physically disturbed habitats. To be used appropriately, extensive data and/or expert knowledge may be necessary.

Histopathology: Histopathological indices have been useful in assessing the toxicological impact of contaminated sediments (Burton, 1992). Effects can be measured directly and quantified in terms of frequency of incidence (Ingersoll, et al., 1997). However, histopathological indices may be influenced by factors other than chemical contaminants.

4.3 CHEMICAL-SPECIFIC CONSIDERATIONS

Although the above described assessment tools are well-known and available to all ecological risk assessors, their value considerably differs depending upon the chemical of concern. Each of the following groups of chemicals has distinctive abilities to bioaccumulate and/or causes a toxic response. Contaminant groups may be divided into metals, polycyclic aromatic hydrocarbons (PAHs), PCBs and Dioxin/Furans. Because mercury significantly differs in its toxicity and degree of bioaccumulation when compared to other metals, it is discussed separately. Tables 2 and 3 summarize the following discussion.

4.3.1 Metals

Concentrations of metals in aqueous environments often are compared to the USEPA Ambient Water Quality Criteria (AWQC) (USEPA, 1998) and available sediment quality guidelines. Effects may be

more directly measured using sediment toxicity tests with field-collected sediments and through benthic macroinvertebrate community assessments. These bulk and porewater toxicity tests do not measure bioaccumulation, however, accumulation in benthic invertebrates may occur with or without toxicity.

An example of a freshwater sediment bioaccumulation test is provided by the USEPA (2000B). Metals, with the exception of mercury and possibly cadmium, generally do not bioaccumulate as extensively as do non-polar organics. Nevertheless, bioaccumulation tests such as this show exposure and may be used as measures of potential effects if one knows the concentrations (i.e., dose) that may cause injury to predators. For example, Woodward et al (1994) demonstrated that feeding metal-contaminated invertebrates to juvenile rainbow trout (at concentrations in invertebrates comparable to those found in the Clark Fork River in Montana) resulted in reduced growth and survival of the trout. Although bioaccumulation of most metals is relatively low, tissue residue values can still be compared to the Jarvinen and Ankley (1999) and USACE (2000) databases to estimate potential effects. Lastly, partitioning of metals from sediments to overlying waters conceivably could cause avoidance by certain aquatic species (Hansen, et al., 1999).

Table 2. Summary: Exposure Assessment

Contaminant Group	Sediment Chemistry	Tissue Chemistry: Invertebrates	Tissue Chemistry: Fish	Biomarkers
METALS	X	X	*	*
MERCURY	X	X	X	
PAHs	X	X		X
PCBs	X	X	X	X
DIOXINS	X	X	X	X

* Cadmium is the best example of a metal that can be used to show exposure through fish tissue chemistry and biomarkers

4.3.2 Mercury

As for the metals discussed above, using the available sediment screening guidelines may aid in the assessment of mercury in sediment. However, most available sediment effects databases are based on total mercury measurements rather than on the more toxic methylmercury. In addition, these empirical sediment quality guidelines often have low accuracy in predicting adverse effects. As for other metals, sediment toxicity testing and benthic macroinvertebrate community assessments comprise the principal tools in estimating mercury effects to benthic organisms. Because mercury (especially methylmercury) readily bioaccumulates and biomagnifies, tissue chemistry is of relatively great value; tissue concentrations in invertebrates and higher trophic level organisms are appropriate targets to demonstrate exposure. In situ collections for tissue chemistry are preferred to laboratory bioaccumulation tests because of the importance of methylation to bioavailability. An example of a well-designed bioaccumulation study is one using caged, pre-sized bivalves to measure potential availability of inorganic and methylmercury, along with effects on growth. Toxic effects from mercury tissue residues

are found in the Jarvinen and Ankley (1999) USACE (2000) databases; lethal and sublethal effects are shown whereby, for example, impaired behavior in adult fish is found at lower concentrations than is mortality.

Table 3. Summary: Effects Assessment

Contaminant Group	Sediment Toxicity: Literature	Sediment Toxicity Tests	Benthic Community Assessment	Tissue Residue Effects	Biomarkers
METALS	X	X	X	*	
MERCURY	X?	X	X	?	
PAH	X	X	X		X
PCBs				X	
DIOXINS				X	

* Cadmium is primary example of a metal that can be used to show effects through tissue chemistry.

Uncertainty exists concerning the confidence of using tissue concentrations to predict effects based on literature sources.

4.3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Effects to invertebrates from PAH contamination in sediments are first assessed using the sediment triad methods discussed above, which incorporate sediment chemistry, sediment toxicity and benthic community assessment. A PAH model was presented by Swartz et al. (1995) to estimate the toxicity of PAH-contaminated sediments which involves using a combination of equilibrium partitioning, QSAR, toxic units, additivity, and concentration-response models. Highly contaminated sediments often result in harmful effects to fish species such as reproductive impairment, liver lesions and other histopathology, much of which can be assessed when examining field-collected fish. Although toxicity in fish is related to biotransformation to toxic metabolites, biomarkers such as the presence of PAH metabolites in fish bile, cytochrome P-450 induction, or DNA adducts are usually considered measurements of exposure. However, cytochrome P-450 induction may be linked to toxic effects in fish including reproductive effects and carcinogenicity. Other exposure measures are tissue residues in resident invertebrates and resident or caged bivalves; in the latter study example, one may assess growth effects if juvenile bivalves are measured before deployment. It should be pointed out that recent studies have noted that PAH toxicity can be significantly increased if organisms are exposed to UV light (e.g., sunlight). Thus, toxicity assays for organisms and sediments in shallow water or the intertidal should be carefully designed.

4.3.4 PCBs and Dioxins/Furans

The standard sediment triad methods may also be used to estimate effects of PCBs and Dioxins/Furans. MacDonald et al. (2000) shows total PCB sediment concentrations that may injure benthic organisms based on toxicity tests. Iannuzzi et al. (1995) review the available sediment guidelines for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin. Likely improvements to standard toxicity tests are recent draft long-term toxicity tests, 42 day *Hyalella azteca* and 50 to 65 day *Chironomus tentans*, that measure survival, growth, and reproduction in moderately PCB-contaminated sediments (USEPA, 2000B; ASTM, 2000). PCBs readily bioaccumulate, especially into fish, via the foodweb pathway. In fact, fish may be more sensitive to toxic effects of PCBs and dioxins/furans than are invertebrates because the latter lack the aryl hydrocarbon receptor; the presence of this protein makes these compounds toxic to a species. Exposure of invertebrates to these chemicals is measured by analyzing tissue residue concentrations in resident species, in situ exposures of caged organisms, and laboratory sediment bioaccumulation tests. Fish PCB exposure, like exposure to some of the other contaminant groups described above, is measured using tissue residue concentrations or biomarkers in resident species. Considering tissue concentrations (along with lipid content) and comparable sediment concentrations (including TOC levels) provides a biota-sediment accumulation factor (BSAF) that may be compared against literature values, if available.

Direct effects measures for PCBs and dioxins/furans generally are more intricate than are the previously discussed contaminants. Tissue residue concentrations can easily be compared to literature effects values (USACE and Jarvinen and Ankley databases), although much uncertainty may result from such an approach. More complex studies include transporting sexually mature fish to the laboratory where fecundity of females, fertilization success, egg hatch, survival to the yolk resorption stages and gross abnormalities can be measured. Corresponding sediment chemistry data would allow for a determination of a threshold sediment concentration and correlated tissue residue levels associated with the above measurements. Because PCBs show dioxin-like effects (i.e., coplanar PCBs have the same mode of action as dioxin), the most sensitive endpoint is often reproductive effects.

In order to compare toxicities of environmental samples that have different concentrations of coplanar dioxins, furans, and mono-ortho and nonortho-substituted coplanar PCB congeners, toxic equivalent factors (TEFs) have been developed, most recently by the World Health Organization (Van den Berg, 1998). To apply TEFs, individual chemical concentrations within a sample are multiplied by their respective TEF and all products are summed to give a value expressed in toxic equivalency units (TEQs). Separate TEFs are provided for human/mammals, fish, and birds but not directly for sediments. To estimate the sediment TEQ that is associated with effects on fish, it is necessary to back-calculate the sediment TEQ from the fish tissue residue effect level using congener-specific biota-to-sediment accumulation factor or BSAF (defined below) and the fish TEFs.

4.4 FOOD WEB BIOACCUMULATION AND RISK ASSESSMENT TECHNIQUES

Except for the tissue residue data, the above assessment tools rarely address potential adverse impacts from bioaccumulation. Because bioaccumulation of contaminants may result in adverse effects to resident natural resources, models to predict such uptake from nonpolar organic chemicals and mercury from sediments have been developed. Most models use the BSAF as a means to estimate risk and ultimately derive clean-up levels of sediment. The BSAF is the ratio of the chemical concentration in the organism on a lipid-normalized basis to the chemical concentration in the sediment on an organic-carbon basis; hence the units are grams of organic carbon per gram of lipid. One can determine sediment clean-up by dividing a maximum allowable tissue level (MATL) by the BSAF. However, this requires several assumptions: 1) that the MATL is known, 2) that the BSAF values are defined by accepted measures (either site-specific or literature values), and 3) that a constant relationship (i.e., steady-state) exists between the biota and the sediment. In addition, trophic transfer of contaminants is not considered. The

Army Corps of Engineers have used the BSAF concept to create a Theoretical Bioaccumulation Potential, which is an estimate of the equilibrium concentration of a chemical in the tissues of an organism exposed to contaminated sediment (USACE, 2000B). The BSAF approach can be linked with a simple modeled food web to better understand the accumulation of a sediment-borne chemical by organisms (Thomann and Komlos, 1999).

Thomann et al. (1992) and Gobas (1993) introduced more advanced mechanistic food web models that predict bioaccumulation of hydrophobic organic chemicals in aquatic organisms. These models improve and interpret the BSAF values by including the bioaccumulation process, food web structure, bioenergetics, and toxicokinetics while limiting the uncertainty. Burkhard (1998) compares the two models and finds they are, in many ways, quite similar; differences, for example, stem from methods linking aqueous and sediment chemistry to concentrations in lower food chain organisms.

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5. CHARACTERIZING THE SPATIAL EXTENT OF SEDIMENT CONTAMINATION AT IMPACTED SITES

5.1 INTRODUCTION

For decades, pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), heavy metals, and pesticides were discharged into many U.S. rivers, lakes, estuaries and coastal areas, either from point or non-point (primary) sources. A large percentage of many of these contaminants became associated with organic and mineral particles that subsequently settled out across the bottoms of surface water bodies. Impacted sediments act as secondary sources of organic and metal contamination, posing significant direct and indirect environmental risks through bioaccumulation in aquatic organisms and by incorporation into aquatic and upland food webs. Episodic physical redistribution of contaminated sediments within dynamic waterways over time can also literally disperse such environmental risks, potentially impacting biological and water quality conditions far from the original sediment source. Despite today's strict environmental laws that restrict "end-of-pipe" discharge of pollutants into U.S. waterways, the problem of contaminated sediment persistently remains.

In order to make appropriate and cost-effective risk management-based decisions for a site once sediment contamination has been discovered, there is often a need to characterize the full nature and spatial extent of sediment contamination at the site. Such a characterization evaluates the vertical as well as lateral distribution (or effective boundaries) of contaminants.

This chapter comprises: (1) a generalized summary of an iterative regulatory framework within which the spatial extent of sediment contamination occurring across a site can be characterized; (2) a brief description and discussion of several items integral to implementation of such a framework; and (3) a brief summary of tools or field approaches that can be used to accomplish resource-effective spatial characterization.

For the purposes of this short review, several simplifying assumptions are made: (1) the *nature* of sediment contamination occurring at a given site has already been determined, based on results of preliminary (or exploratory) sediment sampling and chemical analysis as well as perhaps toxicity testing; "contaminant X" is deemed the principal constituent of concern in site sediments (although several sediment contaminants, *including* contaminant X, may collectively pose toxic conditions to biological receptors at the site); (2) a more definitive characterization of the vertical and lateral distribution of contaminant X within site sediments (referred to herein as *spatial characterization*) has been deemed necessary; (3) contaminant X is associated nearly exclusively with (bound to) organic and mineral sediment particles, and displays minimal interaction with adjacent pore, ground, and surface waters; and, in a related note; (4) sediment is the only impacted medium at the site, with insignificant contributions from surface water, ground water, or air. Additionally, it is assumed that the sediment management approaches being considered for a given site - including the threshold concentration of contaminant X in sediments for which action will be deemed necessary - is *risk-based* in nature; that is, the cleanup action level is dependent on the level of risk that such a sediment concentration may pose to human and/or ecological receptors at the site.

5.2 GENERAL FRAMEWORK FOR CHARACTERIZING THE SPATIAL EXTENT OF SEDIMENT CONTAMINATION

The end goal for collecting definitive sediment data across the site (using either direct sampling or inferential [remote] approaches) is clear: to obtain an adequate characterization of the spatial extent of

sediment contamination X for the site. However, what process should be followed to accomplish this goal?

Determining the spatial extent (and nature) of contaminated media is a principal goal for conducting remedial investigations at CERCLA (Superfund) sites and RCRA facilities. The Data Quality Objectives (DQO) Process, recently published by the US EPA (US EPA, 2000), offers a logical framework for accomplishing such an end goal, not only at federally recognized sites, but also at other impacted sites. Specifically, the DQO Process "…provides a systematic approach for defining the criteria that a data collection design should satisfy, including: when, where, and how to collect samples or measurements; determination of tolerable decision error rates; and the number of samples or measurements that should be collected" (US EPA, 2000). The DQO Process generally considers a variety of impacted media potentially occurring at hazardous waste sites, including surface and subsurface soils, ground water, surface water, and air, but not specifically sediments. Nevertheless, the Process should be applicable to sediment-related issues as well, particularly when considered in concert with a previously published, and sediments-specific, document entitled *Sediment Sampling Quality Assurance User's Guide* (US EPA, 1985).

Application of the DQO Process generally involves following seven discrete steps, which culminate (at Step 7) in the development and optimization of a site-specific and statistically viable sampling design plan for collecting the data necessary for satisfying the DQO Process. Following is a brief and technically biased description of each of the seven steps, including an example of how each step may hypothetically apply to the definitive spatial characterization of contaminant X in sediments occurring across a riverine site. It is important to note at the outset that the DQO Process is meant to be used in an iterative fashion. For example, Process steps may be re-addressed in light of, for example: obtaining new information related to site conditions; subsequent refinements to site models; a re-consideration of appropriate, risk-based action levels; and/or changes in project funding. Through such iterations, the end result should be the development of a more focused and resource-effective sampling design plan.

1. State the Problem. In this step, the contamination problem is summarized and described through development of a conceptual site model and scenarios for potential contaminant exposure to human and/or biological receptors are identified. *For example, sediments polluted by contaminant X have been identified for the site, although the vertical and lateral extent of this contamination is unknown. It is further believed that sediments represent the only significantly contaminated media at the site, and that the only complete pathways for receptor exposure occur for benthic organisms exposed directly to the contaminated sediments.*

2. Identify the Decision Statement. In this step, the principal study question is developed, along with alternative actions, and both are combined into a decision statement. *For example, do the concentrations of contaminant X in site sediments exceed ecological risk-based concentration limits in certain portions of the site and therefore warrant remediation, or are sediment levels below such concentration limits, for which remedial action (or further investigative study) may not be necessary?*

3. Identify Inputs to the Decision Statement. In this step, the information needed to resolve the decision statement is identified (including the sources for such information) and the action level is determined based on the appropriate health- or risk-based criteria. *For example, an ecological, risk-based criterion published by the US EPA could be used to determine the preliminary action level by which to judge concentrations of contaminant X occurring within site sediments.* Given the iterative nature of the DQO Process, subsequent refinements to the site conceptual model or site-specific risk assessments may call for a change in action level for contaminant X in site sediments.

