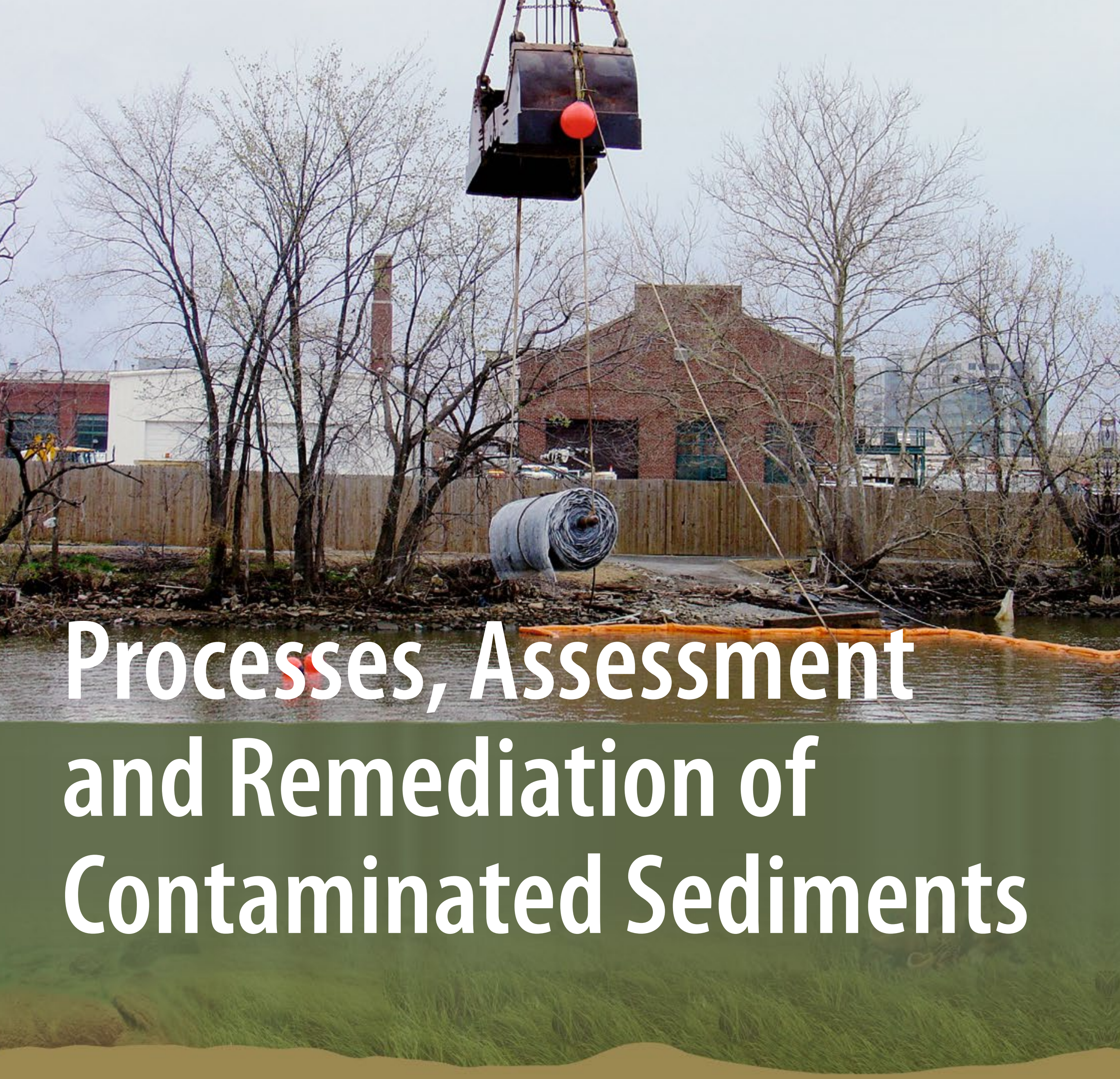

Processes, Assessment and Remediation of Contaminated Sediments

Danny D. Reible
Editor

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Processes, Assessment and Remediation of Contaminated Sediments

SERDP and ESTCP Remediation Technology Monograph Series
Series Editor: C. Herb Ward, Rice University

Processes, Assessment and Remediation of Contaminated Sediments

Edited by

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SERDP and ESTCP have joined to facilitate the development of a series of monographs on remediation technology written by leading experts in each subject area. This volume is intended to help engineers and scientists better understand contaminated sediment sites and identify and design remedial approaches that are more efficient and effective. Volumes previously published in this series include:

- *In Situ* Bioremediation of Perchlorate in Groundwater
- *In Situ* Remediation of Chlorinated Solvent Plumes
- *In Situ* Chemical Oxidation for Groundwater Remediation
- Delivery and Mixing in the Subsurface: Processes and Design Principles for *In Situ* Remediation
- Bioaugmentation for Groundwater Remediation

The following volume is planned for publication in the near future:

- Chlorinated Solvent Source Zone Remediation

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Preface

In the late 1970s and early 1980s, our nation began to grapple with the legacy of past disposal practices for toxic chemicals. With the passage in 1980 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, it became the law of the land to remediate these sites. The U.S. Department of Defense (DoD), the nation's largest industrial organization, also recognized that it too had a legacy of contaminated sites. Historic operations at Army, Navy, Air Force, and Marine Corps facilities, ranges, manufacturing sites, shipyards, and depots had resulted in widespread contamination of soil, groundwater, and sediment. While Superfund began in 1980 to focus on remediation of heavily contaminated sites largely abandoned or neglected by the private sector, the DoD had already initiated its Installation Restoration Program in the mid-1970s. In 1984, the DoD began the Defense Environmental Restoration Program (DERP) for contaminated site assessment and remediation. Two years later, the U.S. Congress codified the DERP and directed the Secretary of Defense to carry out a concurrent program of research, development, and demonstration of innovative remediation technologies.

As chronicled in the 1994 National Research Council report, "Ranking Hazardous-Waste Sites for Remedial Action," our early estimates on the cost and suitability of existing technologies for cleaning up contaminated sites were wildly optimistic. Original estimates, in 1980, projected an average Superfund cleanup cost of a mere \$3.6 million per site and assumed only around 400 sites would require remediation. The DoD's early estimates of the cost to clean up its contaminated sites were also optimistic. In 1985, the DoD estimated the cleanup of its contaminated sites would cost from \$5 billion to \$10 billion, assuming 400–800 potential sites. A decade later, after an investment of over \$12 billion on environmental restoration, the cost to complete estimates had grown to over \$20 billion and the number of sites had increased to over 20,000. By 2007, after spending over \$20 billion in the previous decade, the estimated cost to address the DoD's known liability for traditional cleanup (not including the munitions response program for unexploded ordnance) was still over \$13 billion. Why did we underestimate the costs of cleaning up contaminated sites? All of these estimates were made with the tacit assumption that existing, off-the-shelf remedial technology was adequate to accomplish the task, that we had the scientific and engineering knowledge and tools to remediate these sites, and that we knew the full scope of chemicals of concern.

However, it was soon and painfully realized that the technology needed to address the more recalcitrant environmental contamination problems, such as fuels and chlorinated solvents in groundwater and dense nonaqueous phase liquids (DNAPLs) in the subsurface, was seriously lacking. In 1994, in the "Alternatives for Ground Water Cleanup" document, the National Research Council clearly showed that as a nation we had been conducting a failed 15-year experiment to clean up our nation's groundwater and that the default technology, pump-and-treat, was often ineffective at remediating contaminated aquifers. The answer for the DoD was clear. The DoD needed better technologies to clean up its contaminated sites and better technologies could only arise through a better scientific and engineering understanding of the subsurface and the associated chemical, physical, and biological processes. Two DoD organizations were given responsibility for initiating new research, development, and demonstrations to obtain the technologies needed for cost-effective remediation of facilities across the DoD: the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

SERDP was established by the Defense Authorization Act of 1991 as a partnership of the DoD, the U.S. Department of Energy, and the U.S. Environmental Protection Agency; its mission is "to address environmental matters of concern to the Department of Defense and the Department of Energy through support of basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations." SERDP was created with a vision of bringing the capabilities and assets of the nation to bear on the environmental challenges faced by the DoD. As such, SERDP is the DoD's environmental research and development program. To address the highest-priority issues confronting the Army, Navy, Air Force, and Marine Corps, SERDP focuses on cross-service requirements and pursues high-risk and high-payoff solutions to the DoD's most intractable environmental problems. SERDP's charter permits investment across the broad spectrum of research and development, from basic research through applied research and exploratory development. SERDP invests with a philosophy that all research, whether basic or applied, when focused on the critical technical issues, can impact environmental operations in the near term.