4. Define the Study Boundaries. In this step, the spatial (geographic) as well as temporal boundaries of the study are established, as well as the scale of decision-making (i.e., the smallest unit to which the decision rule [Step 5] will be applied). Spatial boundaries for the study could be set coincident with

surveyed site boundaries, or could be set "scientifically", coincident with the outermost locations at which contaminant concentrations drop below the pre-defined action level (without regard to the location of site boundaries). Furthermore, placement of an additional, temporal boundary on the study will likely depend on the nature of the media and contaminants involved. Setting boundaries around a site characterized, for example, by subsurface soil contaminated by an immobile metal contaminant may not require such a boundary extension, whereas a situation in which the same, strongly sorbed contaminant is found in sediments occurring within a hydrologically dynamic, riverine ecosystem may require temporal boundary considerations. *For example, the overall study boundaries for a riverine site in which contaminant X occurs in sediments may encompass not only the area immediately adjacent to the primary, albeit historical, point source for X, but also encompass areas located some distance downstream from X, to where sediment-bound contaminants may have migrated over time.*

5. <u>Develop a Decision Statement Rule</u>. In this step, a logical "if…then…" decision statement rule is developed that defines conditions that would cause the decision makers to choose among alternative actions, and that integrates the statistical parameter chosen for decision making as well as the action level to which the parameter value will be compared. *For example, a decision rule could state that if the mean concentration of contaminant X in sediment at the site or a portion thereof is less than Y mg/kg (the action level), then neither further investigation nor remedial action are needed. Otherwise, if the mean concentration is greater than the action level, then further investigation and/or remedial action may be warranted.*

6. <u>Specify Tolerable Limits on Decision Errors</u>**.** In this step, quantitative performance criteria for the sampling design are established, and tolerable probability values are assigned for each type of potential decision error. *For example, a goal for spatial characterization of contaminant X in sediments, within the context of null hypothesis testing, could be to collect and analyze enough data so that – when comparing mean concentrations for contaminant X with the action level - the chance of making either a false rejection (Type I) or a false acceptance (Type II) decision errors is one-in-a-hundred. Meeting such stringent decision error limits would require the collection and analysis of a large amount of data, which may be beyond the scope of project funding. Consequently, target action levels and/or decision error limits, among other factors, may need to be reconsidered during the iterative DQO process, and the consequences of such choices need to be explicitly addressed.*

7. <u>Optimize the Design for Data Collection.</u>   In this final step of the DQO Process, a resource-effective sampling and analysis design plan for generating data consistent with the above-described DQOs is developed. Development of the final sampling design will likely involve iterative reviews of existing data and comparisons of the costs, quantity, and quality of data required for implementing different statistically based sampling design alternatives. *For example, a simple random sampling design for collecting additional sediment characterization data for contaminant X from across the site may offer the most appropriate and cost effective approach to satisfying project DQOs.*

   Because of their importance to the DQO Process, two items discussed above – the **conceptual site model** and **statistical design** – deserve additional mention. The need for **site-specific information** and its overall importance in developing a viable sampling design plan are also discussed.

5.3 SITE-SPECIFIC INFORMATION

   Development of an appropriate, site-specific sediment sampling design plan is contingent upon knowing as much about the site as possible with respect to contaminant sources; prevailing environmental conditions related to site hydrology, sedimentation, and biologic colonization; and other anthropogenic influences to the site. An inventory of historical data or information already available for the site (over and above existing sediment chemical data) will facilitate timely and cost-effective development of the

site-sampling design plan – and will also help determine what types of site-specific data may still be needed. Information related to *contaminant source(s)* would include knowledge of the location and status of primary (e.g. end-of-pipe) sources, including whether or not the contaminant source(s) have been eliminated and, if so, when. Information related to *environmental conditions* would include a spatial understanding of: surface water depths and flow velocities; site bathymetry; areas and types of sediment accumulation occurring at the site, including an estimate of sedimentation rates; areas characterized by scoured conditions, which may be more-or-less free of sediment accumulation; and the nature and extent of colonization of site sediments by benthic macroinvertebrate organisms, as well as the overall health of such communities. Information related to *anthropogenic influences,* other than the issue of contaminant source, may include knowledge of past dredging at or near the site or significant boat or ship activity; other similar considerations may include knowledge of significant physical changes to the site over time, such as the installation or removal of storm water drainage ditches adjacent to the site.

The application of hydrologically based, sediment transport and deposition models (e.g. US EPA, 1985), when integrated with available site information, may prove useful in assisting in the development of sampling design plans, particularly when attempting to simulate (or retroactively characterize) temporal influences on the spatial extent of contaminant distribution at the site. Finally, if not already apparent from existing sediment chemical data, an integration and evaluation of site-specific information may also, for example, assist in qualitatively estimating the potential vertical distribution of sediment contamination at the site (through collective consideration of the age and duration of the primary contaminant source; sediment deposition rates; and past surface water flow velocities, including whether or not a 100- or 500-year storm event has occurred in the recent past). In summary, an overall picture of the site and its spatial/temporal workings- as derived from a variety of site-specific information - will be necessary for developing an appropriate sediment sampling design, and, to that end, will be critical in preparing (and refining) the conceptual site model.

5.4 THE CONCEPTUAL SITE MODEL

A Conceptual Site Model (or CSM) is a functional, often graphical, depiction of the contamination problem (US EPA, 2000) at a site that illustrates the qualitative relationships between: (1) locations of contaminant sources or locations where contamination exists; (2) types and expected concentrations of contaminants; (3) potentially contaminated media and migration pathways; and (4) potential human and ecological targets or receptors. Development of an appropriate CSM will be highly dependent upon knowledge of the site-specific conditions described above, and its continued refinement towards a more and more accurate and complete portrayal of a site's contamination problem (as it exists in both time and space), is integral to successful completion of the DQO Process. For the purposes of this short review, we have assumed that sediment contamination (by constituent X) represents the only significantly impacted media, thus implying that benthic organisms represent the only biological receptors directly impacted by the contamination (indirect impacts to the food web aside). However, the assumptions that no other media are impacted by contaminant X (or other contaminants) and that no other pathways or routes for receptor exposure to such contaminants exist at the site would obviously need to be justified.

In summary, an appropriately developed CSM can be used to prioritize areas of greatest concern at a site characterized by impacted sediments through the reconciliation of the issues of spatial distribution of contaminant X with the bioavailability of contaminant X. For example, the areas of greatest potential risk to benthic receptor organisms – and therefore the areas requiring application of the most intense sediment management efforts (e.g., removal through dredging) - may be delineated by more-or-less superimposing a map of the spatial distribution of contaminant X for the site overtop a graphical depiction of the spatial occurrence of the greatest populations of the most sensitive macroinvertebrate organisms occurring at the site. More information on the CSM concept can be found in Chapter 3.

5.5 STATISTICAL DESIGNS FOR SEDIMENT SAMPLING OR CHARACTERIZATION

As described in a number of regulatory documents (US EPA, 1985, 1991, 2000), a variety of statistical designs and procedures can be employed to determine the array, number, and locations for sediment data collection at a site, including: simple random sampling; systematic sampling; stratification; or composite sampling. Another sampling approach, referred to as judgmental sampling, may also be employed and is generally based on historical information for the site (including knowledge of historical source locations), visual inspection, and professional judgment (US EPA, 1991); however, judgmental sampling is not a statistically based (randomized) approach to sediment characterization, and does not generally allow for drawing defensible conclusions about conditions in areas of a site beyond the exact locations from which samples were collected (US EPA, 2000).

There are pros and cons associated with the use of any one of the above approaches to sampling design (e.g. US EPA, 2000), as related to variability in: (1) the confidence with which the assumption of a normal distribution for site data can be justified (which is required when using statistically based, randomized sampling approaches); (2) the level of knowledge of site-specific conditions and characteristics; (3) the relative ease of design implementation; (4) the ability to focus sampling efforts in more critical areas of the site; (5) the range in contaminant concentrations that may occur across the site; and (6) relative cost effectiveness. Some of these drawbacks may be overcome by collecting a large amount of data, but this may not be cost effective. In contrast, fewer samples or data may be needed to adequately characterize spatial extent of sediment contamination if a field-validated sediment transport and deposition model has been developed for the site (US EPA, 1985).

In summary, the statistical design ultimately chosen for data collection at a site, during Step 7 of the DQO Process, will be a function of not only cost considerations and the quantity and quality of data required, but also other factors as well, as described in this section.

5.6 TOOLS FOR ACCOMPLISHING SPATIAL CHARACTERIZATION STUDIES

The vertical and lateral extent of sediment contamination occurring across a site may be determined using direct and/or indirect (inferential or remote) approaches, each of which may be enhanced or improved upon using computer or mathematical modeling techniques.

5.6.1 Direct Characterization

Pursuant to the final data collection design plan, sediment samples can be retrieved from pre-defined sampling points systematically positioned across the site (with the sampling points located using GPS technology). The collected samples can then either be returned to the laboratory and chemically analyzed for the targeted constituents of concern using appropriate laboratory QA/QC procedures, or evaluated directly in the field using screening-level analytical procedures (US EPA, 1994); see also Chapter 6.

The type of sediment samples collected will depend on specific goals of the spatial characterization project. Collection of intact, continuous sediment core samples presumably encompassing the entire vertical extent of contamination, followed by depth-discrete chemical analysis of portions of the core to determine vertical contaminant distribution, will be required if a definitive statement is to be made related to the vertical extent of contamination. These types of data would likely be required, for example, if dredging is anticipated as a probable risk-management option for the site, in order to determine the depth to which dredging should occur. In contrast, grab samples may instead be collected from the sediment surface (e.g. the upper several inches) if project concerns focus primarily on the degree of sediment contamination to which benthic organisms across the site, which live in these upper several inches of sediment, are currently being exposed. In many cases, cost-effective fulfillment of sampling design requirements may involve implementing a combination of coring and grab-sample techniques.

5.6.2 Inferential Characterization

It can generally be assumed that the greatest majority of sediment contamination occurring at a site is associated with finer-grained materials like clays and silts rather than coarser-grained deposits (including sands or gravels), free product issues aside. Often, then, sediments in contaminated or urbanized areas are considered to be made up of mixtures of contaminated fine-grained material and uncontaminated coarse-grained material. There are, however, many exceptions to this rule, see for example, Apitz and Kirtay, 1999. These caveats aside, using this assumption, acoustic profiling (NRC, 1997; US EPA, 1994), including side-scan or multi-beam sonar techniques, can be employed to remotely characterize the spatial distribution of different sediment types – including the finer-grained sediments having a higher likelihood of contamination (if sediment contamination does, in fact, occur at the site). These methods, however, may have difficulties in sediments of mixed grain size.

These types of remote sensing tools can neither reliably identify nor quantify chemical contaminants in sediments, thus the continued need for the collection and analysis of core or grab sediment samples. Particularly if contamination is site-specific rather than regional, sediments with contaminated fines may be adjacent to, mixed with or interlayered with sediments with less- or un-contaminated fines. The data collected with such acoustic equipment would also need to be carefully calibrated to site sediments to confirm, for example, that a particular type of data signal uniquely pertains to the finest-grained sediments occurring at the site. Despite such drawbacks, however, remote-sensing tools may be highly useful during the process of refining the sampling design plan, particularly at larger sites. For example, this approach can be used not only to delineate portions of a site in which the potential for the occurrence of sediment contamination is the highest (i.e. in areas characterized by thick deposits of fine-grained sediments), but also areas in which such sediment contamination is *not* likely to occur (i.e. in areas characterized either by granular sediments or scoured areas, which are essentially free of water-borne deposits). Again, knowledge of site-specific conditions, such as the spatial/temporal variability in surface water flow (which will dictate sedimentation conditions at the site) will assist greatly in remote-sensing efforts.

Finally, standardized sediment toxicity tests (see Chapter 8) can be conducted to infer the spatial distribution of biologically relevant concentrations (and/or suites) of sediment contaminants occurring across a site. Sediment samples collected for toxicity testing should be collected at the same time (and near to) those samples collected for chemical testing. Development of an adequate, site-specific correlation between results of sediment toxicity and chemical testing could potentially be used to justify a more focused use of toxicity testing to characterize the spatial distribution of biologically relevant sediment contamination. Such an approach may ultimately prove to be an efficient use of project funds in that it could minimize, for example, the need for conducting costly replicate chemical analyses which, in turn, could enable more thorough toxicity testing of site sediments. In terms of ecological and human-health protection, a more substantial set of toxicity testing data may provide for a better spatial understanding of sediment contamination at the site, and the biological effects of such contamination.

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6. THE USE OF FIELD SCREENING OR RAPID SEDIMENT CHARACTERIZATION (RSC) TOOLS FOR SEDIMENT ASSESSMENTS

6.1 ABSTRACT

The primary goals of a sampling and analysis plan for an Ecological Risk Assessment (ERA) or a sediment site assessment are to identify potential contaminant sources and to delineate areas of contamination. However, traditional sampling and analysis approaches do not always provide all the information necessary to support the risk assessment process in a cost- and time-effective manner. Site assessments performed in the marine environment are often hindered due to the complexity and heterogeneity of marine ecosystems. One measure that can be implemented at various stages of the assessment or ERA process at sediment sites is the use of field screening or rapid sediment characterization (RSC) technologies. These are field transportable screening tools that provide measurements of chemical, biological or physical parameters on a real-time or near real-time basis. When used appropriately, these tools can streamline many aspects of the assessment process. The tools can be used to delineate areas of concern, to fill in information gaps and to assure that expensive, certified analyses have the greatest possible impact.

This chapter provides information about several of the rapid sediment characterization technologies that can be used at marine sediment sites. Examples are provided to illustrate the efficacy of applying rapid sediment characterization tools to different stages of the ERA process. Finally, recommendations are given for the evaluation, selection and application of RSC tools for the assessment process.

6.2 INTRODUCTION

Traditional sampling and analytical approaches do not always provide the information necessary to support the Ecological Risk Assessment (ERA) decision-making process in a cost- and time-effective manner. Because of the complex nature of marine ecosystems, sampling programs should focus on the identification of potential contaminant sources and on delineation of areas of contaminated media. Implementation of rapid sediment characterization tools at different stages of the ERA process can aid in focusing sampling requirements and ultimately facilitate reaching final decisions in a cost- and time-effective manner.

Ecological Risk Assessment evaluates the likelihood that exposure to one or more stressors (i.e., contaminants) will result in adverse ecological effects (USEPA, 1997). The purpose of the assessment is to provide information relevant to the management decision-making process. Ideally, Ecological Risk Assessments should be scientifically based, defensible, and done in a manner that is cost effective and protective of human health and the environment, (e.g., CNO, 1999). Collection of data necessary to support decisions at sediment sites in a cost-effective manner is often hindered by the complexity and heterogeneity of marine ecosystems. Detailed site investigations require extensive sampling and subsequent laboratory analyses for both metal and organic contaminants. Samples are often collected without any *a priori* knowledge of the nature and extent of contamination. Due to the high cost of laboratory analyses, the number of samples taken is often cost-limited. Thus, zones of contamination can be missed, or, if located, over- or under-estimated. For more detailed spatial information on the extent of contamination, sites of interest must often be sampled and analyzed in an iterative manner. Chemical assays are often combined with additional laboratory analyses; including one or several bioassays to determine whether there are adverse biological effects of these contaminants in various media (e.g., sediment, elutriate, water column). This approach can be prohibitively costly, slow and labor-intensive. When used appropriately, RSC tools can streamline many aspects of the ERA process, delineating areas

of concern, filling information gaps and assuring that expensive, certified analyses have the highest possible impact.

6.3 RAPID SEDIMENT CHARACTERIZATION

Rapid sediment characterization (RSC) can be defined as utilization of near real-time screening techniques to rapidly delineate extent of contamination, physical characteristics and/or biological effects. Rapid sediment characterization tools are field transportable analytical tools that provide measurements of chemical, physical or biological parameters on a real-time or near real-time basis. A wide variety of tools exist which are capable of making these types of measurements. Many technologies have been tested and/or successfully used to characterize different types of environmental media (e.g., soil, sediment, water and air). A compendium of these technologies is listed in "Field Analytical and Site Characterization Technologies, Summary of Applications" (USEPA, 1997) and in "Field Analytical Measurement Technologies, Applications, and Selection" (CMECC, 1996). The EPA has also compiled an online Field Analytical Technologies Encyclopedia (FATE) that is intended to provide information about technologies that can be used in the field to characterize contaminated soil and ground water, monitor the progress of remedial efforts, and in some cases, for confirmation sampling and analysis for site close out (see additional references/sources for details). Although not all of the technologies currently available are applicable to sediment sites, several of them have been tested and demonstrated in sediments.

Table 4 lists those screening-level tests and tools recommended by the USEPA's Assessement and Remediation of Contaminated Sediments (ARCS) program (USEPA, 1994). Examples can also be found in standard environmental textbooks such as Gilbert, 1987, which provides specific examples of using screening and laboratory data together to optimize for reduction in cost or data variability.

Table 4. Screening- Level Analyses Recommended by the ARCS Program for Freshwater Sediments

Analytical Technique	Parameter(s)
X-ray Fluorescence Spectrometry (XRF)	Metals
UV Fluorescence Spectroscopy (UVF)	Polycyclic Aromatic Hydrocarbons (PAHs)
Immunoassays	PCBs Pesticides PAHs
Microtox®	Acute Toxicity

In order to determine if RSC tools are appropriate to assess contamination at a given site, several questions should be asked. For example: What are the goals of the investigation? What are the contaminants of concern? Are the contaminants known? What are the action limits? What are the strengths and weaknesses of the analytical methods being considered? Do instrument detection limits meet action limit requirements? By asking these questions before sampling is started and considering the

advantages and disadvantages of different techniques, appropriate decisions can be made on how best to implement a technology or suite of technologies to facilitate the ERA process.

The relative advantages and limitations of rapid sediment characterization methods and standard methods are provided in **Table 5**. A brief description of some RSC technologies that have been tested in sediments is provided below. All of the technologies described below are commercially available.

Table 5. Advantages and Limitations of Screening and Standard Laboratory Methods

Rapid Sediment Characterization Analysis	Standard Laboratory Analysis
Benefits ❑ rapid results can guide sampling locations ❑ potential for high data density for mapping ❑ reduced cost per sample	Benefits ❑ standard methods that are very quantitative ❑ can often remove interferences
Limitations ❑ often non-specific ❑ semi-quantitative ❑ matrix sensitive	Limitations ❑ often blind sampling ❑ long delays to results ❑ expensive ($K/sample)

6.4 RAPID SEDIMENT CHARACTERIZATION TECHNOLOGIES: GENERAL PRINCIPLES

6.4.1 X-ray Fluorescence Spectrometry (XRF): Metals

This technique measures the fluorescence spectrum of x-rays emitted when metal atoms are excited by an x-ray source. The energy of emitted x-rays reveal the identity of the metals in the sample and the intensity of emitted x-rays is related to their concentrations (Swift, 1995, USEPA, 1998). Rapid, multi-element analysis can be performed by XRF. An XRF spectrometer can analyze a wide range of elements (i.e., sulfur through uranium), with a wide dynamic range, from parts per million to percent levels, encompassing typical element levels found in soils and sediments. Detection limits are different for each element. For metals such as Pb, Zn and Cu the detection limits typically range from 50 ppm to 150 ppm (USEPA, 1998). Field portable XRF (FPXRF) instruments can be calibrated using several different methods: 1) internally, using fundamental parameters determined by the manufacturer, 2) empirically, based on site-specific calibration standards, or 3) using the Compton Normalization Method which is based on the analysis of a single, certified standard and normalization for the Compton peak (USEPA, 1998). Field portable XRF units provide near real-time measurements with minimal sample handling, allowing for extensive, semi-quantitative analysis on site. Several examples can be found in the literature in which FPXRF has been used for the analysis of soils and sediments. Sediments in a Norwegian fjord (Skei et al., 1972), San Diego Bay (Stallard et al., 1995) and a large number of sites (Kirtay et al., 1998) have been screened for heavy metal content by XRF. FPXRF has been certified by the USEPA as a field screening method for metals in soils (USEPA, 1998).

6.4.2 UV Fluorescence Spectroscopy (UVF): PAHs

1. This screening method is based on the measurement of fluorescence observed following UV excitation of organic solvent extracts of sediments. In general, this method is used to measure fluorescent organics (especially PAHs), though some care must be taken to reduce signals from

natural organic compounds (e.g., humics) that fluoresce. Because fluorescence measurements are matrix sensitive, it is currently necessary to make measurements on solvent extracts rather than directly on the wet, solid sediment sample in order to achieve detection limits appropriate for marine sediment PAH benchmark criteria and typical levels in many marine sediments. Solvent extraction requires additional time for sample extract analysis, so although fluorescence is a near real-time measurement, the total time for analysis may be up to half an hour. Solvent extraction makes it possible to improve detection limits by several orders of magnitude. Detection limits range from one ppm to five ppm total solid-phase PAH. Many studies have used UVF to assess total PAH levels in various types of sediment (Hargrave and Phillips, 1975, Filkins, 1992, Owen et al., 1995).

6.4.3 Immunoassays: PCBs, PAHs, Pesticides

An immunoassay is a technique for detecting and measuring a target compound through use of an antibody that binds only to that substance. Quantitation is generally performed by monitoring solution color changes with a spectrophotometer. The technology can be used to measure concentrations of a variety of organic contaminants including PCBs, PAHs and organic pesticides. Detection limits range from hundreds of ppb to low ppm levels (USEPA, 1997, CMECC, 1996).

6.4.4 Laser Particle Scattering: Grain Size

Laser Particle Scattering operates on the principle of small-angle (Rayleigh) laser scattering to obtain the size distribution of particles suspended in water. The small-angle intensity distribution of light scattered by particles suspended in water is recorded. This distribution, which is the sum of particle scattering, is inverted to obtain the particle concentration and size spectrum. Theoretically, the particle size range is 0.1 µ to 500 µ. Commercial instruments, such as the LISST (Laser In Situ Scattering Transmissometry) instruments are available for making both in situ measurements (submersible) as well as measurements of samples in the laboratory, on the manufacturing line, or in a small boat (Sequoia Scientific, 1999). The operating range (particle size range) of these instruments is typically 1.25 µ -250 µ. Grain size measurements are made because contaminants generally are associated with the fine-grained particles (Förstner, 1987). This information can be useful in helping to delineate contaminated areas. Furthermore, grain size can be used to normalize other measurements and, at times, to predict when bioassays may encounter confounding factors.

6.4.5 IR Moisture Analyzer: Moisture Content

Moisture content measurements can be made quickly in the field or laboratory using commercial infrared drying instruments. Measurements are typically made by spreading a five gram sample of wet sediment on an aluminum sample dish, placing it in the analyzer, weighing it, initializing the drying procedure and then re-weighing it. Percent moisture is determined by the difference between wet weight and dry weight. Drying time is typically 5 – 15 minutes, depending upon moisture content. These results are used for conversion of data from wet weight to dry weight, for comparison with benchmarks and reference values, which are generally resolved in dry weight units. In some cases, percent moisture can be used as a proxy for grain size.

6.4.6 Screening Bioassay Tests

The QwikLite and QwikSed Bioassays measure the inhibition of light emitted by marine bioluminescent dinoflagellates (e.g., *Gonyaulax polyedra*) exposed to a test solution (effluents, elutriates, or sediment porewaters). Any decrease in light output relative to controls suggests bioavailable contaminants or other stressors. The bioassays are capable of measuring a response within 24 hours of test setup and can be conducted for a standard four-day acute test or seven-day chronic test. QwikSed can

be used to evaluate sediment toxicity. If the contaminated sediment is found to be toxic and requires cleanup, QwikSed can be used to assess the toxicity reduction. A "Standard Guide for Conducting Toxicity Tests with Bioluminescent Dinoflagellates" can be found in ASTM, 1999.

The Microtox® bioassay is a commercial test which measures the inhibition of light emitted by a bioluminescent microorganism. Any decrease in light output relative to controls suggests bioavailable contaminants or other stressors. A number of studies have compared Microtox® response to other bioassays (e.g., Giesy, 1990).

6.4.7 Summary

Implementation of rapid characterization tools in ecological risk assessments will improve sampling and reduce uncertainty at several steps of the RI/FS process without the enormous cost of traditional re-sampling efforts. Use of these tools moves the ERA process forward in the most time- and cost-effective manner with minimum uncertainty.

6.5 COST BENEFIT COMPARISON: EXAMPLE

An example of integrating rapid sediment characterization tools into the assessment process is provided in **Table 6**. In this example, in order to adequately delineate the area of concern for metals and PAHs, 400 sampling positions were identified. By measuring samples from each station using two RSC tools (XRF and UVF), and selecting 25% of those samples for confirmatory laboratory analysis, the overall analytical cost could be reduced by approximately 50% as compared to the cost of analyzing all of the samples using standard analytical methods. The cost could also be reduced by taking fewer samples for standard laboratory analyses, however adequate coverage/delineation of the site would be compromised. By using RSC tools with lab validation better delineation of a site could be accomplished in a cost- and time-effective manner.

Table 6. Cost Benefit Comparison for 400 Samples

Analysis Method	RSC Tool (# of samples)	Standard Method (# of samples)	Total Cost
XRF (metals) ($90/sample) (40 samples per day)	n = 400	n = 100	$71K
ICP/MS (metals) ($350/sample) (30 – 90 days turnaround)	n = 0	n = 400	$140K
UVF (PAHs) ($100/sample) (20 – 30 samples per day)	n = 400	n = 100	$80K
GCMS (PAHs) ($400 – 550/sample) (30 – 90 days turnaround)	n = 0	n = 400	$160K
Total Cost (RSC + Lab validation)			$151K
Total Cost (Laboratory Only)			$300K

6.6 RECOMMENDATIONS

A few recommendations are provided below for consideration in the selection and application of RSC tools to the ERA process.

6.6.1 Determine Which Tools are Appropriate

In order to determine if RSC tools are appropriate to define the nature and extent of contamination at a given site, site-specific project goals and parameters as defined by the Data Quality Objective (DQO) Process must be considered. It is critical to assure that the contaminants or criteria that are deemed to be decision drivers are detectable with the RSC tools that are available. In most cases, even if screening tools are not available for all the contaminants of concern, the tendency for classes of contaminants to co-associate allows for use of those parameters which are more easily measured to act as proxies for a suite of contaminants, to guide sampling and to interpolate between samples where a full suite of analyses is undertaken. In all cases, RSC technologies should be supplemented with a subset of samples for which thorough, traditional, standard laboratory analyses are carried out.

6.6.2 Data Quality

As with any method or technology, certain limitations exist. The primary limitations to RSC technologies are that they are often 1) non-specific, 2) semi-quantitative and 3) matrix sensitive. Because of these limitations, the data produced by RSC tools/methods are not necessarily equivalent to those generated by standard methods. Data are typically classified as either "screening data with definitive confirmation" or "definitive data" (USEPA, 1993). Screening data are those data generated by rapid, less precise methods of analysis with less rigorous sample preparation such as those produced using RSC methods, whereas, definitive data are generated using rigorous analytical methods, such as the approved EPA reference methods. Definitive data are analyte-specific, with confirmation of analyte identity and concentration (USEPA, 1993). Depending on the data quality requirements established during the DQO Process, a well-designed RSC protocol, paired with laboratory validation, will be able to provide data which can be of sufficient quality and great value to the risk assessment.

6.6.3 Documentation and Reporting of Data

Documentation and reporting is a very controversial subject in environmental analytical chemistry, because it affects how data are received and perceived by the user and often the public (Keith, 1991). The advent of database and GIS tools for the presentation and processing of environmental data allows for an unprecedented level of data manipulation and interpretation not just by data generators but also other users, regulators and stakeholders. While this ability has many benefits, there are potential dangers as well, particularly when data from many sources are combined. Results can be misleading if non-equivalent data are combined together without careful intercalibration.

A few different approaches to the documentation and reporting of data can be used to avoid such problems when reporting results, particularly those from RSC methods. The first is to always flag numbers generated by a non-standard method in spreadsheets and data reports, and to include text, references or qualifiers that address any potential offsets from standard analyses. This has the advantage that all data are available to regulators and stakeholders, but information necessary for proper interpretation is also provided. A second approach is to carry out site-specific calibration of RSC analyses and to report only corrected, calibrated data. This has the advantage of providing results that are more easily interpolated between or contoured with standard data. However, site-specific calibration requires a higher level of effort at a site (possibly more samples sent for laboratory analyses) and may reduce the cost-effectiveness and utility of using RSC tools in the ERA process. A third option, particularly for RSC analyses that generate only qualitative data (i.e., data which identify the presence or

absence of target analytes, but may have no relationship to true concentrations of the analytes) is to not report values. In such an approach, samples are either ranked (e.g., from highest to lowest levels) or ranges are reported (e.g., below detection limit, detected but not quantifiable, below action limit, above reference levels, etc.).

6.6.4 Obtain Regulatory Acceptance Prior to Use

It is particularly important that bioassay protocols to be applied are acceptable to all parties. While there is a substantial body of literature comparing screening bioassays to more "standard" bioassays, it is important that the assay selected in some reasonable way mimics or models the exposure pathways of concern, and that all parties are comfortable with the sensitivity and appropriateness of a selected protocol. While this document addresses screening bioassays, this recommendation is valid for all bioassay approaches, screening or "standard".

A concern voiced by many potential users of RSC tools is that, since they are not subject to the same QA/QC protocols and rigors as are standard procedures, they will make the user vulnerable by not standing up to regulatory or legal scrutiny. While these concerns are not trivial, it is clear that there are a growing number of case studies in which RPMs, regulators and the user community have accepted RSC data as a critical, though not stand-alone, part of the analytical and decision making process. A number of case studies can be found in the recent literature (USEPA, 1997, CMECC, 1996).

In any case, the intent to use RSC tools, and how the resulting data will be interpreted and managed, should be addressed up front with regulators and other stakeholders. Furthermore, it should be pointed out that RSC tools are only one part of the ERA process, which should always be balanced with and supplemented by standard, certified analyses. When used appropriately, RSC tools can streamline many aspects of the ERA process, delineating areas of concern, filling in information gaps and assuring that expensive, certified analyses have the highest possible impact.

6.7 REFERENCES

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6.8 ADDITIONAL INFORMATION

6.8.1 XRF

❑ EPA Method 6200: http://www.epa.gov:80/epaoswer/hazwaste/test/6200.pdf

6.8.2 QwikSed

❑ ASTM Standard: http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/PAGES/E1924.htm?L+mystore+rbmv5448

6.8.3 Federal Regulatory Guidance Documents

❑ Field Analytical Measurement Technologies, Applications and Selection: http://www.epa.gov/region09/qa/r9-qadocs.html

6.8.4 Field Analytical Technologies

❑ http://fate.clu-in.org/

6.9 LIST OF ACRONYMS AND ABBREVIATIONS

BERA:	Baseline Ecological Risk Assessment
COPEC:	Contaminant of Potential Ecological Concern
Cu:	Copper
DQO:	Data Quality Objective
ERA:	Ecological Risk Assessment
FPXRF:	Field Portable X-ray Fluorescence Spectrometry
FS:	Feasibility Study
LISST:	Laser In Situ Scattering and Transmissometry
PAH:	Polycyclic Aromatic Hydrocarbon
PCB:	Polychlorinated Biphenyl
Pb:	Lead
PPB:	Parts per Billion
PPM:	Parts Per Million
QA/QC:	Quality Assurance/Quality Control
RI/FS:	Remedial Investigation/Feasibility Study
RPM:	Remedial Project Manager
RSC:	Rapid sediment characterization
SRA:	Screening Risk Assessment
μ:	Micron
UVF:	Ultra Violet Fluorescence Spectroscopy
XRF:	X-ray Fluorescence Spectrometry

7. EVALUATING REFERENCE AREA CONDITIONS IN SEDIMENT ASSESSMENTS

7.1 THE ISSUE

Reference areas can be used as benchmarks for comparison of biological, chemical or physical sediment data that might be collected from potentially impacted study areas. Thus, they serve as potential control sites for these complex and multivariate studies. Lack of appropriate criteria for selecting the reference area may result in an inappropriate location being selected, and inappropriate sediment remedial actions being taken.

7.2 WHY THIS IS IMPORTANT

A proper approach to assessing and selecting a reference area is a key element of the overall sediment assessment process. Currently, there is no definitive approach to selecting a reference area; however, criteria can be established that would permit a more systematic process for making this selection. Establishing these criteria is critical because if reference areas are not highly similar to the areas under study, misleading or inappropriate conclusions may be drawn when making data comparisons. If this occurs, decisions on the risks associated with the sediment contamination and actions to reduce those risks may also be inappropriate.

7.3 APPLICATIONS

Reference areas are often utilized in sediment assessments so that data collected from an area potentially contaminated with various substances can be evaluated against a similar area that does not contain these substances. The underlying assumption is that the differences that might be observed between the two areas result from the presence of the substances in the sediments at one area vs. their absence at the other area.

There are three main applications for reference areas. One is where a reference area is used in determining whether a contaminated area may require remediation. That is, by reducing or eliminating exposure pathways to the substances in the sediment in the contaminated area, over time it may achieve the same or similar biological, chemical or physical characteristics as the reference area. A second is to determine incremental risk between a specific site with site-specific levels of contamination and a reference site in the region with some, but less elevated, but regionally ubiquitous levels of impact. Such a comparison is often valid in urbanized or industrialized areas. A third application is when a reference area is used in a post-remedial monitoring program. By making comparisons between a remediated area and the reference area over some time period, scientists and managers may be able to determine whether the remediation achieved its intended goals and objectives.

7.4 APPROACHES – STRENGTHS AND WEAKNESSES

The selection of the reference area can be based on a number of factors or criteria, including: (1) proximity to the study area; (2) physical, chemical and biological similarities, etc. A discussion of many of these criteria can be found in the references cited at the end of this document, as well as in the section below.