A DoD partner organization, ESTCP, was established in 1995 as the DoD's environmental technology demonstration and validation program. ESTCP's goal is to identify, demonstrate, and transfer technologies that address the DoD's highest-priority environmental requirements. The program promotes innovative, cost-effective environmental technologies through demonstrations at DoD facilities and sites. These technologies provide a large return on investment through improved efficiency, reduced liability, and direct cost savings. The current cost and impact on DoD operations of environmental compliance are significant. Innovative technologies are reducing both the cost of environmental remediation and compliance and the impact of DoD operations on the environment, while enhancing military readiness. ESTCP's strategy is to select laboratory-proven technologies with potential broad DoD application and use DoD facilities as test beds. By supporting rigorous test and evaluation of innovative environmental technologies, ESTCP provides validated cost and performance information. Through these tests, new technologies gain end-user and regulatory acceptance.

In the 18–22 years since SERDP and ESTCP were formed, much progress has been made in the development of innovative and more cost-effective environmental remediation technology. Since then, recalcitrant environmental contamination problems for which little or no effective technology had been available are now tractable. However, we understand that newly developed technologies will not be broadly used in government or industry unless the consulting engineering community has the knowledge and experience needed to design, cost, market, and apply them.

To help accomplish the needed technology transfer, SERDP and ESTCP have facilitated the development of a series of monographs on remediation technology written by leading experts in each subject area. Each volume is designed to provide the background in process design and engineering needed by professionals who have advanced training and 5 or more years of experience. The first volume in this series, *In Situ Bioremediation of Perchlorate in Groundwater*, meets a critical need for state-of-the-technology guidance on perchlorate remediation. The second volume, *In Situ Remediation of Chlorinated Solvent Plumes*, addresses the diverse physical, chemical, and biological technologies currently in use to treat what has become one of the most recalcitrant contamination problems in the developed world. The third volume, *In Situ Chemical Oxidation for Groundwater Remediation*, provides comprehensive, up-to-date descriptions of the principles and practices of *in situ* chemical oxidation for groundwater remediation based on a decade of intensive research, development, and demonstration. The fourth volume, *Delivery and Mixing in the Subsurface: Processes and Design Principles for In Situ Remediation*, describes the principles of chemical delivery and mixing systems and their design and implementation for effective *in situ* remediation. The fifth volume, *Bioaugmentation for Groundwater Remediation*, covers the history, current status, and the exciting future prospects for deliberately adding bacteria and other agents to treat contaminated groundwater.

The purpose of this volume, *Processes, Assessment and Remediation of Contaminated Sediments*, is to help engineers and scientists better understand contaminated sediment sites and identify and design remedial approaches that are more efficient and effective. Contaminated sediment management is a difficult and costly exercise that is rarely addressed with easily identified and implemented remedies. It is hoped that this book can help identify and implement management approaches that provide an optimal, if not entirely satisfactory, solution to sediment contaminant problems.

In order to accomplish our goal, this volume contains a variety of topics needed to understand, assess, and manage contaminated sediment sites:

- An introduction to contaminated sediment management that summarizes the trade-offs between natural attenuation, containment, and active removal (Chapter 1).
- A series of chapters describing key sediment processes that separate sediments from contaminated soil sites and make understanding sediment processes difficult. These include:
    - An introduction to the processes that are uniquely associated with contaminated sediment sites including sediment resuspension, groundwater upwelling, hyporheic exchange, and bioturbation (Chapter 2).
    - A chapter detailing current understanding of sediment erosion and transport and how these processes are modeled (Chapter 3).
    - A chapter describing the physical and biological processes operative at the sediment-water interface (Chapter 4).
- A series of chapters describing sediment risk assessment approaches including:
    - A chapter on how to design risk assessment programs to support risk management decisions (Chapter 5).
    - A chapter on biological effects that usually define the risks that contaminants in sediments represent and the biological assays used to assess those risks (Chapter 6).
    - A chapter on assessing bioavailability via chemical measurements, primarily through the use of porewater concentration measurements (Chapter 7).
- A series of chapters describing sediment risk management, i.e., remedial approaches and their design, including:
    - A chapter on processes describing how to develop and implement risk management efforts (Chapter 8).
    - A chapter on each of the key approaches to managing contaminated sediments: monitored natural recovery (Chapter 9), intrinsic biotransformation and biodegradation (Chapter 10), *in situ* treatment via carbon amendments (Chapter 11), *in situ* containment via capping either with inert material or with active amendments (Chapter 12), and dredging and excavation (Chapter 13).
    - A chapter on the design and implementation of a monitoring program to evaluate remedy performance (Chapter 14).

In addition to the above, the final chapter in the volume (Chapter 15) seeks to identify key uncertainties and resulting research and development needs for the assessment and management of contaminated sediments.

In any single volume covering an area this broad, there are many topics that are not discussed, but it is hoped that the topics that are emphasized represent the state of the practice of contaminated sediment assessment and management and that the most important and commonly needed topics are adequately addressed. It is sincerely hoped that the volume will be useful to the technical practitioner as well as the research scientist and engineer in the field.

SERDP and ESTCP are committed to the development of new and innovative technologies to reduce the cost of remediation of soil, groundwater, and sediment contamination as a result of past operational and industrial practices. We are also firmly committed to the widest dissemination of these technologies to ensure that our investments continue to yield savings for not only the DoD but also the nation. In facilitating this monograph series, we hope to provide the broader remediation community with the most current knowledge and tools available in order to encourage full and effective use of these technologies.

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About the Editor

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Dr. Reible is the Bettie Margaret Smith Chair of Environmental Health Engineering in the Department of Civil, Architectural and Environmental Engineering and the Director of the Center for Research in Water Resources at the University of Texas at Austin. He received his MS and PhD degrees in Chemical Engineering in 1979 and 1982, respectively, from the California Institute of Technology after a BS in Chemical Engineering in 1977 from Lamar University, Beaumont, TX. Prior to joining the University of Texas in 2004, he was the Chevron Endowed Professor of Chemical Engineering at Louisiana State University and the Director of the Hazardous Substance Research Center/South and Southwest.

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CHAPTER 1

INTRODUCTION

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1.1 HISTORY OF SEDIMENT CONTAMINATION

The decades of the 1960s and 1970s reflected an awakening of an environmental consciousness in America and increasing efforts to reduce the uncontrolled or poorly controlled releases into the natural environment that had characterized past human activity. It is perhaps hard to understand today the common belief that the air, soil and water were effectively limitless and therefore appropriate for largely uncontrolled disposal of our wastes. It is also hard to imagine that during the 1940s through the 1960s there were acute air pollution episodes in various cities around the globe that led to the premature deaths of people at a rate that was easily observable. More than 4,000 excess deaths occurred during a "killer smog" episode in London in 1952 due to the combination of normal air emissions and adverse atmospheric conditions. These acute episodes helped galvanize public opinion, leading ultimately to regulations such as the Clean Air Act amendments of 1970. Following passage of these regulations, air quality improvements were rapid in many areas although we continue to work to manage the more difficult air pollution problems.

Similarly, Love Canal in New York helped focus public and regulatory attention on contaminated soil. The identification of severe soil pollution problems associated with past disposal options led directly to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or "Superfund", legislation of 1980. This and other regulatory actions led to a significant focus on soil and groundwater contamination in the decades that followed.

Our experience with water quality was less driven by specific events but by a general recognition of the problems with the surface waters. It is difficult to imagine that until the 1960s many of our cities had minimal waste treatment and the water quality of many of our streams and rivers was very poor. The improvements in waste treatment practices and control of industrial and municipal effluents, for example after the 1972 Clean Water Act, led to dramatic improvements in the quality of our waters.

The resulting reduction in releases of contaminants into surface waters, however, led to recognition of the persistence of many of these same contaminants in the sediments. As the quality of the surface waters improved we began to recognize the legacy of contaminated sediments as the ultimate sink for strongly solid-associated persistent contaminants. Initially, it was hoped that these sediments would recover relatively rapidly with the reductions in releases and attention was focused on the more acutely contaminated soils and groundwaters near sources. Ultimately, for many persistent compounds this was found not to be the case. Thus, while contaminated site activities in the decades of the 1980s and 1990s were focused on soil and groundwater, it was not until this century that many contaminated sediment sites began to receive remedial attention.

There are many reasons for the delay in focusing on contaminated sediments, in addition to belief that they would recovery naturally. The risks posed by sediments are often ecological

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risks with limited connection to human health risks. Contaminated sediments often exhibit incomplete exposure pathways, particularly for human health risks. Contaminants in sediments that remain below the biologically active zone of the near surface (typically 10–15 centimeters [cm] in depth or less), pose little risk to ecological or human health. If the contaminants are sufficiently mobile to migrate into the biologically active zone, or if sediment processes (such as erosion) can expose these buried contaminants, however, they can pose significant risk. Even then, however, the risks posed by the contaminants in sediments are moderated by limited bioavailability under certain conditions. Moreover, exposure pathways leading to human health risks are typically associated with movement into the food chain, often across several trophic levels. This makes it more difficult, for example, to quantitatively link contaminated sediment to a fish to human health pathway. Fish levels of mercury, for example, may sometimes be more directly linked to atmospheric deposition than to a substantial inventory of mercury in sediments. Superfund legislation, in particular, is focused on human health risks and the link to human health must be established and confirmed to trigger the full weight of the regulatory process. Finally, the risks themselves are typically chronic risks that lack the strong incentives to act as with acute risks and effects.