One important criterion for selecting a reference area could be that it has received little or none of the same substances as the study area. This is often difficult to fully achieve since there can be analytically detectable levels of a variety of substances in sediments. It might be possible however to reach agreement

on the selection based on the magnitude of the difference between the levels in sediments at the reference area vs. the study area. In other words, selection should not be based on the total absence of substances in the reference area, but perhaps on some percentage difference between the levels in both areas. This is particularly important for assessments in highly industrialized aquatic systems.

A second criterion could be the physical nature of sediments in the reference area. These measurements are relatively simple to conduct, and provide important information that can be utilized in the decision making process later on. Ideally, comparisons of areas with fine-grained, silt-clay sediments should be made with reference areas of the same or very similar composition. As noted previously this may not be feasible in all situations given the diversity of aquatic systems in the US.

A third criterion could be the chemical composition of the sediments in the reference area. Comparable levels of total organic carbon (TOC), and other characteristics such as acid volatile sulfides (AVS), oxidation-reduction potential and pH can be important to selecting the reference area. Data for some of these parameters are more time consuming and expensive to collect (AVS, for example) than others (TOC, for example), and results can be very heterogeneous within a particular area. Even so, some of these measurements can be very useful in evaluating the potential bioavailability of substances in the sediments since TOC and AVS can help bind substances and make them non-bioavailable under certain conditions.

A fourth criterion could be physical proximity to the study area. Ideally, the reference area would abut or be adjacent to the study area. Unfortunately, sources of contaminants may be sufficiently widespread and influence a geographically large area outside the study area. In this situation the reference area may need to be some distance from the study area.

A fifth criterion could be flow dynamics, especially where the study and reference areas are located on rivers and streams. In this case, it would be inappropriate to compare sediment data collected from high-flow rivers systems to those in more flow-restricted lakes or ponds. In estuarine and marine systems, it is important to compare erosional or depositional areas with reference sites of similar sedimentation regimes. In addition, substances in sediments can attach to particulates and become entrained during high flow conditions. An area where sediments can be scoured and transported would not offer the same type of physical bottom characteristics, contaminants or biological features as one where such flows were restricted.

A sixth criterion could be the composition and abundance of the benthic invertebrate community. Unfortunately, this may be even more difficult to rectify, as benthic invertebrate communities can be very heterogeneous, within even small distances. These communities also vary significantly with seasons, and are, themselves, a collective function or result of many of the above factors, which is another complicating factor. Similarly, measurements of the abundance and diversity of benthic invertebrate communities are routinely used as assessment tools for determining the potential impacts of sediment contamination. Pre-selecting a reference area on the basis of the benthic invertebrate community characteristics might obscure important differences between the reference and study areas.

When using statistical evaluation to compare site and reference parameters, an important goal, is that sampling design and abundance should be comparable in study and reference sites to make statistical comparisons meaningful. Largely due to cost considerations, this requirement is rarely met. The consequences of this issue to the design, interpretation and validity of statistical comparisons should be carefully and explicitly addressed in data evaluations.

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8. APPLICATION OF SEDIMENT TOXICITY TESTING IN SITE REMEDIATION ACTIVITIES

8.1 INTRODUCTION

Bioassay, defined as the use of biological media (whole organisms, cells, etc.) to measure contaminant concentration and/or potential biological response in environmental samples, has become an integral component of environmental assessments. Bioassay is a feature of many regulatory programs in the U.S. (e.g., CWA, FIFRA, TSCA, CERCLA/SARA, RCRA, MPRSA). Numerous sediment bioassays have been developed over the years for a variety of purposes. Most of these bioassays have been designed to assess the toxicity of sediments to make regulatory-based decisions (e.g., identifying acceptable disposal alternatives for dredged material; determining cleanup levels; or evaluating the effectiveness of a cleanup remedy). Since sediments serve as the ultimate repository for many environmental contaminants, the use of sediment bioassay as a tool in site assessment and site remediation activities logically follows. However, these tools should not be applied without proper consideration of the strengths and weaknesses of the individual procedures. The purpose of this chapter is to provide an overview of the general types sediment toxicity testing procedures currently available, as well as a discussion of strengths and weaknesses of those procedures, especially in context of their potential application to site assessment, remediation, and post-remedial monitoring. While testing procedures exist for evaluating the potential for exposure and/or uptake of contaminants (e.g., biomarker and bioaccumulation tests), these issues are addressed in other chapters. The scope of this review is limited solely to toxicity testing procedures.

Sediment toxicity tests can be categorized by exposure scenario, duration, endpoint, and/or laboratory versus in situ procedures. While the majority of sediment toxicity tests have been designed to look at the effects of whole sediment, there are other procedures for the evaluation of effects associated with unique sediment exposure scenarios. For example, there are procedures for evaluating effects associated with suspended sediments, sediment extracts, sediment porewater, and contaminant flux from bedded sediment. Selection of the most appropriate procedure is dependent upon the type of exposure scenario being evaluated. There are relatively quick and inexpensive screening procedures (which typically have somewhat higher false-positive rates and/or reduced ecological relevance relative to more conventional procedures) and there are longer-term, full lifecycle procedures (which may have higher ecological relevance, but are generally more complex and costly than are conventional acute toxicity tests). There are tests to evaluate potential effects at the cellular level (e.g., mutagenic potential), other tests that focus at the organismal level (e.g., survival, growth), and still others that look at reproductive endpoints and potential linkages to population level responses. Finally while many tests are laboratory-based, there are also procedures to evaluate effects to organisms exposed in situ. For organizational purposes, this review will consider the range of available sediment toxicity test procedures by exposure scenario (i.e., whole sediment, suspended particulate, etc) and discuss the general strengths and weaknesses of these procedures in context of their potential applications in site remedial activities.

8.2 WHOLE SEDIMENT TESTS

A number of procedures have been standardized for the evaluation of whole sediment (e.g., ASTM 2001, USEPA 1994a & b). In general, the majority of these tests focus on (acute) lethality in whole organisms (e.g., typically benthic infaunal species) following short-term or acute exposures (<14 days). More recently developed protocols focus on measurement of (chronic) sublethal responses (e.g., reduced growth and/or reproduction following longer-term exposures). Both acute and chronic tests provide useful measures of potential toxicity to benthic biota. Selection of appropriate procedures for a specific application depends on the questions being addressed, the nature of the environment and sample matrix,

the nature of the contaminant or contaminants of potential concern and the behavior of the test organisms. Evaluating the toxicity of in-place sediments should be approached differently than examining the potential impact of sediments that are to be removed, relocated and/or treated as part of a remedial action. For the evaluation of in-place sediments, it may be important to maintain sample integrity by evaluating intact sediment cores or using in situ procedures to accurately measure toxicity associated with the bioavailable fraction of sediment-associated contaminants under relatively undisturbed conditions. Whereas, in those instances where the sediment is to be removed, it may be more appropriate to simulate how the material will be handled at the removal site and/or rehandled at the disposal site. For example, evaluating effects associated with a removal/rehandling activity may require sample homogenization and compositing to capture potential changes in bioavailability (e.g., changes in redox affecting metal availability) that could also affect measured toxicity. Application of these tests in the national dredged material evaluation program and other regulatory programs has heightened the awareness of species and test-matrix-specific issues that can potentially confound interpretation of test results. Such things as organism behavior relative to exposure potential, organism health/sensitivity, sediment grain size, porewater ammonia, porewater salinity, porewater sulfides, TOC quality and/or quantity, pH, alkalinity and other factors can affect test organism response independently of any contaminant-induced effects. Consequently, it is important to have good measures of test species health/sensitivity via such parameters as control performance and reference toxicant testing information. It is also critical to characterize the geochemical nature of the sediments and to have a clear understanding of candidate test species' sensitivity to these factors prior to deciding which test to apply. The application of additional control treatments can be useful in establishing the potential influence of a particular factor on test results. For example, the use of a fine-grained or coarse-grained control sample as part of the test series may help elucidate the potential influence of sediment grain size on test results. Since many test species are supplied from wild-caught populations, it is important to employ QA/QC procedures to ensure that test organisms are healthy (e.g., appropriate handling, acclimation and holding) and appropriately sensitive (e.g., reference toxicant testing). Finally, the nature of the contaminant/s under consideration can also influence test selection. For example, compounds such as PCBs generally take a long time to reach steady-state concentrations in exposed organisms, and typically the effects are sublethal. Consequently, it would be more appropriate to evaluate sediments contaminated with PCBs using chronic sublethal tests than using acute lethality tests.

Solid-phase test procedures have a broad range of applicability to sediment remediation activities. Such tests are most commonly used to help delineate the extent and magnitude of contamination in the initial site assessment and in post-remedial monitoring. In the initial site assessment, toxicity test results, in combination with other information (i.e., bulk sediment chemistry), can be used to delineate the aerial extent of bioavailable contamination. In addition, the application of more specialized techniques such as Toxicity Identification Evaluations (TIEs) can be used to help identify the contaminants or contaminant classes most likely responsible for toxicity at the site and/or exclude potentially confounding factors (e.g., ammonia) (USEPA 1991). It should be noted, however, that TIE procedures for whole sediments are not fully developed nor routinely applied at this time. Sediment toxicity tests may be used to assess comparative risks associated with various management alternatives (capping, natural attenuation, etc.). They can also be used to establish efficacy or impact of proposed remediation technologies (soil/sediment washing). Since toxicity of many of the intermediate products are not known, whole sediment tests may provide a useful tool for the integration of potential effects of intermediates formed by a specific treatment process. They can also signal effects of a remedial strategy on non-target contaminants. For example, some treatments may mobilize previously unavailable non-target compounds. However, the ecological relevance of such an application would be limited unless the remediated material is to be returned to an aquatic environment, or if in situ treatment were being considered.

8.3 SEDIMENT POREWATER TESTS

Sediment porewaters, the water in the interstices of the sediment matrix, can be extracted for toxicity testing. Porewater is generally extracted via centrifugation of the sediment sample. However, other methods such as squeezing a sediment sample by applying positive pressure with an inert gas in a specially designed chamber, or passive diffusion through a semi-permeable membrane device placed in the sediments are other techniques that have been employed for the collection of sediment porewater (Ankley and Schubauer-Berigan, 1994). Recently, in situ sampling of porewaters with probes has also been carried out (e.g., Chadwick et al., 1999). Interest in the evaluation of sediment porewater as a unique test matrix stems from the belief that porewater chemistry is more representative of the bioavailable fraction of sediment-associated contaminants than is bulk sediment chemistry. However, the validity of such an assumption is highly dependent upon the organism being examined, and how it interacts with marine sediments. Currently, only a small number of sediment porewater tests have been developed, though in theory any aquatic organism could be used to evaluate sediment porewater toxicity. The small volume of sample that is practicably obtained through conventional porewater extraction methods limits the application of porewater tests to species/life-history stages that can be evaluated in small volumes (e.g., <50ml). Additionally, the exposure of epibenthic or pelagic species/life-history stages to sediment porewater has little direct ecological relevance and such organisms may express heightened sensitivity to sediment-associated factors other than contaminants, thus being poor surrogates for those species that might come in contact with porewater. For example, evidence suggests that urchin embryos lack the multi-xenobiotic transporter mechanisms found in other invertebrates (Toomey and Epel 1993, Galgani et al. 1996). These transporter mechanisms allow organisms to eliminate organic chemicals from their cells and thus are a protective adaptation. This would explain the often-reported sensitivity of the sea urchin porewater assay. Animals that have no evolutionary adaptation for exposure to sediment porewater (i.e., lacking the relevant protection systems) should be more sensitive. However, a porewater exposure for an animal that never comes into contact with sediment porewater over the course of its natural life history makes this heightened sensitivity meaningless for an ecological assessment. In addition, water quality measures (e.g., hardness and alkalinity for freshwater; salinity levels for estuarine/marine) of sediment porewater are highly variable. Consequently, the use of species with narrow tolerance limits for these factors may require that adjustments be made to the test medium to bring it within the acceptable limits for the test species. Such adjustments obviously may affect bioavailability of contaminants and confound the interpretation of test results. Consequently, one must be very careful with the application and interpretation of such tests for site assessments; even the use of infaunal species/lifehistory stages does not preclude the potential influence of confounding factors. For example, absence of sediment (as in a porewater assay) can be a stressor for organisms that normally reside in contact with sediment.

In general, sediment porewater tests have a high propensity to be affected by factors other than sediment-associated contaminants. Consequently, porewater tests are perhaps best suited as screening tools in initial site assessments. Additionally, because TIEs are better developed and more easily performed on water samples, porewater is a useful matrix for conducting such investigations on sediments. Results of porewater TIEs can be used in conjunction with other lines of evidence (chemical analysis, site history information, etc.) to identify the contaminants of concern at a site and help focus selection of the best remedial alternatives.

8.4 SEDIMENT EXTRACT TESTS

Sediment extract tests fall under a special class of test procedures. These are tests that evaluate extracts (i.e. prepared using either water or an organic solvent) of sediment-associated contaminants. Generally, the resultant extract is exchanged into an appropriate medium for subsequent testing. An

example of this type of test is Microtox®. Microtox® utilizes the bioluminescent properties of the marine bacteria *Photobacterium phosphoreum* to assay material for toxicity. The test method assumes that the levels of light emitted by the bacteria can be used to assess the overall biological condition of the bacteria exposed to individual chemical compounds and mixtures of mixtures. Light emitted by the bacteria exposed to potentially toxic samples is compared to light emitted to unexposed bacterial controls. Differences in luminescence are considered an indication of relative toxicity. Because the Microtox® test is most effectively performed in an aqueous marine matrix, sediments are extracted either with water or an organic solvent and then exchanged into test water of the appropriate salinity. Aqueous extracts are increased in salinity (i.e., salted up) while organic extracts are exchanged into water of an appropriate salinity for testing. Similarly, many of the procedures for assaying genotoxic potential of sediment-associated contaminants (e.g., Ames, Mutatox, H4IIE, and the P450RGS assays) rely on methods of extraction and exchange for testing (Inouye, 1999). The most obvious criticism of such procedures is that the issue of bioavailability is confounded in the extraction and exchange process. It should be pointed out that because of these concerns, Microtox® is more commonly applied to porewater extracts of sediments. Even in these cases, the potential influence of confounding factors (e.g., elemental sulfur) on the measurement endpoints may leave the interpretation of test results equivocal.

Sediment extract procedures should only be used for screening purposes. While such procedures can be used to infer a potential for toxicity, they should be applied and interpreted with caution. Sediment extract tests may have application in both site assessments and post-remediation monitoring. They may also be used to evaluate the efficacy of various treatment technologies (e.g. percent reduction of genotoxic potential by various treatment processes).

8.5 SEDIMENT-WATER INTERFACE TESTS

Sediment-Water Interface (SWI) Tests are designed to look at effects on epibenthic species as a result of contaminant flux from the sediment surface to overlying waters. They involve collection of an intact sediment core from the field. Test animals are then placed within a screened tube that rests on the surface of the sediment core. The screen prevents the animals from coming in direct contact with the sediment but permits exposure to contaminant flux from the sediment surface. Originally developed to assess the potential effects of contaminant flux on echinoid development (specifically the urchin, *S. purpuratus*), the same procedure can be applied to other epibenthic species/life-history stages (Anderson et al., 1996). While these tests can be applied to assess toxicity of sediments, they are best adapted for assessing affects associated with contaminant flux. The exposure represents a reasonable approximation of actual exposure conditions in the field to epibenthic organisms, assuming quiescent conditions. It should be pointed out, however, that a core in a laboratory will be subject to diffusional fluxes, but will not esperience advective fluxes from processes such as groundwater flow, wave pumping, bioirrigation, etc., which may dominate transport in situ (e.g., Apitz and Chadwick, 2000). As with other tests, one must be cognizant of the potentially confounding influences of factors other than sediment associated contaminants. For the SWI test, sediment features affecting overlying water quality (salinity, pH, ammonia and sulfide) are of greatest concern in addition to organism health. A clear understanding of these factors and their potential influence on test organism response is critical for test interpretation. The SWI test does require specialized testing equipment; however, the equipment is easily fabricated using readily obtainable supplies.

Sediment Water Interface tests can be used to delineate the extent and magnitude of potential toxicity as part of the site assessment process and in post-remediation monitoring. Because the test uses independent sediment cores (i.e., field replication), its application permits greater spatial coverage and potentially a better measure of field variability for test dollar expended relative to more conventional tests with laboratory replication. However, SWI tests are focused on a specific route of exposure (contaminant flux) and may not capture effects associated with direct contact and/or ingestion of sediment-associated

contaminants. SWI tests may be useful for assessing the comparative risks associated with various management alternatives (capping, natural attenuation, etc.), and can also be used to establish efficacy of proposed remediation technologies (soil/sediment washing).

8.6 SEDIMENT ELUTRIATE TESTS

Sediment elutriate tests were originally designed to assess potential water column effects associated with suspended sediments and/or dewatering discharges related to dredging and disposal activities (USEPA/USACE 1991, 1998). Since these types of activities are of generally short duration, nearly all of these tests have focused on effects associated with short-term or acute exposures. In addition, most of these tests focus on effects in pelagic species/life-history stages. Briefly, these tests involve combining the sediment with dredge-water from the site in a 1:4 ratio, then mixing the slurry for 30 minutes. The mixture is allowed to settle for 1 hour and the overlying supernatant is used as the 100% fraction. Typically, the 100% fraction is then used to create series of dilutions (e.g., 50, 25, 12, and 1% elutriate concentrations using disposal site water) that are then evaluated in an elutriate test to estimate a LC_{50} or EC_{50} value.

There are two general types of endpoints for these tests, standard lethality of whole organisms and/or effects on larval development. Like whole sediment test, the selection of the most appropriate type of test for a particular application depends on the questions being addressed, the nature of the environment and/or sample matrix, and the nature of the contaminant or contaminants of potential concern. For example, such tests are probably not useful for assessing potential effects of whole sediment on infaunal invertebrates (such effects are better addressed via whole sediment testing methods, as described above). Elutriate tests are better suited for the evaluation of potential water column impacts during removal and/or disposal. Like other test procedures, selection of appropriate test species for elutriate tests should be driven by the environment being evaluated (i.e., freshwater, estuarine, marine) and the types of species present at the removal or disposal site. Ideally, the candidate test species would actually be present at one or the other of these sites. However, this is not always possible. Consequently, one should look for species closely related to resident species. Application and interpretation of sediment elutriate tests should also include careful consideration of potentially confounding factors. Many of the same factors that can confound solid-phase test results can also affect elutriate tests. Two principle confounding factors in elutriate tests are ammonia and TOC. Most of the pelagic species and nektonic life-history stages commonly employed in sediment elutriate tests never encounter ammonia levels commonly associated with sediment matrices. Consequently, they tend to be more sensitive to ammonia toxicity than are Benthic organisms. Since ammonia is a relatively refractory constituent and generally not considered a persistent contaminant of potential concern at sediment clean-up sites, it is important to distinguish between effects induced by ammonia and effects potentially induced by the contaminants of potential concern. High levels of TOC have also been shown to potentially interfere with interpretation of elutriate tests (Bridges et al. 1996). Since animals are not fed during the course of exposure, TOC can represent a potential food source for those species requiring exogenous food sources. Larval mussels and echinoderms, among others, however, do not feed at the test stages that are used. In some cases, then, it is possible to see effects in elutriates with very low TOC and low contaminant levels and not see effects in elutriates with high TOC and higher contaminant levels. The interpretation of these observations may also be related to the removal of available fractions of contaminants by their association with TOC. By measuring these parameters and/or running appropriate controls, one can account for the influence of these potentially confounding factors on test results.

In terms of their potential application to site remediation activities, elutriate tests are best suited for monitoring activities. Such applications would include evaluating potential water column effects during remediation or removal/disposal of sediments and/or assessing the quality of return water associated with dewatering of material placed upland (e.g., water discharging over a weir at a confined disposal facility).

8.7 OTHER CONSIDERATIONS

Use of Resident Species as Test Organisms: While the use of standardized test procedures and test species offers consistency and permits comparison across sites over time, the use of indigenous test organisms can provide useful information about potential effects to resident species. Both ASTM (ASTM E1850-97 2001) and the USEPA (USEPA 1991) provide guidance for the selection of resident species as test organisms. Some species (e.g., commercially important fish and shellfish species) can be obtained through local hatcheries. Other types of organisms may have to be obtained from reference field locations. The intent behind the use of resident species is to increase the site-specific relevance of test results. While detailed information on the life history, care, maintenance, and testing of standardized test species exist, similar information may be lacking for resident species. Consequently, the potential influence of factors other than sediment-associated contaminants may not be well understood.

In Situ Testing: Site assessment and post-remedial monitoring may include in situ testing (i.e., bioaccumulation and/or toxicity). Such tests are useful in that they can provide more realistic measures of exposure accounting for the influence of site-specific conditions on contaminant uptake than do laboratory tests. However, like laboratory bioassays, in situ tests can be confounded by factors unrelated to sediment exposure (e.g., short-term changes in turbidity, current flow, etc.). Conversely, they may capture effects of contaminant transport conditions not replicated in the laboratory. Unlike laboratory bioassays, which are conducted in a controlled setting, there is a greater potential for such factors to go undetected. In situ tests have been conducted successfully and there are many examples in the published literature where such tests have helped to elucidate environmental effects (Rice et al. 1987, Brickson-Sasson et al. 1991, Ireland et al. 1996). Methods for conducting in situ exposures are determined largely by the site characteristics and species being evaluated.

8.8 SUMMARY

Sediment toxicity tests are useful tools for the evaluation and remediation of contaminated sediment sites. Used in conjunction with other information (e.g., chemical analysis of sediment and tissues of resident organisms, geomorphology, hydrology, etc.), sediment toxicity tests can help delineate the extent and magnitude of contamination, aid in the selection of appropriate management alternatives and ensure effective remediation.

The selection and application of such tests should be made with careful consideration of the questions to be addressed, the environment being evaluated, and the strengths and weaknesses of individual procedures and test species.

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9. BIOAVAILABILITY OF CONTAMINANTS IN SOIL AND SEDIMENT SYSTEMS

9.1 DEFINITION

The bioavailability of a contaminant controls the relationship between the absolute concentration of a chemical in a specific environmental matrix and the accessibility of the chemical for incorporation and possible toxicity (Alexander 2000). Reduced bioavailability via sequestration plays a significant role in soil and sediments systems where the toxicity of a chemical in aqueous or gaseous phase has been shown to be mitigated once the chemicals come in contact with soil or sediments (Hrudey et al., 1996). Sediments of different compositions and histories but the same bulk COC concentrations may have very different toxicities. Thus, it is important to consider the bioavailability, rather than just bulk concentration, of COCs in sediments.

Bioavailability addresses the fundamental issue of the potential for exposure of contaminants to a specific receptor. Exposure is not the result of the total concentration of a chemical in which the potential receptor is found, but only of that portion which is biologically available. Exposure occurs once a chemical is released from a soil/sediment particle and then transported to receptor. It has been shown that exposure of soil/sediment-borne contaminants can be impacted by physico-chemical properties of the chemical and environmental parameters including solubility, sorption, chemical form (speciation), and compartmentalization within the environment. These physico-chemical processes often result in environmental sequestration of the contaminant, with the potential for exposure the result of the availability of non-sequestered fraction. Exposure is further affected by the interaction of the non-sequestered fraction of the contaminant with an organism through its life history, which takes into account route and duration of exposure. Ultimately, bioavailability is species-specific because the dose that reaches an organism's target organs or tissues, and results in a biological response, may differ between receptors.

9.2 ISSUE

As the shift to risk-based cleanup continues, it is critical to establish "How clean is clean?" or "When is a site clean enough?" (NEPI, 1988). Although the concepts of bioavailability are well established (Kelsey and Alexander, 1997; Reible et al., 1999; Mark, 1995), incorporating these principles into risk assessments and into regulatory frameworks has proven problematic. Current regulatory decisions often assume the amount of chemical detected equals the amount, which could cause an effect to a receptor. This assumption, which ignores issues of bioavailability, can result in conservative estimates of transfer of contaminants from soils/sediments to the biota. The requirement for "zero presence" of a specific contaminant in soil or sediments is incompatible with the existing literature, which has shown that the toxicity of many contaminants decreases with time. The question to be asked is "How do we incorporate bioavailability when setting soil/sediment limits for regulatory purposes?" or alternatively, "What concentration of a chemical has the potential to pose a significant risk?" Since endpoints or targets for remediation for soil and sediment based on these issues may ultimately determine the removal volumes and costs of remediation, this decision process has significant implications.

Considering bioavailability when setting regulatory limits may at times result in an overall reduction in impact of the biota to contaminants. For example, the bioavailability of a contaminant sequestered in sediment systems could increase during dredging due to changes in the physico-chemical environment. In such a case, release of contaminants during resuspension and direct exposure of buried sediments to the aqueous environment (water column) may pose a greater hazard than leaving the contaminant in place. Bioavailability considerations suggest that at times leaving residual contamination in place may pose less

of a threat to surrounding organisms. Therefore, it is important to consider the principles of bioavailability in establishing endpoints for remediation and for setting realistic soil/sediment quality cleanup limits for regulatory purposes.

9.3 PROCESSES IMPACTING BIOAVAILABILITY

Contaminants can exhibit a wide range of toxicities across different types of soils/sediments. Bioavailability is impacted not only by soil/sediment type, but also by contact time between soil/sediment and aging, which can reduce the level of contaminant available for degradation/bioremediation (Hatzinger and Alexander, 1995). There are important physical-chemical-biological processes occurring in soil and sediment systems that have a significant impact on the bioavailability of organic and inorganic (metal) contaminants.

The sorption of a chemical onto soil/sediment plays an important role in determining its bioavailability. The sorption process often results in the sequestration of organic compounds within the soil/sediment particles, resulting in an overall decrease in bioavailability of the sorbed compound. Organic chemicals exist in soils in free or bound form; "free" indicates that the compound can be extracted from soil without altering chemical structures while "bound" chemicals are those resistant to extraction.

Enzymes and minerals can mediate oxidation of organic compounds to free radicals, which then results in coupling the contaminant to the organic fraction of soils/sediments. For example, enzymes found in soil fungi (e.g. laccases) have been shown to oxidize phenolic compounds and initiate the polymerization process (Gianfreda and Bollag, 1999). This results in the oxidative coupling of the organic contaminant to the organic fraction, resulting in the incorporation of these materials (covalently) into humic material. Studies have shown that certain pesticides become covalently bound to the humic fraction and the bioavailability of these humic bound fragments was practically negligible (Bollag and Huang, 1998).

Both sorption and sequestration can result in reduction of the potential for exposure of contaminants to biota. Where the rates of reaction for sorption usually occur quickly (within minutes), sequestration can take up to weeks or months to reach equilibrium. Organic contaminants that have been sequestered are usually harder to extract with organic solvents than are unsequestered contaminants. Sorption processes involve weak attractive forces such as electrostatic attraction, H-bonding, van der Waals forces, mechanisms that occur nearly instantaneously when contaminant and soil/sediment particle come in contact. In contrast, contaminant sequestration into soil or sediments is a diffusion phenomenon into inaccessible microsites within the soil/sediment environment.

Metals in a solid phase are usually unavailable and the uptake of metals by an organism usually occurs when metals are soluble. Thus, processes influencing the equilibrium between soluble and solid or bounds phases for heavy metals impact their overall bioavailability. Specific physical-chemical factors influence dissolution and precipitation of metals into the mineral phase ultimately defines their aqueous concentrations. Precipitation refers to the formation of a solid phase (mineral) from a dissolved phase of the chemical and occurs when the concentration of the chemical exceeds its aqueous solubility. Precipitation is a common phenomenon and controls the solubility of many elements including aluminum, iron, manganese, magnesium, and calcium. For example, orthophosphate can complex metals such as Pb, Cd, and Zn to form precipitates that are insoluble, relatively stable, and reduce the overall toxicity of the metal contaminants (Traina and Laperchie, 1999). However, ingestion and inhalation of particulate-bound metals can represent a significant route of contaminant exposure. Redox state in sediments affects metal form, solubility, and thus, bioavailability. Thus, tests for metals bioavailability should be designed and evaluated carefully, based upon the scenario being examined.

Chemical reactions, either abiotic- or biologically mediated, can result in changes in chemical structure, which in turn may alter chemical solubility. Changes in the geochemical equilibrium, which can result due to oxidation-reduction reactions, complexation, or sorption, can result in the precipitation of a chemical due to a change in the chemical's structure and solubility. A primary objective in many remediation strategies is either the elimination of the reactive heavy metal or conversion of the toxic metals (e.g., Pb) to geochemically stable forms, usually through precipitation reactions.

9.4 MEASURING BIOAVAILABILITY

As ecological risk assessment moves toward more quantitative exposure assessments, it becomes increasingly important to accurately estimate bioavailability. Although the routine and consistent consideration of bioavailability in eco-risk assessment is desirable, incorporating these concepts into quantitative estimates of exposure must be scientifically justifiable.
In order to facilitate incorporation of bioavailability data into risk characterization and cleanup remedies, additional work needs to be conducted on the development of a range of simple bioavailability tests. Significant effort is being directed toward developing simple chemical measures of bioavailability. Recent work has shown that mild solvent extractions may serve as surrogates for the prediction of bioavailability. Alexander and Alexander reported (2000) that a decrease in genotoxicity of benzo[a]pyrene paralleled a decrease in extractability of this material in soil suspensions. Others have shown the decrease in toxicity of phenanthrene and pyrene to earthworms correlated well with the resistance of these PAHs to mild solvent extraction (Chung and Alexander, 1999). Although these simple chemical assays look promising, more research is needed to establish correlation of the results for these tests with actual exposure to receptors and establish the validity of these tests as protective. Others have used the gut juices of deposit feeders to examine a bioavialable fraction (e.g., Mayer et al., 1996).

Alexander (1995) proposed that three lines of evidence are necessary to demonstrate the reduction of the bioavailability of toxic chemicals in soils/sediments. First, abiotic processes render the chemical less available to microorganisms, which are more able to assimilate organic chemicals than are plants and animals. The lack of bioavailability of these compounds can be observed by an overall decrease in the rates and extent of biodegradation of sorbed organic compounds in aged soils. Second, as the residence time of organic compounds increases in soil, they become more resistant to extraction by solvents; this fact is particularly noticeable for some chlorinated organics that are highly reactive with organic substances in soil or sediments. For example, Sarkar and coworkers (1988) demonstrated the enzymatic coupling of 2,4-dichlorophenol to fulvic acid by several oxidoreductases. Beyerle-Pfnur and Lay (1990) reported that chloroanilines can react with a variety of soils and sediments and remain bound, with subsequent extraction with solvent resulting in recovery of less than 10% of the chloroanilines. These strong interactions were likely the outcome of covalent bonding between the amino groups and the oxygen-containing group of the humic fraction resulting in an overall decrease in the bioavailability of the chloroanilines. Third, as the residence time of organic compounds increases in soils (and, presumably, sediments), there is a corresponding decrease in toxicity to test organisms. Taken together, these three lines of evidence demonstrate that as chemicals become sequestered in inaccessible microsites or covalently bind to the organic fraction of the soil/sediment particles, their overall bioavailability and toxicity diminish.

Novel molecular technologies are becoming available which will assist in evaluating the in situ bioavailability of contaminants (Kohler et al., 2000). Luminescence-based microbial biosensors have been constructed (e.g. genetically) and are being used to predict the bioavailability of metals and organic contaminants such as PAHs. Ripp and coworkers (2000) reported on a biosensor, which had been successfully introduced and maintained in soil for over 2 years. This study demonstrated the successful use of a lux-based bioreporter microorganism to assist in determining a contaminant's bioavailability as

well as serving as an on-line monitoring method for bioremediation. Future development of this technology will assist in more accurately determining the in situ bioavailability of contaminants.

9.5 UNCERTAINTIES

Although the precepts of bioavailability have been established, there are still many uncertainties to consider when quantifying potential contaminant exposure to organisms. When considering multiple receptors, the pathway through which exposure occurs is likely to differ between species. For example, contaminants sequestered in soil or sediment may prove unavailable to organisms in the water while sediment-dwelling organisms may prove quite sensitive. Contaminants can exhibit a wide range of toxicities across different sediment types; this variability has often been attributed to the variability in interstitial (pore) water concentration and not to the total chemical concentration in sediments. The toxicity reduction for nonionic organic chemicals (via sorption) is affected by the organic carbon content of the sediment, while for metals the reduction has been shown to be related to the acid volatile sulfide concentration of sediments (Mark, 1995). However, more recent studies with heavy metals such Cd, Ni, Zn, and Ag have shown that dietary uptake, not metal concentrations in pore-water, controls bioaccumulation (Lee et al., 2000).

There is evidence that long-term sequestration can be altered by changes in the physical-chemical-biological environment of soil/sediments systems. Changes in redox state have been shown to effect metal binding and dissolution. Oxidation of soil humic material can be responsible for releasing organic contaminants, which were previously bound to the soil organic fraction. White and coworkers (1999) reported the bioavailability of PAHs (phenanthrene) in aged soil could be enhanced by the addition of PAHs such as athracene/pyrene. Since contaminants immobilized in soil/sediment systems may be released back to the aqueous environment, one of the key issues concerns the long-term stability of non-bioavailable fraction.