The delay in focusing on sediments was also a reflection of the difficulty of managing those risks. Whereas many contaminated soil sites are relatively small, often 1–10 acres in surface area, contaminated sediment sites may involve tens of miles of a river and millions of cubic yards of sediment. The sediments themselves also contain large amounts of water and removal approaches can dramatically increase the amount of water that must be handled. The large amounts of water add cost, complexity and environmental impacts to the management of the sediments. Contaminants in sediments are also often confined to a relatively small fraction of the sediments, typically the fine-grained, organic rich fraction of solids. The excess water and diluent solids mean that effectively managing contaminated sediments involves dealing with large volumes of effectively inert and marginally contaminated materials.

The contaminants in sediments are typically persistent and strongly solids-associated. They are also often found in low energy, depositional environments in which fine-grained organic rich solids will accumulate. If it were not for the propensity of contaminants to accumulate in more stable environments we would likely observe substantially more rapid recovery in many sediment systems. Instead, we find persistent contamination often 50–100 years after the introduction of contaminants into an aquatic system.

It is in responding to the legacy of accumulating contaminants in relatively stable sedimentary environments that this volume is dedicated. This volume will introduce many of the somewhat unique processes that influence the fate and behavior of sediment contaminants, including sediment erosion and resuspension, groundwater upwelling, hyporheic exchange and bioturbation (Chapters 2, 3, and 4). Chapters 5, 6, and 7 will describe how risks in sediments can be assessed, focusing specifically on biological assays (Chapter 6) and the assessment of bioavailability using chemical measurements (Chapter 7). The remainder of the volume is focused on management of contaminated sediments, starting with a chapter on management principles (Chapter 8) before turning to the management technologies. The management technologies discussed include four chapters on *in situ* management approaches (Chapters 9, 10, 11, and 12), a chapter on dredging and removal (Chapter 13) and finally a chapter on monitoring remedial actions (Chapter 14). The *in situ* management chapters include a chapter on monitored natural recovery (Chapter 9), a chapter on biological processes and bioremediation (Chapter 10), a chapter on *in situ* physical-chemical treatment with sorbents (Chapter 11), and a chapter on *in situ* capping (Chapter 12). The final chapter (Chapter 15) on research needs draws on the previous ones and attempts to identify technical challenges and opportunities for advancing the practice of management of contaminants in sediments; however, not all potential areas of importance are given comprehensive coverage because of a lack of space or limited applicability to most contaminated sediment sites.

In this introductory chapter, the general features of contaminated sediment management are discussed and illustrated before turning to the details of the processes and technologies involved.

1.2 FRAMEWORK FOR MANAGING CONTAMINATED SEDIMENTS

The assessment and management of contaminated sediments is inherently more complex than managing many small, relatively simple contaminated soil and groundwater sites. Because of the multiple uses and demands placed upon surface waters, it is often difficult to identify the primary goals and objectives of a risk management effort for contaminated sediments. In the Superfund context, the primary goal most likely would be elimination of the risks to human health and the environment. However, a National Research Council (NRC) study (NRC, 2001) recognized that contaminated sediment management efforts could involve societal, cultural, and economic impacts commensurate with human health and ecological risks. Hence, the goals of effective contaminated sediment management are generally broad and complex, frequently conflicting, and often controversial. Identifying these goals and resolving potential conflicts between them may be difficult but will ultimately achieve contaminated sediment management efforts that are considered more successful by a broader spectrum of stakeholders.

Bridges et al. (2011) also recognized the importance of developing a central accepted vision for a remedial effort, using that vision to define objectives as well as achievable short- and long-term goals, and to engage stakeholders in a meaningful way.

The achievement of appropriate remedy goals is illustrated in Figure 1.1.

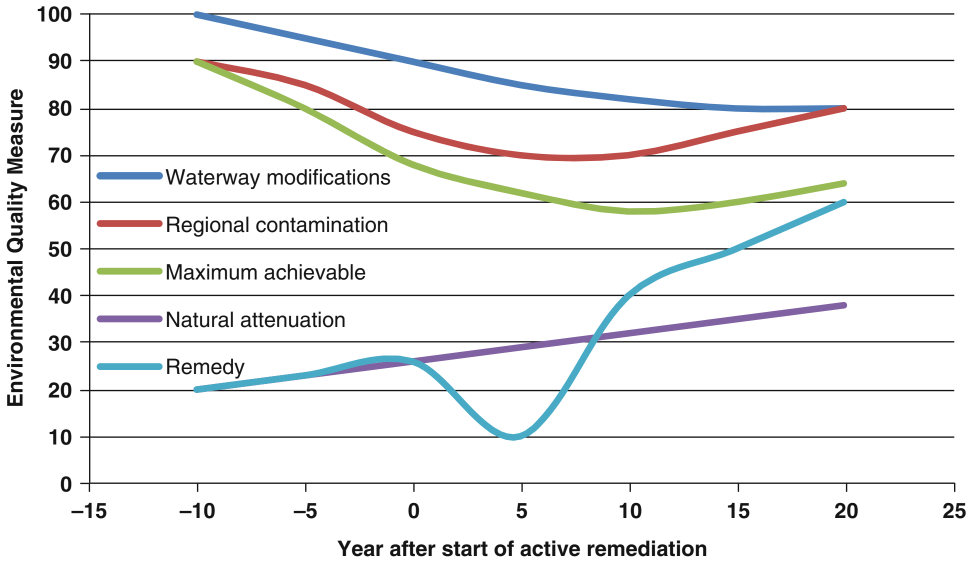

Figure 1.1. Conceptual depiction of environmental quality achievable with a remedy. The *dark blue*, *red* and *green lines* illustrate the effect of non-site related (e.g., watershed) effects on environmental quality at a site while the *purple* and *light blue line* illustrate the effects of recovery or remediation at a site.

Figure 1.1 illustrates that the goals of managing contaminated sediments must take into account the broader watershed issues in which it is placed. Waterway modifications (e.g., channelization) may reduce achievable environmental quality and the achievable goals may change over time. Moreover, other contamination issues in the watershed may have an impact on the recovery or remediation of a site and this may also reduce the achievable environmental quality. Presumably the negative consequences of these other sources may moderate over time as the contributing locations are subject to remediation or control. This is illustrated in Figure 1.1 by the improvement in environmental quality due to a reduction in regional contamination over time. The combined effect of both of these becomes the maximum achievable quality for any isolated efforts at the site of concern.

Remedial efforts then strive to achieve as much of that maximum achievable quality as possible. The final two curves represent the improvement in quality expected from natural attenuation and that actually achieved by an active remedy (e.g., dredging). Natural attenuation may require an excessively long period of time to achieve remedy goals or to approach the maximum achievable quality curve. An active remedy, however, may cause impairment during implementation (e.g., due to resuspension during dredging) and that is shown as the dip in the site quality along the active remediation curve. This initial degradation in quality associated with implementation of the remedy is then hopefully offset by improvements in quality over natural attenuation at longer times, also as shown in the curve. The maximum attainable quality, however, remains that set by the impairments associated with planned modifications and other watershed or regional sources of impairment. The goal of any active remedy is to maximize the improvements over natural attenuation and achieving environmental goals that are as close as possible to the maximum achievable quality, balancing cost and other negative consequences of the remedy.

A framework in which to effectively accomplish effective management of contaminated sediment sites is the Framework for Environmental Health Risk Management (Figure 1.2) of the Presidential/Congressional Commission on Risk Assessment and Risk Management (1997), which was embraced by the NRC (2001).

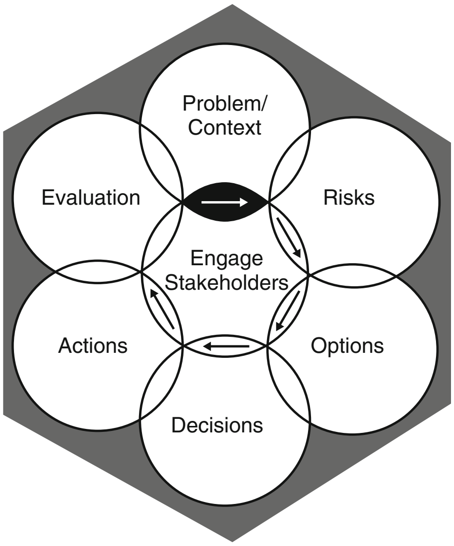

Figure 1.2. Framework for environmental health risk management (President's/Congressional Commission on Risk Assessment and Risk Management, 1997).

This framework provides a systematic approach to risk management and includes the following stages:

- Involving the affected parties early and actively in the process,
- Defining the problem,
- Setting risk management goals,
- Assessing risks,
- Evaluating remediation options,
- Selecting a risk management strategy,
- Implementing the risk management strategy, and
- Evaluating the success of the risk management strategy.

The major advantages of this risk management framework are: (1) it can be applied to any contaminated sediments site that may have both new or ongoing remediation; (2) it is iterative, allowing any stage in the framework to be revisited as new information about the site, its environs, remediation technologies, environmental dynamics, or health effects of contaminants becomes available; (3) it can be used to address risks ranging from human health to societal and economic impacts at a site; and (4) it involves all affected parties in all stages of the management process. The framework also emphasizes evaluating the success of a risk management strategy as integral to the risk management process. Evaluating success was lacking in many early remedies. As noted by the NRC (2007), monitoring has not always been done in a manner to appropriately evaluate success and identify the components of a remedy that most contribute to that success.

The framework is not unique but is a commonly accepted framework that has the features needed to successfully manage risk at complicated contaminated sediment sites. When coupled with the features identified by Bridges et al. (2011) to accelerate remedies, the framework could be a useful organizing tool. The features identified by Bridges et al. (2011) include:

- Develop a detailed and explicit project vision and accompanying objectives, achievable short-term and long-term goals, and metrics of remedy success, beginning at the start of a project and continuing throughout the project,
- Strategically engage stakeholders in a more direct and meaningful process,
- Optimize risk reduction, risk management processes, and remedy selection,
- Incentivize progress toward risk reduction, and
- Pursue remedial projects as a collaborative enterprise.

Together, the risk management framework proposed by the Presidential/Congressional Commission on Risk Assessment and Risk Management and the tools to accelerate remedies proposed by Bridges et al. (2011) represent a useful foundation for assessing and managing contaminated sediments. Regardless of the manner in which remedial goals are developed and a remedial program implemented, however, aiding progress toward those goals is the objective of the technical information presented in this volume.

1.3 PROCESSES AND RISKS OF CONTAMINATED SEDIMENTS

As indicated previously, much of the contamination of concern in sediments is associated with the past legacy of contaminants released to the lakes and waterways or onto soil that subsequently washes into the surface waters and settles on the bottom. The extent to which these deposited sediment contaminants pose a risk is a function of both the contaminants and the processes that control their behavior.

The specific contaminants of primary concern include hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). More soluble and less sorbing organic contaminants are typically not sediment contaminants due to their higher mobility and tendency to rapidly leach or degrade in the sediment environment. There are exceptions to this general rule, particularly when the sediment contamination is the result of migration of an upland groundwater plume. But just as the contaminated sediments of concern are often those found in net depositional, relatively stable environments, the contaminants of concern are typically persistent contaminants. The high molecular weight compounds such as PCBs and PAHs exhibit very low mobility and little degradation under natural conditions and are thus likely to accumulate in these environments. Substantial levels of PCBs are found for example at many contaminated sediment sites even 40 years after their use was banned in the United States. Other common sediment contaminants include metals that do not degrade although they may be found in chemical forms that are largely unavailable as a source of exposure and risk.

Although the contaminants of concern are typically found strongly associated with the solid phase, the dynamics of some environments will lead to release of the contaminants to the water column. This may be caused by resuspension events, site processes that can transport and transform the typically small levels contaminants in porewater, or management efforts that disturb the sediments. Erosion into a contaminated sediment layer can clearly lead to resuspension of sediments, as will be discussed in Chapter 3. Resuspension can dramatically change the sediment redox environment, influencing redox sensitive contaminants, or lead to direct release of contaminants due to partitioning into the water column. Unavailable forms of metals may sometimes be transformed by exposure to oxic overlying waters to more available and mobile forms of the metal. Rapid groundwater upwelling or bioturbation, the normal life cycle activities of organisms at the sediment-water interface, may also cause a significant flux of contamination to the surface and into the overlying waters. Even within a stable sediment environment, however, partitioning or chemical release into the porewaters can lead to contaminant release into the overlying water as a result of groundwater upwelling and hyporheic exchange as well as bioturbation, the normal mixing and transport activities of benthic organisms that live at the sediment-water interface. These mechanisms are largely unique to sediments and difficult to assess and quantify due to their complexity, site specificity and spatial variability within a site. They are, however, critical to assessing the exposure and risks of those sediments. In a sediment environment not subject to significant resuspension and erosion, bioturbation is likely the single most important transport mechanism for strongly solid-associated contaminants in the surficial sediments (Reible, 2008).

The emphasis in sediment risk assessment is often on ecological risk, particularly to the benthic community. This community is in direct contact with the sediments and includes organisms, particularly deposit feeders, that rapidly and efficiently process sediments. This rapid processing of sediments often results in a form of quasi-steady conditions between the benthic community and the underlying sediment and those conditions largely define the rate and potential effects in higher organisms that interact and feed on the benthic community.

Focusing on the benthic community also has the advantage of relatively easy measurement and cost-effective sediment assessment. By focusing on the biological organisms, the discussion recognizes that biological response is paramount in evaluating sediment quality. That is, if properly conducted biological assessments disagree with conclusions reached by physical and chemical measurements, it is often assumed that the biological assessments are likely to provide the better indicator of sediment quality. Sediment quality assessment is inherently a weight of evidence endeavor because of a variety of biological responses and effects, but ultimately risk is defined by the biology and not the physical and chemical measures we use to aid in our assessment of those responses. For example, the porewater assessments discussed in Chapter 7 are useful only to the extent that they mirror biological response. This should always be kept in mind, particularly when using chemical measures that are less well correlated with biological response, such as bulk solid concentrations (Long et al., 1995). Any physico-chemical measure of biological response is effectively a model of that response and inherently incomplete and approximate indicators of the actual response of concern. As is often said of models, "All models are wrong . . . but some are useful" (Box and Draper, 1987). Physico-chemical measures of biological response should be viewed from that perspective.

1.4 MANAGING RISKS OF CONTAMINATED SEDIMENTS

Our ability to respond to the risks that we identify through an assessment process remains remarkably limited. Due to the large size (both area and volume) of contaminated sediment sites and the challenges of large volumes of diluent water and solids, expensive, high technology solutions are not forthcoming. Our basic options remain that of monitored natural recovery, *in situ* management through capping or sequestering amendments (e.g., activated carbon or organophilic clays) and removal followed by disposal in a landfill. It could be said that all contaminated sediment management is through containment, containment by nature through deposition of clean sediment and burial of persistent, low mobility contaminants, containment by capping or sequestering amendments, or containment in a landfill after removal by dredging or excavation. Alternatives to landfill disposal of dredged material have been developed but there is little incentive to employ them due to their cost and complexity. *In situ* degradation may be an alternative to *in situ* containment by capping or sequestering amendments (Chapter 10) but due to the persistent nature of most sediment contaminants, they are not likely to be generally applicable.

The general characteristics of the three basic sediment management options of monitored natural recovery, capping or *in situ* treatment, and dredging are shown in Figure 1.3.

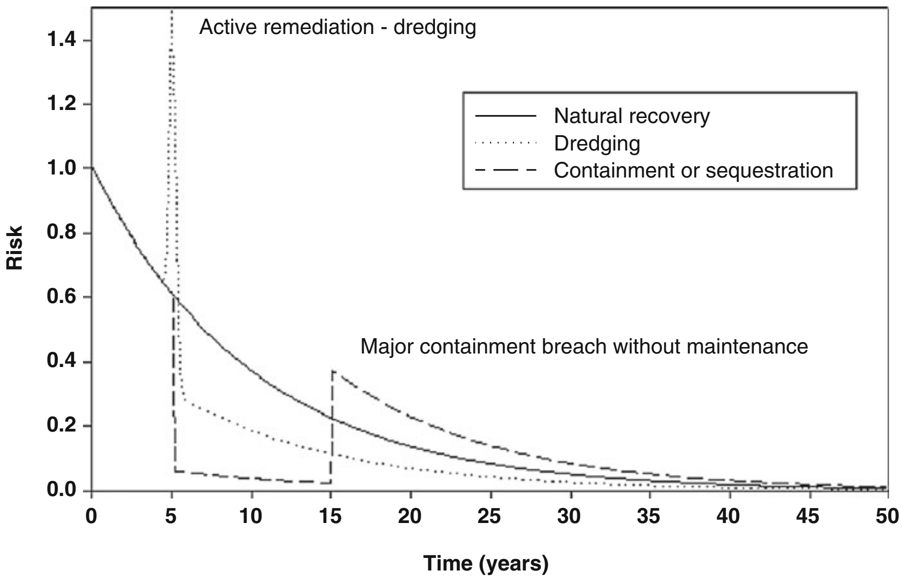

Figure 1.3. Characteristic responses of three primary sediment remedial approaches.