9.6 SUMMARY

A significant amount of effort is being put forth to provide a sound scientific basis for including bioavailability considerations in risk characterization and clean-up strategies. The use of bioavailability data for establishing "environmentally acceptable endpoints" will be impacted by a range of issues including; 1) future land use, 2) nature and extent of contamination, and 3) exposure to receptors (human and ecological). Although the extent of current science and information is significant, further documentation and guidelines are needed to better describe how bioavailability can be aligned with clean-up standards and incorporated into risk assessment methodologies.

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10. IN SITU BIOACCUMULATION TESTS

This chapter presents a brief description and evaluation of in situ techniques that have been used to evaluate bioavailability of sediment-associated contaminants, specifically caged biota studies and semi-permeable membrane devices (SPMDs). In general, these techniques are intended to provide a relatively short-term, reproducible indicator of contaminant bioavailability. These techniques combine the advantages of experimental control offered by laboratory studies with the environmental realism provided by field studies. They are often used to gauge effectiveness of sediment remediation through performance of pre- and post-remediation studies. Furthermore, since they are deployed in situ for a period of time, they will integrate the effects of time-varying exposure caused by storms, currents, tides, etc., which might be lost in a sampling event. A brief description of these techniques is provided below, followed by a discussion of their advantages and disadvantages.

10.1 CAGED BIOTA STUDIES

Caged biota studies typically employ fish or mollusks contained in a vessel that allows exposure to sediments, either directly or indirectly (e.g. via the water column). Organisms may be obtained from commercial sources or from uncontaminated reference sites. Mussels are frequently used in both freshwater and marine environments because they are ubiquitous and sedentary, and can concentrate contaminants to levels that are orders of magnitude greater than environmental concentrations (Green et al., 1985). Certain fish species, such as fathead minnows and channel catfish, have also been used. Preliminary screening of test organisms is usually necessary to verify that they are contaminant-free prior to test initiation. To ensure that data from different test runs are comparable, care should be taken to use organisms of consistent size and age.

Exposure periods depend on the test organism used and the type of site and chemicals being studied. One general principle for such tests is that the exposure period be sufficient for organisms to come to steady-state or equilibrium with respect to contaminant uptake. For example, Jones and Sloan (1989) reported data that suggested a 4-6 week exposure period was sufficient for steady-state to be achieved in fathead minnows exposed to PCBs in the Hudson River. Rice and White (1987) reported uptake maxima occurring within 20 to 30 days in fathead minnows and 9 days in fingernail clams exposed to PCBs. Curry (1977) proposed that caged mussels (*E. complanata*) could be used to detect trace organic chemicals in water after 4 to 6 weeks' exposure. Generally, exposure periods should be sufficient to achieve steady-state, but should be short enough to reduce the chances of mortality due to disease or lack of food.

If the methodology has not been well developed, samples may be taken periodically throughout the test to monitor uptake kinetics and identify when steady-state is reached. Alternatively, if the protocol has been used extensively, samples may only need to be taken at the end of the recommended exposure duration. Samples would typically be analyzed for tissue residue concentrations of the chemicals of interest.

Caged biota studies offer the advantages of monitoring in situ chemical uptake by organisms, while also providing a degree of control and reproducibility of experimental conditions. By limiting mobility of the organisms, the tests can provide a good indicator of chemical bioavailability at a particular time and place. The major limitation of these types of studies is that the artificial exposure regimen may not accurately reflect uptake by resident biota, which can move and forage freely.

10.2 SPMDS

SPMDs are passive sampling devices designed to mimic the uptake of organic chemicals from water by aquatic organisms. Typically, they consist of polyethylene tubing or membranes filled with a solvent (e.g. hexane, triolein) that are mounted on some type of frame and suspended in the water column. Hydrophobic organic chemicals are taken up into the solvent, and concentrations can subsequently be measured when the SPMDs are retrieved. Exposure durations differ, but may be similar to or less than those used in caged biota studies.

SPMDs are especially useful in detecting chemicals that are present at very low and/or variable concentrations in the water column, since they concentrate hydrophobic chemicals from the water into the solvent. As such, they can be valuable tools in investigating potential sources of contaminants. A significant drawback, however, is the relative lack of calibration data to relate SPMD data to environmental concentrations (Meadows et al., 1998). SPMDs also do not address potentially significant processes affecting bioaccumulation in organisms, most notably uptake via feeding and metabolism/elimination.

10.3 DISCUSSION

Caged biota studies and SPMDs have several advantages and disadvantages in common. Both provide short-term indicators of relative bioavailability. Both employ somewhat artificial protocols in an attempt to control for sources of variability and to obtain a consistent measure of chemical concentrations at a specific place and time. As such, they are more useful as relative indicators of remedial effectiveness (through comparison of pre- and post-remediation data) than as measures of baseline risk. Their utility in assessing baseline conditions and risk is limited due to their somewhat artificial exposure regimens and the general lack of information correlating their data with more ecologically relevant information, such as tissue residue concentrations in resident biota.

Caged biota studies provide somewhat more realistic data than SPMDs, since they employ actual organisms and thus can encompass most of the processes affecting bioaccumulation, including feeding and metabolism. However, caged biota studies may also experience problems associated with the organisms themselves, including disease and physical stress associated with the enclosure, that SPMDs avoid.

In addition to these in situ techniques, laboratory protocols for measuring bioaccumlation of sediment-associated contaminants have been developed. For example, USEPA (2000) describes a 28-day bioaccumulation protocol for the freshwater oligochaete, Lumbriculus. Many of the same issues associated with caged biota studies apply to laboratory protocols as well, including the need to obtain contaminant-free organisms, and to run tests for sufficient time for uptake and equilibrium to occur.

In general, both caged biota studies and SPMDs provide a relatively inexpensive, rapid, repeatable means to measure chemical availability. In most cases, they should be used in conjunction with tissue residue studies of resident biota to provide an optimal assessment of baseline risks and potential remedial effectiveness.

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11. NATURAL PROCESSES DETERMINING CONTAMINANT AND SEDIMENT FATE

Natural fate and transport processes normally control the recovery of unremediated contaminated sediments, the effectiveness of in situ remedial processes, and the amount and fate of any residual contamination after disturbance of the sediment. Ultimately, it is the portion of the chemical (or constituent or contaminant) of concern (COC) that moves via natural processes into the water or food chain that is the source of exposure and potential risk to human and ecological receptors. Some of the processes that must be considered include,

- In-bed fate processes, including irreversible adsorption and chemical or biological reactions
- In-bed transport processes, including diffusion and advection as influenced by reversible sorption/desorption and colloidal transport
- Interfacial transport processes, including sediment deposition and resuspension, bioturbation, and water-side mass transfer

The purpose of this chapter is to define the basic characteristics of these processes and their role in determining contaminant and sediment fate. The range and significance of natural processes are influenced heavily by site-specific characteristics that must be adequately assessed prior to the selection, design and optimization of any management options for contaminated sediments. Any attempt to summarize and compare management options must recognize the different environments in which contaminated sediments are found. The relative importance of release, transport and fate processes differ significantly between lacustrine, riverine, estuarine, and coastal environments.

The exposure and risks to fish and higher-level organisms depend on the release and availability of the COCs in the sediment. Generally, it is assumed that the only the significant portion of the COC that is directly available is the fraction that partitions into the dissolved phase of the water. In this molecular form, the COC can move across biological membranes and accumulate in fish and other animal tissues. The available portion of the COC is generally limited by transport and/or equilibrium partitioning considerations. The risks of sediment contaminants to higher organisms can arise via one or more of the following three pathways:

- Direct exposure to fish and higher animals by COC release from resuspended contaminated sediment or by incidental ingestion of contaminated bed sediments.
- Indirect exposure to higher animals by predation and harvesting of plants and animals living directly exposed at the contaminated sediment-water interface.
- Direct exposure to fish and higher animals from COC release from bed sediment to the overlying water or through consumption of filter-feeding or benthic infaunal organisms that obtain their food via the water column

These pathways are linked to specific natural processes that should be assessed in any sediment environment in which remediation is needed or planned.

Key factors in defining the exposure and risks to COCs in sediments are the energy of the overlying flow and whether the system is net erosional or depositional. Under high flow conditions, the bed sediment tends to be coarse-grained and noncohesive with little sorptive capacity and low depositional rates. Significant amounts of sediment and associated contaminants may be suspended in the water and the dynamics of the sediment may largely define the dynamics of the contaminants. Since most persistent sediment COCs are associated with the solid phase, any mobilization of this phase dramatically increases COC mobility. It should be emphasized, however, that high suspended sediment loads do not necessarily mean that the bed is unstable in that the source of the suspended sediments may be land surface runoff or simply transport from upstream. In low energy environments, contaminant fate and transport is not controlled by sediment erosion and resuspension. Under low flow conditions, deposits are

typically fine-grained, providing high sorptive capacity and significant slowing of advection and oxygen transport. Often the most important process within stable or depositional sediments is bioturbation, the mixing associated with the normal lifecycle activities of sediment-dwelling organisms.   Many organisms, especially head-down deposit feeders, prefer fine-grained sediments, enhancing uptake and bioturbation in these areas. In the absence of significant bioturbation, physicochemical and/or microbial processes largely govern the release or fate of contaminants from the bed sediment. Important physicochemical processes include advection, diffusion and sorption/desorption. The high sorption capacity associated with fine-grained sediments may also increase the relative importance of boundary layer mass transfer processes in the water near the sediment-water interface. This occurs by a mechanism similar to the enhanced importance of water-side mass transfer processes in the evaporation of highly volatile compounds (i.e. compounds that strongly prefer movement to the atmosphere).

To illustrate the variable importance of sediment resuspension, bioturbation and advection/diffusion, consider that riverine environments are often characterized by seasonal variations in flow. During high flow conditions, for example associated with spring flooding, significant bed resuspension may occur. Such resuspension cannot be assumed, however, even under abnormal flooding events, since many riverine systems exhibit continuous particle and contaminant deposition over many years.   In both riverine and lacustrine environments, bioturbation may dominate contaminant transport and exposure during the lower energy summer and fall periods. Physicochemical processes such advection and diffusion are not as sensitive to temperature and season and may come to dominate contaminant transport and fate during the late fall and winter conditions.   The behavior and implications of the processes important in erosional environments and in net depositional environments are discussed in each of the subsequent sections.

11.1 PROCESSES IN EROSIONAL ENVIRONMENTS

Under high energy conditions such as in a stream, significant erosion of the sediment bed occurs and individual sediment particles can be carried downstream either by sliding along the surface of the sediment or by being suspended in the stream. The process normally results in the formation of dune-like structures that progress downstream by the process of erosion on the upstream face and deposition on the downstream face. During this overturning and migration process, sediment particles are exposed and either scoured and suspended in the stream or reburied by other sediment particles. During exposure to the stream water, COCs sorbed onto the sediment particles can be desorbed, and COCs in the adjacent porewater can be mixed into the overlying water. Once particles are set in motion, the following three types of movement can be recognized:

- Rolling and sliding along the bed surface (i.e., bed load transport)
- Suspension in the free stream (i.e., suspended load)
- A transitional motion characterized by saltation and particle jumps

The ability to predict the onset of resuspension in sediment remains largely limited to cohesionless, coarse-grained particles. Site-specific measurements of bed and/or suspended load sediment transport are needed to characterize cohesive, fine-grained sediment. Current models employ laboratory tests on site sediments to derive parameters that can be used in state of the art sediment transport models. Significant uncertainties remain in 1) defining the flows appropriate to any expected flooding condition, and, 2) defining the resulting sediment transport.

If significant resuspension occurs, the water column contaminant concentration tends to approach equilibrium conditions with the resuspended sediment. If the resuspended sediment load in the overlying water is ρ_s (mg/L) and the bed sediment contaminant loading is given by W_s (mg/kg), the equilibrium loading in the water, C_w (mg/L) is given by

$$C_w = \frac{\rho_s W_s}{1 + \rho_s K_{sw}}$$

K_{sw} is a distribution coefficient between the sediment and the water that should be measured under site-specific conditions. At very high resuspended sediment loads, the water column concentrations approach equilibrium with the bed sediment, while at low resuspended sediment loads, the water column concentrations are proportional to the amount of resuspended sediment. When sediment is dredged, an artificial situation equivalent to high flow rates and sediment resuspension in the water body occurs. Under such conditions, the contaminant concentration in water again tends to equilibrate with concentrations associated with the sediment resuspended by the dredge head as described by the Equation.

11.2 PROCESSES IN DEPOSITIONAL ENVIRONMENTS

11.2.1 Organism Accumulation and Bioturbation

Plants and animals living at the sediment-water interface are often assumed to be equilibrated with the surficial sediments. The partitioning of the COC with the surficial sediments defines the porewater concentration, and the dissolved porewater concentration is often assumed to define the portion that is available for uptake by the plants and animals. It is important to note that the COC concentration in the surficial sediments may not be represented well by the depth averaged composite concentration that is typically measured. Freshwater benthos, for example, may only populate the upper 5 to 10 centimeters (cm) of sediments in significant quantities. In marine sediments, animals living at the sediment-water interface tend to be larger and influence a larger sediment depth. The ratio of the contaminant concentration in the surficial sediments to that in the deep sediments depends on the COC transport rate to the surface layer and the transport rate and fate processes that remove COCs from that layer.

The uptake of the COC into sediment-dwelling animals depends on the ability of the organisms to accumulate the COC. The ratio of the loading in the organism to that in the sediment is termed the biota-sediment accumulation factor (BSAF). For hydrophobic organic compounds, the partitioning of the COC is assumed to be controlled by the organic "solvent" fraction that exists within a particular phase. Thus, a more useful biota-sediment accumulation factor for such compounds is one that normalizes the concentration in each phase with the organic fraction in that phase. For the biota, this is the lipid fraction, f_{lipid}, and for the sediment, it is the organic carbon fraction, f_{oc}.

$$BSAF = \frac{W_b / f_{lipid}}{W_s / f_{oc}}$$

The BSAFs differ as a function of sediment, organism, and time of exposure, but their values for benthic organisms tends to approach unity. This approach to unity implies that the organic-normalized concentration in the organism and the sediment are identical and that the organism is in equilibrium with the dissolved concentration of the COC in porewater. For higher organisms dynamic processes and bioaccumulation may cause the BSAF to differ significantly from unity.

The normalization with organic carbon content assumes that essentially all of the COC in the sediment and organism is available for partitioning to organic matter. A significant fraction of the COC, however, seems largely unavailable and is held in a desorption-resistant fraction. This phenomenon has been noted

most often in aged sediments where significant quantities of COCs appear not to follow the assumed linear, reversible partitioning. At this stage, no predictive guidance is available on the amount or extent of this desorption-resistant and potentially nonbioavailable fraction and either 1) all of it is assumed available or 2) site-specific measurements of availability are required for a more precise characterization.

The concentrations of metals and ionic species are significantly more complicated; however, the dissolved porewater concentrations in the sediment have been seen increasingly as the best indicator of metals and ionic species in both plants and animals. As indicated previously, the fraction that is ultimately leachable into the porewater is typically less than 10% of the total metal loading on the sediment, and the effective partition coefficient for this leachable fraction is typically 3 to 10 (Myers et al. 1996). Another indicator for specific metal contaminants is the ratio of the acid volatile sulfides (AVS) to the simultaneously extractable metals (SEM). A number of metals, including cadmium, copper, lead, nickel, and zinc, tend to form insoluble metal sulfides in sediments. As long as the AVS exceeds the SEM, these metals are essentially unavailable in dissolved form to living organisms.

As a result of the complex and varied behavior primarily of metal species and some other chemicals, toxicity tests often are used to assess the potential for adverse sediment effects rather than specific physico-chemical tests. The USEPA Assessment and Remediation of Contaminated Sediments (ARCS) Program performed a comparative evaluation of a number of toxicity tests for sensitivity and discriminatory power (USEPA 905-B94-002). The discussion of the individual tests and their ability to identify severely contaminated sediments is beyond the scope of the present discussion.

Thus, the assessment of the COC levels entering the food chain via uptake into plants and animals at the sediment-water interface is largely a question of COC availability. In the absence of site-specific toxicity information, equilibrium partitioning for organic carbons and the AVS/SEM for some metals are useful predictors of availability.

Organisms also move sediments and their contaminants by burrowing, foraging and ingestion/defecation processes. It is difficult to quantify their impact in this regard except through observations of high-resolution contaminant profiles in the sediment.   Radioactive tracer profiles have also been used to date sediments and indicate sediment reworking or mixing rates.   Movement of the sediment to the surface followed by release has been shown to be a significant contaminant transport process in stable sediments. Effective mass transfer coefficient measurements are often in the range of 0.3-30 cm/year.