As shown in the Figure 1.3, natural attenuation during monitored natural recovery represents a baseline against which alternative remedial approaches can be compared. In containment or sequestration options, the contaminant is not destroyed or removed from the system but it is isolated through the addition of an amendment or cap (or an amended cap). As is typically the case, very rapid risk reduction can often be achieved by this approach. Capping, for example, can be implemented rapidly and provide near immediate elimination of key exposure pathways. This can result in rapid reduction in risk. Since the contaminants are not destroyed or removed, however, there remains the possibility that a containment breach could occur sometime in the future and increase risk or that long-term containment is not feasible due to active transport processes (e.g., rapid groundwater upwelling). In a cap, in the absence of transport processes such as rapid upwelling that will compromise a cap, the increase in exposure (and subsequently risk) is typically proportional to the area of a cap lost through contaminant penetration or the erosion of a cap. For a sequestering amendment in the sediment, the loss in containment would be proportional to the loss of sequestering amendment and re-exposure of the underlying contaminated sediment. The potential effects of either loss can be assessed by a realistic evaluation of the likelihood and extent of any potential containment loss.

In dredging or other removal options, the reduction in exposure and risk is not immediate due to the resuspension of dredged material during the process of dredging and the exposure of residual contamination after dredging. Increasingly, the exposure of residuals is managed by placement of backfill, effectively a thin layer cap to reduce exposure to the residual contamination. Resuspension losses remain important, however, and a NRC report (NRC, 2007) documents a number of examples to illustrate the significance of this phenomenon. The NRC reports typical resuspension losses of the order of 1% of the sediment dredged and residual sediments exposed at the surface on the order of 5% of the sediment dredged. These estimates are based upon sediment measurements but it is generally assumed that the contaminant losses parallel the sediment losses. This is likely a reasonable assumption for highly hydrophobic compounds but is likely a large underestimate of contaminant losses for less sorbing contaminants and contaminants associated with nonaqueous phase liquids (NAPLs). The assumption of 1% and 5% for resuspension and residual losses or exposures, respectively, may seem to be relatively modest amounts but it should be remembered that the sediment and contaminants released are much more accessible and potentially bioavailable than contaminants left untouched in the sediments. This is particularly of concern for sediment contaminants that were originally buried deep below the sediment surface in that exposing those sediments could dramatically increase exposure and risk to the contaminants. Sediments resuspended or exposed at the surface may also oxidize and release metals that would be largely unavailable if left in reduced form in the underlying sediments (Hong et al., 2011). Contaminants buried below the biologically active zone may pose effectively negligible risk (at least in their buried state) to organisms at the sediment-water interface or higher organisms, but if left as a residual after dredging, organisms will be directly exposed to contaminants within the biologically active zone. Deeply buried (i.e., below the biologically active zone) PCBs in a non-erosive environment, for example, are unlikely to migrate into the biologically active zone but dredging will give rise to exposure at the surface, albeit with a substantial reduction in total mass of contaminants.

The recovery curves depicted in Figure 1.3 are not easy to evaluate and are typically subject to substantial uncertainty. This may blur the relationships among the various alternatives and severely limit the ability to identify an optimum remedy based upon speed and extent of recovery. Again, the challenge of this volume is to aid in the management process and ensure that the development of recovery curves, whether quantitative or conceptual, is based upon the best information available.

1.5 EXAMPLE: COMPARISON OF REMEDIAL ALTERNATIVES

In order to illustrate the relationships shown in Figure 1.3, natural attenuation, dredging and capping were compared in a specific example (text box below). The intent of this example is not to represent the behavior of the remedy approaches at all sites but to indicate how one might construct such a curve and illustrate the characteristics of a site that influence the recovery curves. The assumptions and environmental setting for the example are shown below.

Comparison of Remedial Alternatives

This example compares remedies for a hypothetical sediment site containing a 2 foot (ft) (0.6 meters [m]) layer of sediment containing 100 milligrams per kilogram (mg/kg) of a hydrophobic organic contaminant with properties equivalent to that of benzo[a]pyrene (log Kow = 6.04). The sediment contains 1% organic carbon and partitioning is assumed linear and reversible with the sediment-water partition coefficient, Ksw, given by the product of the organic carbon based partition coefficient and the fraction organic carbon, $K_{oc}f_{oc}$, where $\log K_{oc} = (0.903)(\log Kow) + 0.094$ (Baker et al., 1997) and log Kow is the octanol-water partition coefficient. Bioturbation is assumed to mix the upper 10 cm of sediment in all remedies and lead to a slow recovery of the surface layer due to contaminant release at the sediment surface. The conditions for each of the remedies were as follows:

- ***Natural Attenuation***
  - Bioturbation in upper 10 cm of sediment with an effective particle reworking coefficient of 1 centimeter per year (cm/yr) (Reible et al., 1996).
  - No sediment erosion or mixing between biologically active zone and deeper sediment layers.
- ***Dredging***
  - Five year dredging activity focused on upper 2 ft of sediment with 20% of the sediment surface dredged each year.
  - One percent resuspension and loss during dredging.
  - A residual of 5% of 2 ft layer redistributed over upper 10 cm biologically active layer at conclusion of dredging (either due to intermixing of residual layer with clean underlying sediment by bioturbation or intermixing of the residuals with a backfill layer containing surficial average of 1% organic carbon).
- ***Capping***
  - Five year capping activity with a 1 ft layer of sand with sorption equivalent to a sediment with 0.01% organic carbon (Ksw ~35 liters per kilogram [L/kg]).
  - The concentration at the surface of the sand at the conclusion of capping is assumed to be 5% of the underlying sediment concentration as a result of sediment resuspension during capping.
  - The cap is assumed to be governed by diffusional processes in the layer between the upper 10 cm (bioturbation layer) and the underlying sediment. The 1 ft layer of sand with 10 cm in a bioturbation layer results in an effective chemical isolation layer in the cap of approximately 20 cm or 8 inches (in).

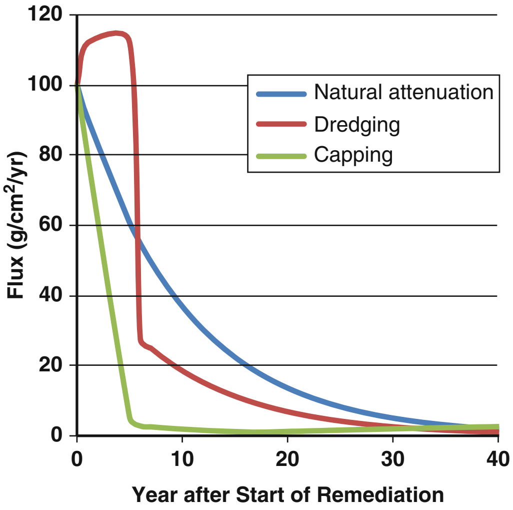

Figure 1.4. Comparison of flux into surface water by each remedy in the hypothetical example.

The comparison of the various remedial alternatives is shown in Figure 1.4. The comparison is on the basis of flux to the overlying water in grams per square centimeter per year (g/cm^2/yr). Natural attenuation results in a continuous reduction in concentration as a result of bioturbation induced mixing and release at the sediment-water interface. As a result, the flux decreases exponentially with a characteristic time (1/e time) of 10 years (characteristic time of release assuming any contaminant brought to the surface is released to the overlying water is h_{bio}/k_{bio}, where h_{bio} is the thickness of the biologically active layer, 10 cm, and k_{bio} is the effective particle reworking coefficient in the biologically active layer, 1 cm/yr).

For dredging, there is a modest increase in flux (12% greater than original flux) during the period of dredging. While this is a modest increase in flux, it offsets the rate of natural attenuation and thus there is a significant "cost" of dredging in terms of average flux to the overlying water. At the end of the period of dredging, the surface layer is assumed to be given by the dredge residuals (equivalent of approximately 3 cm of sediment) mixed throughout the 10 cm bioturbation layer. Intermixing of the dredge residual throughout the bioturbation layer would normally require a period of years but for purposes of this calculation, it is assumed to be immediately after the conclusion of dredging. Due to the low concentration of dredge residuals in the intermixed layer (approximately 30% of the initial sediment concentration) flux from the post-dredging surface is assumed to be reduced dramatically over the pre-dredging conditions. The sediment then continues to recover by natural attenuation due to bioturbation.