11.2.2 Advection/Diffusion/Reaction Processes

COC movement from the bed to the overlying water is inherently a dynamic process controlled by the transport processes within the bed and at the sediment-water interface. Rarely are these processes sufficiently fast that the overlying water is equilibrated with the surficial sediments (although, as described in the previous two pathways, equilibration of contamination in the overlying water with any suspended sediment and between benthic organisms and surficial sediments is often assumed). The direct exposure of fish and higher animals to COCs in stable, noneroding beds is a rate-limited process controlled by the natural fate and transport processes. Among the processes that control contaminant transport from stable sediments are bioturbation, as described above, the physico-chemical processes of advection and diffusion, and the fate processes of sorption and microbial degradation. The latter processes all involve transport and fate via porewater processes while bioturbation involves particle as well as porewater transport. Because most contaminants are strongly sorbing and the porewater constitutes only a small fraction of the total contaminant mass, advection, diffusion and microbial degradation are generally intrinsically slow processes. All porewater processes are retarded by a factor, R_f, which is the ratio of unavailable (sorbed) fraction of the contaminant to the available (porewater) fraction,

$$R_f = \varepsilon + \rho_b K_{sw}$$

Here, ε is the void fraction (porosity) of the sediment while ρ_b is the bulk density of the sediments. K_{sw} is the sediment-water partition coefficient that is preferably measured for the particular contaminant under the system conditions. Although porewater processes are slowed by this factor, they still may be important under conditions of no particle transport and limited bioturbation.

11.3 SUMMARY

This paper has attempted to emphasize that natural processes largely control contaminant transport and fate and the effectiveness of either natural recovery or an active management option for sediments. These processes must be adequately characterized in order to assess the impact of natural recovery of the sediments and to compare natural recovery to active management options. Among the most important natural processes that must be considered are those in which particles are transported or released from the sediment, as in active erosion of the bed or in bioturbation. Only when these processes are not significantly operative do physicochemical and microbial processes dominate contaminated fate.

11.4 REFERENCES

U.S. EPA. 1996. *Estimating Contaminant Losses from Components of Remediation Alternatives for Contaminated Sediments.* Great Lakes National Program Office, EPA 905-R96-001.

12. ASSESSMENT OF MONITORED NATURAL RECOVERY OF SEDIMENTS

12.1 ABSTRACT

Monitored Natural Recovery (MNR) of sediments as a remedial option relies upon natural environmental processes to permanently reduce risk and requires careful assessment, modeling, and monitoring. Pertinent natural processes include sediment deposition (burial), dispersion, irreversible adsorption, and chemical and biological reactions. MNR differs from "No Further Action" in that the assessment, modeling, and long-term monitoring are required to verify remediation is taking place.

Given that a site possesses appropriate conditions, benefits of MNR include reduction or elimination of secondary impact on habitats caused by construction, lower risk to workers, avoidance of possible resuspension, avoidance of disposal requirements, and lower potential cost than more invasive remedies.

This chapter provides a table of assessment tools for evaluating MNR, broken into three categories: 1) Sedimentation/burial by clean sediments, 2) Contaminant weathering, bio-transformation/ degradation, and 3) Ecological recovery. The paper also discusses the role of modeling. A reliable site conceptual model is needed, which is a qualitative or quantitative statement and diagram of how the various physical, chemical, and biological processes affect risk. For more complex sites, there are many available mathematical models, including hydraulic, sediment transport, physical and chemical transport, and biological/ecological. They are generally applied in sequence, the outputs of the more basic models becoming the inputs to the more advanced.

When assessing a site for MNR, it is also important to identify parameters that are counter-indicative for MNR. These include ongoing sources, immediate and significant harm, insufficient clean deposition, ongoing or potential high energy resuspension, low sediment sorptive capacity, microbial processes that enhance bio-availability, and instances where active remediation can achieve risk-based objectives much more rapidly.

MNR should never be assessed by itself, but rather in comparison with other remedial alternatives, and the assessment should encompass "cradle to grave" risks.

12.2 INTRODUCTION

Monitored Natural Recovery (MNR) of sediments is a remedial option which relies upon natural environmental processes to permanently reduce risk, and which includes careful assessment, modeling, and monitoring to ensure success. The natural processes most often associated with this remedy, discussed below, include sediment deposition (burial), dispersion, irreversible adsorption, and chemical and biological reactions. MNR differs from "No Further Action" in that the assessment, modeling, and monitoring required by the regulator likely will be more rigorous than those associated with other remedial alternatives, and the duration of monitoring will likely exceed that of other alternatives. By definition, MNR is a risk management strategy. The most fundamental applicability requirement for MNR is that the remedial action objectives (RAOs) be risk-based. If mass removal is required for reasons other than risk reduction, MNR will not fulfill that requirement. Acceptance of MNR as a protective alternative requires recognition that the risk posed by a contaminant is closely associated with its spatial and temporal proximity to receptors, and that natural processes often function to eliminate or limit that proximity.

Natural recovery processes play an important role in any remedial action, by reducing margin risks and repairing unavoidable damage of more invasive alternatives. The object of the remedial alternative

assessment for MNR is to weigh its advantages as a primary alternative against other combinations of alternatives, which ultimately include natural recovery as a "polishing step", or which include natural recovery for the less contaminated margins. Another important assessment function, including measurements and modeling, is to help quantify and put in perspective the effectiveness of clean sediment layers in isolating contaminants, and the effects of rare events (storms).

12.2.1 Physical, Chemical, and Biological Processes Important to MNR

Although the application of monitored natural recovery as a remedial alternative for sediments is not as well understood or studied as monitored natural attenuation (MNA) is in its application to groundwater (Science Advisory Board (SAB), 2000), there are a number of physical-chemical–biological-parameters to consider when evaluating sediments. Use of MNR is largely based on the identification of in situ factors controlling the fraction of the constituent (or contaminant or chemical) of concern (COC) bioavailable to the sensitive receptor group(s). Sensitive receptor groups and the natural processes that either ameliorate or exacerbate the exposure of these organisms to the COC are specific to both the contaminant in question and the site. Consequently, success of MNR as a remedial strategy is dependent upon an accurate and specific understanding of the contaminated environment and the dynamics (fate and mobility) of the COC in that environment.

At all sites where MNR is to be considered a possible management strategy for contaminated sediments, identification of the source of the COC is crucial. Physical processes that support MNR by sequestration of the COC deep in the sediment (e.g., burial with clean sediment) are dependent upon developing a contaminant-free physical barrier between contaminated sediments and sediments in contact with the sensitive receptors. Within contaminated sediments the microbial processes catalyzing the transformation and/ or mineralization of the COC can be slow and are often constrained spatially and/or temporally. For these reasons, MNR as a remedial strategy is generally incompatible with a continuing input (i.e. point sources) of fresh contaminant.

Successful use of MNR to manage risk associated with contaminated sediments requires an understanding of the specific natural processes acting in the environment that affect the fate, mobility, and availability of the COC. Once the source of contaminant has been eliminated, management of contaminated sediments using an MNR strategy is largely a matter of limiting flux of the COC out of the sediment and limiting mobility of the contaminated sediments. As such, a number of interacting physical, chemical and biological processes contribute to natural recovery in sediments. Burial and sequestration of the contaminated sediments under a fresh layer of clean sediment often limits the bioavailability of the COC. For instance, in Lavaca Bay (TX) sediments total mercury extends deeper into the sediment than methylmercury, suggesting that the buried total mercury is less available for mobilization through microbial methylation than mercury found closer to the sediment/water interface (Bloom et al, 1999). Additionally, Frazier et al (2000) suggest that gradual burial of mercury-contaminated sediments in Fairhaven Bay and the Sudbury River (MA) reservoirs has reduced the amount of mercury available for methylation in these sites. If burial of the COC is anticipated to be an aspect of MNR for the site, it will be important to determine if the environment has a source of clean sediments adequate to cover and protect the contaminated sediment layer. Hydraulic characteristics of the environment that limit the resuspension and transport of the sediments will also contribute to minimizing the mobility of the COC in the environment.

While mechanical/physical processes limit the bulk movement of the contaminated sediments in the environment, chemical and biological processes will be the most important in determining the mobility and bioavailability of the COC itself. For example, sediment mixing associated with the activities of sediment dwelling organisms (bioturbation) can significantly impact the interfacial transport processes. Surface characteristics and the organic content of the sediment substrate will affect partitioning of the COC between the porewater (available for flux out of the sediment) and the sediment as well as the

reversibility of the binding of the COC to the sediment. Partitioning processes often result in the sequestration of chemicals in inaccessible microsites or as residues covalently coupled to the organic fraction of the sediment particles. This binding often reduces the overall bioavailability, toxicity, and bioaccumulation potential of the contaminant. For example, chloroanilines have been shown to react and bind with sediments as demonstrated by their resistance to subsequent extraction with solvents. These strong interactions are likely the outcome of covalent bonding between the amino groups and the oxygen-containing group of the humic fraction of the sediment (Beyerle-Pfnur R, Lay JP. 1990).

The surface characteristics, redox potential, pH, and chemistry of the sediments are also important determinants of the speciation of the COC and will influence the partitioning of contaminants between the solid and aqueous phases of the sediment. For example, toxicity of metals is often related to their interstitial porewater concentrations rather than total mass in sediments. In many sediments, the concentration of acid-volatile sulfides (AVS) is the key factor in determining interstitial water metal concentrations since AVS/metals form insoluble sulfide complexes with minimal biological activity (Ankley 1996)

Microbial processes are capable of supporting the goals of MNR in sediments in a number of ways. For example, the in situ biological degradation of hexachlorobenzene (HCB) has been shown to occur over a 16 year time period in the anaerobic sediments from a lake in the Netherlands. The reported half-life for HCB was determined to be ~7 years and HCB degradation was shown to be biologically mediated since there was a concomitant increase in di- and tri-chlorobenzenes (Beurskens 1993). Natural degradative processes have been shown to play an important role in the recovery of estuarine and marine sediments contaminated with DDT (1,1,1-trichloro-2,2,bis[p-chloro -phenyl]ethane) and DDE (1,1-dichloro-2,2,bis[p-chlorophenyl]ethylene), a toxic degradation product of DDT (Quensen et al., 1998). However, microbial contributions to NR through transformation and/or mineralization of contaminants may be limited for reasons previously discussed. Yet, microbial activities in sediments are largely responsible for the sediment oxidation/reduction potential, local pH as well as the precipitation and dissolution of minerals that compose the surfaces of sediments. As such, microbes are important determinants of the bioavailability of the contaminants in sediments. For example, the AVS that may precipitate and sequester metal contaminants is a by-product of microbial sulfate reduction. Likewise, microbially-mediated iron reduction produces surface-associated reduced iron minerals that are important environmental reductants in the reductive transformation of different nitroaromatic compounds (Heijman et al, 1995)

Clearly, there are a number of natural processes that support NR of contaminated sediments. Given that a site shows evidence of such processes, benefits of monitored natural recovery of sediments include minimal secondary impact on habitats potentially disturbed by construction, elimination of possible resuspension, and elimination of the need for disposal of contaminants. MNR is less costly than most invasive remedial alternatives, although not necessarily inexpensive.

When assessing a site for MNR it is also important to identify those parameters that will work against the RAOs set for the site. The incompatibility of an ongoing source of contaminant with MNR has already been discussed. Even without an ongoing source, risk assessments may show that the COC presents an immediate and significant harm to human health and the environment, and that active remedies can achieve RAOs much more rapidly than a MNR solution (SMWG, 1999). Site-specific characteristics that will work against the processes that support MNR include insufficient deposition of clean sediments and/or a high-energy environment in which sediments are constantly resuspended and transported. Sediments with a low organic content may not sorb the contaminant, leaving it available for diffusion to the water column. Microbial processes may transform the contaminant to a more soluble and/or bioavailable form. Microorganism may dissolve solid phase minerals that can be responsible for precipitating and sequestering the contaminants. Methylation of inorganic mercury in surficial sediments to produce the more toxic and bioaccumulative methylmercury is an example of a microbial process

acting against MNR goals. In addition to these undesirable site-specific processes, a drawback to natural recovery is the fact that the contaminants stay in place. Therefore MNR as a remedial option may be most effective in systems that show little bottom scour and high sedimentation rates. Nevertheless, MNR is potentially a favorable remedial measure when the site-specific ecological risk is low, the habitat is mostly healthy, and other site conditions are favorable.

Sites exhibiting natural processes ineffective for or antagonistic to controlling the mobility and availability of the COC are not necessarily contraindicated for MNR as a remedial strategy. Engineered remedial solutions such as active capping methods or limited removal of contaminated materials can be designed to overcome undesirable site-specific characteristics while taking advantage of the processes already acting at the site in support of NR.

Where natural processes are to be relied upon to achieve cleanup objectives, long term monitoring and performance standards will need to be developed for the successful application of MNR. It is critical to choose accurate and relevant indicators for an evaluation of permanence at a given site including data that confirms the presence of MNR mechanisms and quantifies rates, trends, and expected permanence.

12.2.2 Tools for Measuring and Assessing Processes Contributing to MNR

Unlike monitored natural attenuation (MNA) for contaminated groundwater, MNR for sediments has no prescribed approach or list of chemicals to measure to establish the extent of natural recovery through contaminant weathering. In order to support MNA as a remedial option for contaminated groundwater, three lines of evidence are often required: a) loss of contaminant mass in the field, b) contaminant and geochemical analysis (presence and distribution), and c) microbiological evidence. MNA correlates electron acceptor gradients with contaminant gradients in groundwater to establish ongoing electron acceptor processes, such as aerobic respiration or anaerobic respiration under nitrate-, iron-, manganese-, or sulfate reducing conditions or methanogenesis. In contrast, because of higher organic material content of sediments, contaminants exist primarily sorbed to sediment solids so they do not create contaminant plumes that affect electron acceptor gradients. Oxidizing conditions in sediments generally exist only at the top few centimeters of surface sediments, providing a very limited zone where oxygen is available for aerobic biotransformation of sediment contaminants. Beneath the aerobic zone, sediments typically are dominated by a single electron acceptor process, such as sulfate reduction in marine sediments or methanogenesis in freshwater sediments.

Tables 7, 8, and 9 show a variety of field measurement and analytical tools that may be used to evaluate the effectiveness of MNR in sediments. Table 7 shows physical transport measurement tools; Table 8 shows tools to evaluate the magnitude and extent of contaminant weathering (including biotransformation/biodegradation) studies; and Table 9 shows tools to evaluate ecosystem impacts due to contaminated sediments and ecosystem recovery studies that may be conducted.

The tools identified in Tables 7 and 8 focus on sedimentation and weathering, because these are the two principal mechanisms contributing to the natural recovery of sediments. Sedimentation (Table 1) acts to provide a clean layer and protect the benthos, water column, and resident fish from contaminant exposure. Weathering serves to stabilize contaminants and can provide permanent reductions contaminant bioavailability and toxicity. Weathering processes (Table 8) include physical (adsorption, sequestration, dilution and volatilization), chemical (sequestration, hydrolysis, photolysis), and biological (biodegradation/biotransformation) mechanisms and can be measured by comparing weathered sediments with less weathered sediments or with known contaminant profiles from the literature. For example, existing PCB histograms are commonly compared to known histograms of Aroclors reported in the literature, if the Aroclor source is known.

Table 7. Field Measurement and Analytical Tools for Sedimentation and In Situ Burial of Contaminated Sediments

Process	Measurement	Tools
Sedimentation under differing hydraulic loading conditions	Establish the natural sedimentation, resuspension and scouring rates	• Measure in situ sediment depths over time (e.g., bathymetric surveys) • Evaluate historical sedimentation using ^{210}Pb, Cs_{137}, or similar dating of sediment cores • Develop a hydraulic sedimentation model to characterize sedimentation
Sedimentation under high flow conditions (turbulent mixing)	Examine the effect of surface sediment mixing with clean sediment, and examine sediment resuspension, particularly during high flow periods	• Examine the water velocity distribution under differing flow conditions • Measure sedimentation and sediment scouring processes under differing flow conditions (bathymetric surveys, sediment traps)
Sedimentation under storm conditions	Examine the effect of surface sediment mixing, sediment scouring, and sediment transport and deposition under storm events	• Conduct storm event sediment and water column sampling (grab samples, sediment traps) • Measure sedimentation and sediment scouring processes under differing flow conditions (bathymetric surveys, sediment traps) • Measure critical shear stress with in situ or laboratory flumes
Vertical diffusive flux	Determine the depth at which sediments need to be buried by natural sedimentation to protect the water column, surface biota, and fish	• Measure the diffusive flux for surface sediments using laboratory column studies • Measure the diffusive flux for exposed and buried sediments using in situ benthic flux chambers
Vertical advective flux	Determine the advective contaminant flux, and depth at which clean sediments need to bury contaminated sediments to protect the water column, sediment biota, and fish	• Measure the advective flux for exposed and buried sediments using laboratory column studies • Measure the vertical advection of contaminants in situ using seepage flux meters
Vertical groundwater advection	Determine whether there are groundwater advective zones	• Perform hydraulic studies: • Dye studies • Piezometer studies • Seepage flux meters • Multilevel pressure transducers • Radon isotope studies
Sediment mixing through bioturbation	Evaluate the extent of sediment mixing and contaminant transport through bioturbation	• Sediment age dating analyses (e.g., 210Pb) may be used to assess bioturbation • Assess macroorganisms and their reported mixing depths • Underwater photography can be used to assess surface benthic activity

Table 8. Evaluation of In Situ Contaminant Weathering, Including Biotransformation/Biodegradation

Process	Measurement	Tools
Contaminant weathering using forensic analyses	Examine the magnitude and extent of contaminant weathering that has occurred in the sediments for historically deposited contaminants	• Conduct contaminant fingerprinting at various sediment depths to establish a historical contaminant profile • Use conservative tracers (e.g. hopane for petroleum hydrocarbons) or other biomarker to assess the magnitude and extent of contaminant weathering • Examine organic/inorganic geochemical indicators (e.g., redox, dissolved oxygen, total organic carbon, etc.) • Conduct laboratory weathering experiments
Anaerobic biotransformation	Determine whether anaerobic biotransformation occurs under natural conditions and establish biotransformation rates	• Establish the occurrence of anaerobic biotransformation in laboratory by comparing contaminant losses in live and killed sediments and/or by conducting 14C-contaminant studies. • Conduct long-term microcosm studies using aged contaminated sediments to develop contaminant biotransformation rates • Examine contaminant distribution shifts (e.g., accumulation of higher-molecular weight PAH or lower chlorinated PCB) that may reflect contaminant biotransformation (it may not be possible to distinguish biotransformation from other weathering phenomena) • Use biomarkers (e.g. genetic) to positively identify biological activity
Aerobic biotransformation	Determine whether aerobic biotransformation occurs under natural conditions and establish biodegradation rates	• Establish the occurrence of aerobic biodegradation in laboratory microcosms by comparing contaminant losses in live and killed controls and/or by conducting 14C-contaminant studies. • Conduct long-term microcosm studies using aged contaminated sediments to develop contaminant biodegradation rates • Examine contaminant distribution shifts (e.g., accumulation of higher-molecular weight PAH or lower chlorinated PCB) that may reflect contaminant biotransformation (it may not be possible to distinguish biotransformation from other weathering phenomena) • Use biomarkers (e.g., genetic) to positively identify biological activity
Bioavailability	Assess availability of contaminants at low concentrations to microorganisms, to establish a low-concentration threshold where biotransformation does not occur.	• Conduct microcosm studies using unamended sediments with a range of initial contaminant concentrations, from < 30 ppm to the maximum observed concentration • Compare sediment contaminant concentrations to literature-reported bioavailability limits
Contaminant partitioning	Assess contaminant sorption in sediments, and compare to literature sorption values	• Conduct batch contaminant laboratory sorption studies using sediments and water from the site • Use literature values for sorption coefficients

Table 9 focuses on ecological measurements that can be used to assess the health or recovery of the sediment and surrounding ecosystem. As discussed above, MNR is by definition a risk management strategy. Thus, an assessment of the efficacy of MNR necessitates an assessment of risks posed by sediment contaminants on the ecosystem and on ecosystem recovery or the potential for recovery.

Table 9. Evaluations for Ecological Recovery by Natural Attenuation

Process	Measurement	Tools
Water column recovery	Monitor changes to the water column before and after source control measures are implemented. Determine if low-level contamination persists in the water column, in the absence of measurable contaminant concentrations.	• Monitor sediment, water column, and air (e.g. atmospheric) contaminant concentrations along contaminated portions of the site to assess sediment and water column recoveries • Use caged fish, caged mussels, trapped fish to measure contaminant bioaccumulation from exposure to the water column. • Use resin traps to measure the potential for bioaccumulation from exposure to the water column
Fish and biota recovery	Examine how quickly fish and sediment biota respond to source control measures and sediment remedial actions	• Conduct fish and sediment biota sampling over time to assess in contaminant concentration reductions in plant and fish tissue • Conduct population assessments to examine population changes due to sediment contamination and recovery • Conduct bioassays to assess the health of sediments or water and potential toxic impacts of contaminants on resident biota
Bioaccumulation studies	Establish primary bioaccumulation pathways from sediment biota to fish and/or mammals; determine whether deep or shallow sediment biota (or both) contributes to fish contamination	• Conduct sediment biota and fish surveys and develop an ecological or human health contaminant exposure model • Use caged fish, caged mussels, trapped fish to measure the potential for contaminant bioaccumulation.

12.2.3 Role of Modeling in Assessment of MNR

Modeling of some sort is always needed in the assessment of MNR; that is, a careful understanding of sedimentation rates, contaminant sources, sediment transport, benthic mixing, and bioaccumulation of sediments is required to understand and effectively implement MNR. The most effective sediment models are those which have a strong basis in physics, chemistry, and biology and which contain a minimum number of adjustable parameters. Models strive to match/explain past history and to accurately predict future performance. For MNR, they should match any recovery that has already occurred. To suggest that MNR is a viable alternative, the model should also predict that recovery will continue to occur, or that it will at least be adequate, and sustainable. There are at least two site situations in which modeling is used in the assessment of MNR: 1) Where effects have been observed (e.g. fish concentrations), and one wishes to evaluate whether the sediments are or are not the cause, or that the effects will diminish with time. 2) Effects have not been observed, although sediment concentrations have been observed, and one

wishes to evaluate whether effects will result in the future. In both instances recovery processes, permanence, and stability are key issues.

At a minimum, a reliable site conceptual model is needed (refer to Chapter 3: The Conceptual Site Model). This conceptual model should consist of a qualitative or quantitative statement and diagram of how the various physical, chemical, and biological processes affect the overall risk at the site. Under certain circumstances, for example a reliably low energy environment with no ongoing sources and no measurable effects in water column or biota, a qualitative conceptual model might suffice for the selection of an MNR remedy. For a more complex site, a more detailed mathematical model is usually necessary.

Mathematical models for sediments have been developed independently in groups that build sequentially upon one another. One group, the hydraulic models, forms the main foundation in describing the flows and associated stresses. They are generally open-channel models, which include as their inputs the size and shape of the streambed or water body and the range of flows expected from various sources. Sediment transport models, built on the previously described hydraulic models, are well developed for non-cohesive sediments (i.e. sands) but less reliable for cohesive forms (i.e. muds). Next in sequence are the models for physical and chemical transport and transformation of contaminants that are linked to the hydraulic and sediment transport models. All models must be site-specific and contaminant-specific in their application, particularly when progressing beyond hydraulic and sediment transport models. Beyond physical and chemical transport models are those that describe the biological processes, including food chains. In utilizing sediment modeling tools, the outputs from the more basic model groups provide the inputs to the next group, and so on. Normally the mass transport and biological processes are not expected to feed back to the more basic processes such as hydraulics, but one must always be alert to site-specific exceptions, for example, the effects of bioturbation on the mass transfer of contaminants.

Models are "calibrated" using measured data to set the values of any adjustable parameters. A strong basis in science and a minimum number of parameters gives the model credibility in predicting the future performance. Data gathering tools and techniques discussed elsewhere in the chapter are used to develop the data required for model calibration. Once calibrated, an important function of a model is to predict the rate at which recovery will occur. Often MNR is assessed relative to the time frame in which overall risk is reduced, relative to other remedial approaches – particularly relative to removal of the contaminated sediments. To assess MNR against other alternatives, the same model should be applied as much as practical to each of the alternatives. For consistency, the same model might be asked to predict not only the recovery scenario for MNR by itself, but also the recovery rate by natural processes following a removal action.

With all their strengths, there is a fundamental rule that always applies to models. Models and other predictive tools should never take precedence over something that can be measured directly. For example, models and other surrogates should not be used to predict current levels of contaminants in fish tissue, if fish can be caught and measured directly. The true usefulness of models is to predict future states that cannot be measured directly, or to guide sampling and data collection. It is the real utility of measurement tools to characterize the present state.

12.3 CONCLUSIONS

Ideally, MNR should not be assessed by itself, but in comparison to other remedial approaches. There is economy in combining assessment steps or data gathering for multiple remedies into a minimum number of field investigations, and the complexity of most sites does not render them amenable to single, ideal solutions. Many sites must be addressed using multiple remedial approaches. Natural recovery will always play a key role, either as the main approach (with extensive monitoring), or as a means of attenuating residues or dispersed materials left after a remedial action. Other remedies that should be assessed along with MNR include removal, capping, assisted natural recovery, hydraulic modification,

and all combinations. The overall assessment question should not be whether MNR achieves some idealized state where all contaminants are destroyed or otherwise inactivated. Instead, the fundamental question is whether MNR can achieve protective levels, in a time comparable to other remedial approaches, or in a way that is less damaging to health and the environment than other remedial alternatives.

12.4 REFERENCES

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13. MONITORING REMEDIAL EFFECTIVENESS

A wide range of technologies is applicable to the management and remediation of contaminated sediments. The selection of these technologies, either alone or in combination, depends on a wide range of considerations, including:
- Effectiveness
- Permanence
- Implementability
- Risks associated with implementation
- Cost
- State and community acceptance

Many of the technologies potentially applicable to contaminated sediments were initially developed to manage contaminated soil and groundwaters. Unfortunately, many of these technologies are difficult to apply or impose potentially unacceptable risks when applied to contaminated sediments. Contaminated sediment sites are often poorly controlled, dynamic systems containing large volumes of moderately contaminated material. An analysis of Superfund Record of Decisions from 1982-1997 showed that the average contaminated soil site considered for ex situ treatment contained 38,000 cubic yards of contaminated material and that the average site considered for in situ treatment contained approximately 105,000 cubic yards of contaminated material. Contaminated sediment sites, however, often contain in excess of 1,000,000 cubic yards of contaminated material and generally are not directly accessible. The ability to control contaminant releases during the application of these technologies is also generally much poorer for contaminated sediments than for contaminated soils and groundwaters.

Selection, design and optimization of remedial technologies for contaminated sediments requires an understanding of the following factors:
- Ultimate effectiveness of the technology with contaminated sediments
- Potential risks associated with application of the technology or resulting from the residual contamination left by the technology
- Methods for measuring and evaluating the performance of the technology when applied to contaminated sediments
- Economics of the technology when applied to contaminated sediments, including the effects of scale and the balance between capital and operating costs
- Uncertainties in application of the technology or in evaluating its potential risks and benefits

Unfortunately, many of these factors are not well understood. More importantly, however, the lack of standardization in how to measure and evaluate the performance of a remedial technology and the lack of adequate monitoring during implementation of these technologies suggests that our ability to select, design and optimize is not improving. The goal of this chapter is to identify these inadequacies and push for improved monitoring of remedial actions both during implementation and afterward in order to enhance our ability to define appropriate management approaches for contaminated sediments.

The primary goal of the application of sediment management or treatment technologies is the reduction of human health and ecological risks. In general, an environmental resource, for example human health, an endangered animal, or commercial fishing stocks, is at risk. The ultimate goal of any remedial monitoring program is to identify the success at protecting or restoring that resource. Because the ultimate goal may require many years to achieve, interim goals are required that provide more immediate feedback into the success or failure of the sediment management option. The monitoring program must then be directed toward the measurement of these interim goals as well as the ultimate goal. In addition, any monitoring program should include efforts to evaluate the effectiveness of the implementation. Thus a three-pronged program for monitoring remedial effectiveness is recommended:

1. Monitor to assess effectiveness of remedial action in achieving ultimate goal, i.e. protection or recovery of the resource at risk.
2. Identify interim goals and monitor to evaluate the effectiveness of the remedial action in achieving those interim goals.
3. Monitor implementation of the remedial action to evaluate effectiveness of meeting both engineering and environmental protection goals.

Each of these is discussed in more detail below.

Any effort to remediate or manage a site containing contaminated sediments is driven by the risk to one or more environmental resources. Commonly, the resource at risk may be human health related, for example protection of commercial or recreational fishing stocks, or related to ecological health, for example the protection of a migrating fish or bird species or protection of biological diversity in the watershed. Ultimately, the measure of success of the remedial or management option is the degree to which the effort was successful in restoring or protecting that resource. The type of monitoring program required to measure success depends on the resource being protected. The end use of any dredged material must also be considered in that there may be influences on the resource or on other resources that may be put at risk.

It is often difficult to monitor the resource at risk, i.e. to measure improvements in human or ecological health resulting from a particular action. There may be sources of exposure other than the sediments being remediated or managed. The water body containing the sediments is likely receiving inputs from nonpoint runoff, sediments in other portions of the surface waters and the atmosphere. In addition, it is even more difficult to measure the success of the chosen management options relative to other options that might have been chosen. Such an effort is critical, however, to learning from the site and improving the decision making process at other sites. Over time, results of many such evaluations will make monitoring efforts easier and more standardized.

Because of the difficulty and time required to define success in restoring or protecting the primary resource at risk, interim goals are needed to provide more immediate feedback that the remediation or management option is progressing. Often, these interim goals are relatively short-term physico-chemical and bioassay measurements. Any remediation or management technology seeks to reduce risk by reducing the contaminants that are or may be introduced to the biologically active zone which includes the upper layers of sediment (which may change with time or due to storm events), the water column, and the air above and surrounding the water body. Monitoring of physical, chemical and biological parameters within this biologically active zone often serves to evaluate effectiveness in meeting interim goals. Examples may include chemical concentration measurements in the water column or in the upper layers of sediment, or density and speciation of benthic organisms. Contaminant uptake in species that respond rapidly to sediment contamination can also be useful as an interim measure. The dynamics of the response of many higher organisms, such as fish or birds, however, may be too slow for these ecological end points to be used as interim measures.

The previous two components of a monitoring program are focused on its long-term effectiveness. A monitoring program is also required for the evaluation of the effectiveness of the implementation of the remedial or management plan. This monitoring effort has three goals, 1) to evaluate the implementation of the particular technology to ensure that it met the engineering construction goals, 2) to evaluate and minimize risks to human and ecological health during implementation, and, 3) to evaluate the appropriateness of the technology at this and future sites. The goal of protecting human and ecological health also has at least three important components.

- Ensuring the safety and health of the workers implementing the technology.
- Minimizing environmental risks to human and ecological health during implementation.
- Evaluating any natural resource damages that may result from the implementation.

The goal of evaluating the appropriateness of the technology is rarely included in current monitoring plans but is necessary to ensure that the best remedial or management plan was selected and to collect data to help assess the applicability of the technology at other sites. For relative comparisons of sediment management technologies, it may be appropriate to employ contaminant mass flows as a surrogate measure of exposure and, ultimately, risk. That is, a technology may generally be assumed to pose less exposure and risk if it leaves less residual contamination and loses less contaminants to the air and water than does an alternative technology. A comparative analysis of mass flows can also identify those components of an overall management strategy that largely control the overall risk and therefore should receive the most resources and effort. As a result it is recommended that the monitoring plan during implementation be directed toward closing the material balance on sediment and contaminant (i.e. identifying the fate of all sediment and contaminants). It is hoped that a similar analysis of mass flows helped lead to the decision to remediate and the selection and design of the remedial option. Thus the monitoring will serve to test assumptions and confirm that the remedial technology is operating as designed. The primary advantage of employing contaminant mass flows as a surrogate for exposure and risk is to avoid the additional uncertainties associated with detailed exposure modeling and translation of that exposure to human health and ecological risk. The latter cannot be avoided in the assessment of the risks posed by the unmanaged sediments or in assessing the adequacy of any particular management approach. It can be useful, however, in the comparative evaluation of potentially applicable technologies. Although uncertainty in the relative comparison is reduced by the use of contaminant mass flows, it cannot be eliminated. In keeping with common practice in such assessments, one approach would be to compare technologies on the basis of both average and 95% upper confidence limit contaminant mass flows.

13.1 SUMMARY

This chapter has attempted to summarize the three types of monitoring desired to support a sediment remediation program, 1) long term monitoring of resource driving the remediation, 2) short-term monitoring of interim measures of remedial success, and 3) short-term monitoring of implementation of remedial technology. Closure of the material balance on sediment and contaminants during implementation of a remedial technology is recommended as a means of maximizing our understanding of the specific project as well as improve our ability to undertake similar projects in the future. Clear definition of the goals of the remediation and how these goals will be measured help to ensure that the effectiveness of the remediation is measured and that this information will improve our ability to select, design and optimize remedial or management approaches at other locations.

13.2 REFERENCES

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