For capping, there is a rapid linear decrease in flux as a greater proportion of the site is capped. The surface of the cap is assumed to contain contaminants at an average concentration of 5% of the underlying sediment as a result of sediment resuspension and intermixing during cap placement. At the end of the assumed 5 year capping period (normally this could be accomplished more rapidly than dredging), this contamination defines the post-capping flux. This contamination is then subject to natural attenuation by bioturbation-related mixing and natural attenuation of the upper 10 cm of the cap layer. The biological community is assumed to immediately repopulate the surface layer of the cap at the conclusion of capping. Similar to the time required for mixing a dredge residual through the biologically active zone, the development of a bioturbation layer in the surficial cap sediments would require 1 or more years, but this is neglected in this example. Normally there would need to be deposition of fresh organic material and then development of a robust population of benthic organisms.

In the capping scenario, there is also the potential of migration through the cap layer leading to recontamination of the surface layer (here assumed to be at the rate of diffusion through the thin cap). The time until the flux at the surface of the cap is 5% of the flux into the cap layer from the underlying sediment is approximately 13 years given the sorption characteristics of the sand layer, using the approach of Palermo et al. (1998) and based upon the relatively weak sorption (and thus low sorption related retardation) of the contaminant in this scenario. After approximately 32 years, the flux from the sediment cap is approximately equal to that of the surface undergoing natural attenuation after dredging. The flux under the cap scenario will continue to increase slightly after this time and continue to exceed that of the natural attenuation after dredging scenario since it is assumed (unrealistically) the sediment underlying the cap maintains a constant concentration. The maximum flux in the cap scenario is, however, less that 4% of the maximum during dredging.

A more realistic capping scenario would be to recognize that the flux through the cap would also decrease due to depletion of the concentration in the underlying sediment (due to contaminant flux even if no degradation mechanisms are operative). This would be true even for a large inventory of contaminants in the underlying sediment since the migration rate of the contaminant through the relatively nonsorbing cap is relatively fast compared to that in the underlying sediment. This reduction over time is not considered in this example.

While the specific shape of the curves in Figure 1.4 will vary depending upon conditions at a particular site, it is worthwhile to note that the curves agree qualitatively with those in Figure 1.3. That is, both figures capture the general characteristics of the three remedy types. The relative performance may vary at any individual site due to problems such a breach of cap containment that was not appropriately designed, especially high (or low) rates of resuspension or residuals due to dredging, or more rapid or slower natural attenuation.

1.6 SUMMARY

The purpose of this volume on contaminated sediments is to help remedial managers and their technical support teams better understand contaminated sediment sites and identify and design remedial approaches that are more efficient and effective. Contaminated sediment management is rarely a win-win proposition and is instead a delicate balancing act among a variety of management options that are incomplete, marginally effective and costly. It is hoped that this treatise can help identify and implement management approaches that provide a workable, if not entirely satisfactory, solution to sediment contamination problems. In any single volume covering an area this broad, there are many topics that are not discussed but it is hoped that the topics that are emphasized represent the state of the practice of contaminated sediment assessment and management, and that the volume will be useful to the technical practitioner as well as the research scientist and engineer in the field.

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CHAPTER 2

SEDIMENT AND CONTAMINANT PROCESSES

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2.1 INTRODUCTION

Contaminated sediments exhibit many features and challenges that differentiate its assessment and remediation from that of contaminated soil. Both soils and sediments tend to accumulate the hydrophobic organic and inorganic constituents that give rise to environmental contamination and risk. Sediments, however, are often found in dynamic environments that can lead to substantial contaminant migration. In general, contaminated sediment sites are a legacy of past contaminant discharge practices and the contaminants have accumulated in environments that are most conducive to such accumulation. Thus, a preponderance of contaminated sediment sites are in fine-grained, often organic-rich, sediments that are more likely to absorb hydrophobic contaminants and in environments where such sediments tend to accumulate, i.e., low energy depositional environments. Contaminated soils, however, often represent the source areas themselves and may exhibit a broader range of environmental and media properties. In addition, many of the processes that influence contaminant migration and fate in sediments (erosion, bioturbation, hyporheic exchange) are less pronounced or nonexistent at contaminated soil sites. Even when soils and sediments exhibit similar properties, there may be significant differences due to sediment characteristics. For example, the erosion characteristics of sediments are often controlled by the cohesive nature of fine-grained sediment deposits compared to the minimal cohesion of dry, wind-blown soils. Moreover, sediments are often confined by one or more spatial dimensions, for example the containment of river sediments to the banks of a river and the adjacent floodplain, limiting the dilution often associated with migration. Thus, contaminated sediment sites may exhibit elevated concentrations and potential risks over large areas or distances compared to many contaminated soil sites. Contaminated sediment sites, by definition, are also associated with large amounts of water, which both complicates their assessment and management but also enhances the potential exposure and risk, for example to aquatic animals and organisms that depend upon them for food.

This chapter will lay the foundation for the subsequent chapters by examining the unique characteristics of sediments and sediment environments. This chapter will start with a short discussion of sediment and contaminant characteristics and then turn to sediment processes that influence contaminant fate and behavior. Among the transport processes that influence sediment and contaminants are:

- Erosion and deposition,
- Porewater diffusion and advection processes,
- Bioturbation, and
- Hyporheic exchange.

These and related sediment processes are shown in Figure 2.1. Each of these processes will be discussed in turn.

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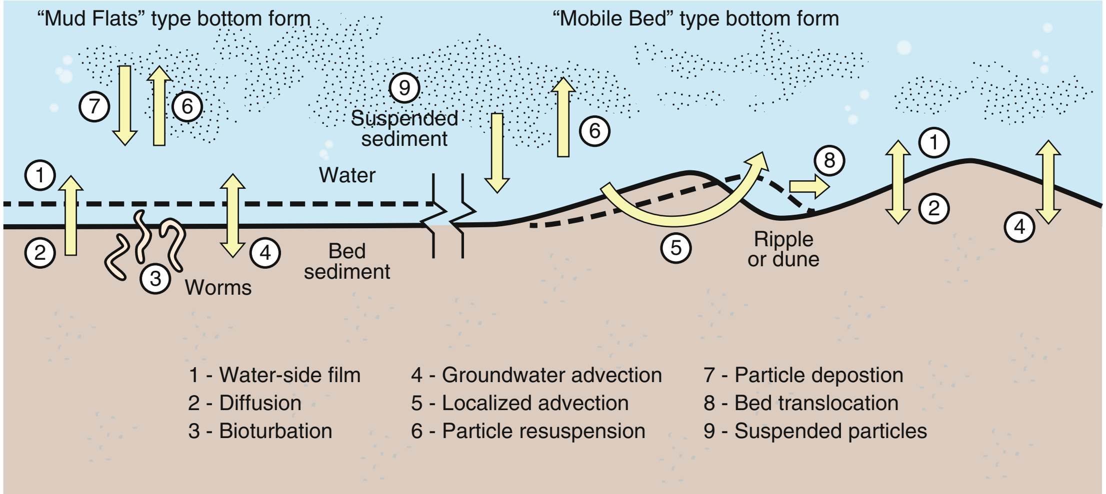

Figure 2.1. Sediment contaminant fate and transport processes (adapted from Reible, 2008).

2.2 SEDIMENT AND CONTAMINANT CHARACTERISTICS

2.2.1 Sediment Characteristics

Many sediments simply represent the accumulation of soil that has eroded from the terrestrial surface. As a result of their accumulation in the subaqueous environment, however, the sediment environment develops much differently than the terrestrial environment.

Eroded soils that run off into bodies of water are first subjected to a grading process associated with the energy environment. Solids suspended in the water environment may contain significant quantities of sand (particle diameters >60 micrometers [μm]), silt (2–60 μm) and clays (<2 μm), but sediments will accumulate these fractions at different rates due to their different settling characteristics. Much fine-grained material may remain suspended in a high energy environment but may settle and accumulate in a low energy environment. A low energy environment may be one that exhibits continuous low flow or one that is only temporarily low energy until the next high flow event in more dynamic systems. Fine-grained deposits are also typically enriched in organic matter. As will be discussed in Section 2.2.2, many contaminants of concern are hydrophobic organics and inorganics that will preferentially associate with these fine-grained sediments and with the organic matter. Thus, many of the most seriously contaminated sediment sites are in low flow, depositional environments that accumulate these fine-grained sediments. Less contamination is typically associated with more dynamic environments in which the sediments are dominated by coarser, faster settling sands.

A fine-grained depositional sediment dominated by silts and clays tends to be strongly cohesive, which may limit its tendency to erode under higher flow conditions. A fine-grained depositional environment will also typically be enriched in organic matter relative to terrestrial soils. Surficial terrestrial soils often contain 0.1–1% organic carbon while fine-grained sediment deposits may contain 1–5% or more organic carbon. Surficial sediments in vegetated marshlands may be considerably higher than this range with 10–20% organic carbon not being uncommon. The combination of low permeability (and therefore low exchange with the overlying water) and high organic carbon means that diagenetic processes have a strong influence on the surficial sediment characteristics. Early diagenetic processes lead to the formation of humic and fulvic acids from the degradation of natural organic matter. These are soluble and lead to substantial quantities of dissolved and colloidal organic carbon (10–50 milligrams per liter [mg/L]) in the pore space of the sediments.

Diagenetic processes consume a variety of electron acceptors, which dramatically influence the redox environment of the surficial sediments. Oxygen is typically rapidly consumed by microbial processes and then less desirable electron acceptors are consumed in turn, leading to strongly reduced sediment environments just a few centimeters below the sediment-water interface. The order of electron acceptor consumption is generally:

$$O_2 > NO_3 > Mn > Fe > SO_4 > CO_2$$

The cumulative effect of oxygen consumption reactions is measured by sediment oxygen demand, a parameter similar in significance to oxygen demand in the overlying water. Sediment oxygen demand serves to reduce available oxygen and encourage anaerobic conditions within the sediment. This may affect the rate of fate processes, such as biological degradation of contaminants in the sediments and the chemical state of metals influencing mobility. The sediment oxygen demand can also impact oxygen levels in the overlying water.

The more reduced conditions associated with the elimination of oxygen and the initiation of iron and sulfate reduction typically slows microbial degradation processes and effectively eliminates degradation of hydrocarbons, which generally proceed rapidly under oxidizing conditions. Iron reduction and sulfate reduction has also been associated with the simultaneous methylation of mercury (Hg) (Compeau and Bartha, 1985; Warner et al., 2003) and carbon dioxide reduction leads to methane formation and gas ebullition. The methane then migrates toward the surface affecting sediment void fraction, strength and, through oxidation of the methane, the oxygen demand of the sediments (Chapra, 1999). Boudreau et al. (2005) describes the growth and migration of gas as a result of methanogenesis. In addition, the reduced nature of fine-grained sediments within a few centimeters of the surface typically limits the vertical extent of macrobenthic activity. The organisms that live at the sediment-water interface are largely limited to the aerobic sediments, although they might extend a portion of their bodies deeper into the sediments or encourage deeper penetration of oxic conditions through burrowing and sediment reworking activities (Reible et al., 1996).

2.2.2 Contaminant Characteristics

Sediment contaminants generally include any constituent that can accumulate in the sediments. Sediments may harbor a significant inventory of the nutrients (nitrogen and phosphorus), release of which may dramatically change the biological characteristics of the overlying water. The impact of these contaminants depends upon the dynamics of the sediment, associated groundwaters and overlying water column. Sediment contaminants are typically strongly hydrophobic and strongly associated with sediment solids. More mobile and soluble contaminants rarely accumulate in sediments. Among the hydrophobic and/or strongly solid associated contaminants of interest are polycyclic aromatic hydrocarbons (PAHs such as pyrene or benzo[a]pyrene), chlorinated aromatics (such as multiple chlorinated benzenes), polychlorinated biphenyls (PCBs), and heavy metals (such as cadmium [Cd], zinc [Zn], nickel [Ni], lead [Pb], copper [Cu] and Hg).

The dominant characteristic of contaminant-solid interactions is physical absorption, characterized by a sediment-water partition coefficient, K_d. The sediment-water partition coefficient is defined by:

$$K_d = \frac{W_s}{C} \tag{Eq. 2.1}$$

where W_s is the solid phase concentration and C is the adjacent water phase concentration. Hydrophobic organic contaminants predominantly sorb into the organic carbon fraction of sediments and thus the sediment-water partition coefficient is often defined as:

$$K_d = K_{oc}f_{oc} \tag{Eq. 2.2}$$

where K_{oc} is the organic carbon-based partition coefficient, a measure of the hydrophobicity of the compound, and f_{oc} is the fraction organic carbon, a single indicator of the sorption capacity of the sediment for hydrophobic organic compounds. This relationship is a good approximation for the sorption of organic contaminants when sorption is dominated by natural organic matter. Natural organic matter is dominated by amorphous carbon, also referred to as soft organic matter. In such cases, the organic carbon-based partition coefficient is related to a measure of the hydrophobicity of the compound. The organic carbon-based partition coefficient is commonly correlated with the octanol-water partition coefficient of the compounds. For example (Baker et al., 1997),

$$LogK_{oc} = 0.903LogK_{ow} + 0.094 \tag{Eq. 2.3}$$

Common PAHs exhibit octanol-water partition coefficients ($LogK_{ow}$) between 3.37 (naphthalene) and 6 or more (e.g., benzo[a]pyrene). Pyrene has a $LogK_{ow}$ of 5.18 and therefore Equation 2.3 suggests a $LogK_{oc}$ of 4.77.

Not all of the organic carbon present in sediments is amorphous. Crystalline "black" carbon, also known as hard carbon, is significantly more sorbing than soft carbon (Ghosh et al., 2003). Accardi-Dey and Gschwend (2002) correlated the sorption into both soft and hard carbon by:

$$K_{sw} = K_{oc}f_{oc} + K_{bc}f_{bc}C^{n-1} \tag{Eq. 2.4}$$

Accardi-Dey and Gschwend estimated K_{bc} for pyrene based upon Boston Harbor sediments to be $10^{6.25\pm0.14}$ (i.e., $LogK_{bc} = 6.25$ or approximately 1.5 more than $LogK_{oc}$) and $n = 0.62 \pm 0.12$. Ghosh et al. (2003) showed a similar increase in sorption onto black carbon in sediments over K_{oc}. The measurement of the fraction black carbon is usually estimated by the fraction of carbon left after combustion of the sediment at the relatively low temperature of 375 degrees Celsius (°C) for 24 hours (Gustaffson et al., 1997).

Metals do not absorb into the organic fraction of the sediment phase. Instead, metals interact with sediments in a much more complicated manner. Metals can absorb directly onto sediment mineral surfaces, specific species can precipitate onto the solids, and metal cations can be electrostatically attracted to charged sediment surfaces (which are typically negatively charged). These metals can be released by cation exchange with other cations or by acidification of the sediment, which will offset the net negative charge at the surface. Metal sorption can be described as an irreversibly sorbed fraction (the metal precipitates), coupled with a reversibly sorbed fraction (the exchangeable and adsorbed portion). The most important of the metal precipitates are metal sulfides that are effectively insoluble and form under strongly reducing conditions. Under the reducing conditions in most sediments, that is a few centimeters below the surface and below, these metal sulfides are quite stable. At the surface, however, oxic conditions can lead to sulfide oxidation and release of the metal ions (Hong et al., 2011a).

Under static conditions, only the exchangeable and adsorbed portion can partition between the sediments and adjacent porewater. This is generally modeled with an effective partition coefficient, K_{sw}, but this is not easily modeled and changes in pH and oxygen conditions can affect the partition coefficient (Hong et al., 2011b).

2.3 SEDIMENT AND CONTAMINANT TRANSPORT PROCESSES

2.3.1 Sediment Erosion and Deposition

Due to the strong sediment association of most contaminants of interest, any migration of the sediment through erosion and resuspension will have a significant impact on contaminant transport. Bioturbation, the sediment processing activities of benthic organisms, can also cause sediment migration but that is discussed separately in Section 2.3.3.

Under high-energy conditions in a stream, significant sediment transport occurs and individual sediment particles can be carried downstream either by bed load or suspended load transport. The process normally results in the formation of dunes, ripples and anti-dunes 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, contaminants sorbed to the sediment particles can desorb, and contaminants in the adjacent porewater can be released into the overlying water.

Should significant erosion and resuspension occur, the water column concentration tends to approach the equilibrium defined by desorbable contaminants in the resuspended sediment. The contaminant concentration in the overlying water, assuming local equilibrium, is given by:

$$C = \frac{\rho_{ss} W_s}{1 + \rho_{ss} K_{sw}} \tag{Eq. 2.5}$$

Here, ρ_{ss} is the suspended sediment density (or concentration), W_s is the concentration of contaminant on the solids and K_{sw} is the effective partition coefficient between sediment and water. At high suspended concentrations, the overlying water approaches equilibrium with the contaminated sediment bed while at low suspended solids density, the overlying water concentration is directly proportional to the suspended solids density, ρ_{ss}.

As shown by Equation 2.5, the concentration and exposure in the overlying water is a function of the concentration of sediment resuspended. The concentration of resuspended sediment is a function of the rate and depth of erosion. The ability to predict the rate of erosion based solely upon physical characteristics of the sediment such as grain size and density remains largely limited to cohesionless, coarse-grained particles. Site-specific measurements of sediment response to shear flows are needed to characterize erosion of cohesive, fine-grained sediment. Erosion of both cohesive and non-cohesive sediments is discussed in detail in Chapter 3.

2.3.2 Porewater Diffusion and Advection

In a stable sediment bed, the transport processes within the mobile phase in the pore space of the sediments become important. In particular, diffusion, dispersion and advective processes dominate.

Molecular diffusion produces a net flux F_{diff} in the x-direction from a region of higher concentration to one of lower concentration that is often described by Fick's first law:

$$F_{diff} = -D_w \frac{\partial C}{\partial x} \tag{Eq. 2.6}$$

where D_w is the molecular diffusion coefficient of the compound in water. Molecular diffusion in a porous medium such as sediments must be corrected for tortuosity and porosity of the diffusion pathways. Millington and Quirk (1961) suggest a combined correction factor of the porosity to the four-thirds power to account for these effects:

$$F_{diff} = -\varepsilon^{4/3} D_w \frac{\partial C}{\partial x} \qquad \text{(Eq. 2.7)}$$

Boudreau (1997) suggests an alternative correction that may be more applicable to fine-grained sediments:

$$F_{diff} = -\frac{\varepsilon D_w}{1 - ln\varepsilon^2} \frac{\partial C}{\partial x} \qquad \text{(Eq. 2.8)}$$

A variety of techniques are available for estimating D_w (Schwarzenbach et al., 2003; Lyman et al., 1990). Values of D_w are typically 10^{-5}–10^{-6} square centimeters per second (cm^2/s) for sediment contaminants.

Advection can be a far more rapid mechanism of contaminant transport. The flow of water in sediments may be upward or downward depending upon local groundwater gradients or both in the case of tidal systems. The nearshore portions of lakes and rivers are common groundwater discharge areas giving rise to upwelling in the sediments. The advective flux, F_{adv}, is related to the upwelling velocity times the porewater concentration:

$$F_{adv} = VC \qquad \text{(Eq. 2.9)}$$

Because of natural heterogeneity, the flow of porewater through sediments is non-uniform, resulting in hydrodynamic dispersion. This results in spreading characterized by an effective diffusion coefficient, D_{disp}, similar to molecular diffusion although related to the flow velocity:

$$D_{disp} = \alpha V \qquad \text{(Eq. 2.10)}$$

The value of α is related to the spatial scale of the heterogeneities in a porous medium. Because the probability of encountering larger heterogeneities increases with travel distance, the value of α is often assumed to be a function of travel distance. A reasonable estimate is 5–10% of travel distance although the sensitivity to this parameter is often not significant for the small travel distances of interest in surficial sediments.

Both advection and diffusion are retarded by the effect of sorption onto solids. Contaminants sorbed to the solid phase are unavailable for advection and diffusion or other porewater processes. The ratio of the total contaminant mass to the concentration in the mobile phase, assuming local equilibrium between the solids and adjacent porewater, is given by:

$$\frac{M_T}{C_w} = \frac{\varepsilon C_w + \rho_s(1-\varepsilon)K_{sw}C_w}{C_w} = \varepsilon + \rho_s(1-\varepsilon)K_{sw} \equiv R_f \qquad \text{(Eq. 2.11)}$$

This ratio is a retardation factor, R_f, in that the effective diffusion coefficient, advection and dispersion coefficient are reduced by this ratio in evaluating the transient migration of the contaminant through the sediments. Advection and diffusion processes transport mass according to the fluxes in Equations 2.6 and 2.9. The accumulation on the solid phase, however, reduces the distance that is influenced by the advection and diffusion processes. Note that the concentration in the denominator in this situation is the total suspended and mobile phase concentration. If colloidal matter or suspended particulate matter increases the mass of contaminant in the mobile water phase, the retardation factor is similarly affected.

Gas ebullition or nonaqueous phase liquid (NAPL) migration can also influence contaminant migration and retardation by sorption. This is primarily important for organic contaminants. Gas ebullition can carry volatile organic contaminants according to:

$$F_{gas} = V_{gas}HC \qquad \text{(Eq. 2.12)}$$

where H is the Henry's Law constant for the compound and V_{gas} is the volume of gas per unit area exiting the sediment. This assumes that the gas is in local equilibrium with the water and neglects other mechanisms for gaseous transport due to sorption of hydrophobics at the gas-water interface of bubbles (Yuan et al., 2009), or mechanical disruption of the surface by gas (Johnson et al., 2002). Values of V_{gas} typically range from 0 to the order of 1 liter per square meter per day (L/m^2/day) (e.g., in the Anacostia river; DiToro, 2001).

The Henry's Law constant for nonpolar volatile organics can generally be estimated by the relationship:

$$H \sim \frac{P_v M_w}{R\,T\,S} \tag{Eq. 2.13}$$

where P_v and M_w are the compound vapor pressure and molecular weight, respectively, R is the ideal gas constant (1 atmosphere [atm]·24.5 L/298 Kelvin [K]/mole), T is the absolute temperature in Kelvin, and S is the solubility of the compound in mass per volume. Due to the relatively small value of H for most hydrophobic compounds of interest, the gas-induced flux is relatively small. A potentially more important concern is the movement of NAPL with gas if the gas moves through a NAPL-contaminated layer.

If a continuing source of NAPL is present, source control efforts are an early and important remedy response. In the absence of gas moving through a NAPL-contaminated layer, however, a NAPL layer is often relatively immobile. Often, the sediment NAPL is often heavily weathered and viscous and the mobile fractions have long since left the sediments. The capacity of the immobile NAPL phase for the organic can also aid in retardation of any chemical migration. Erten et al. (2011) provide a consolidation testing method to evaluate NAPL mobility and expression in soft sediments. This method could also be used to assess gas release and NAPL release with the gas although the gas release by this test is likely more rapid than in the sediment environment.

2.3.3 Bioturbation

Bioturbation is the normal life cycle activity of benthic organisms that lead to mixing of sediment and porewater in the near surface layer of sediments. These activities influence the fate and behavior of contaminants and are often the dominant mixing process in stable sediment environments. This is due to the fact that bioturbation typically involves reworking of the surface layer of sediments through particle mixing and is thus not subject to retardation of processes such as diffusion and advection that limit by retardation in the porewater.

The organisms responsible for the most sediment and contaminant reworking are the macrobenthos. Included in this category are deposit feeders that ingest and process sediment for food and are often referred to as conveyor belt feeders in that they ingest sediment at depth (typically 5–10 centimeters [cm] into the sediment) and defecate at the surface building fecal mounds. Burrowing filter feeders similarly move sediment but for the primary purpose of building a protective burrow from which they can actively pump water that they filter for food. The final category of organisms are surface feeders that tend to forage at the surface consuming organic matter, or sit on the surface filtering water and have a relatively limited impact on the sediment. Amphipods, such as the test organism *Hyallela azteca,* are examples of a surface feeder. *Urechis caupo* is an example of a marine burrowing filter feeder and has been observed to pump an average of 266 milliliters per minute (mL/min) of water through their burrows (Osovitz and Julian, 2002). Tubificid oligochaetes and their marine analogs, polychaetes, are examples of head down, conveyor-belt deposit feeders. These organisms tend to be pollution tolerant and thus are often found in high densities in contaminated sediments. Densities of ~100,000/square meter (m^2) are not uncommon and a sample collected in sediment in Indiana Harbor, Indiana, contained approximately 1,000,000/m^2 (USEPA, 1994). Their individual mass is of the order 0.5 milligrams (mg) dry weight yet they process several times their weight in sediment per day (Reible et al., 1996) and thus even a density of 100,000/m^2 would be expected to process of the order of 100 grams per square meter per day (g/m^2/day). This is the equivalent of reworking the upper centimeter of sediments approximately every 100 days. Given their length of approximately 5 cm and assuming this is the depth of sediments that are reworked (to always maintain a portion of their bodies at the oxic surface), this would suggest that the entire layer may be reworked within 2–3 years (assuming significant activity approximately 150–200 days/yr). Seasonal variations in density and activity may slow the reworking but clearly the organisms have the potential to effectively mix the surface layers of the sediment on a time scale that is very short compared to the lifetime of the sediment contaminants of interest. Marine organisms tend to be larger but present in lower number densities than freshwater organisms.

The high density of the organisms and their effectively random behavior suggest that it might be appropriate to model their effect on contaminants as an effective diffusion process in the biologically active zone. Thoms et al. (1995) summarizes literature reported values of the depth of reworking and intensity of reworking (by effective diffusion coefficient) at more than 200 sites via a variety of different organisms. The primary tool used in these measurements was the distribution of radionuclides in the surface sediments. These measurements were separated into freshwater and estuarine conditions. Deep water measurements were excluded due to their limited significance in contaminated sediment issues and the potential for dramatically different organism density and behavior in deep water, low organic carbon environments.

The observed probability distributions based upon the data of Thoms et al. (1995) are shown in Figure 2.2 (depth of mixing) and Figure 2.3 (intensity of mixing as indicated by an effective particle diffusivity due to bioturbation, or biodiffusion). The arithmetic mean and standard deviation for biodiffusion depths are 5.5 and 3.1 cm (geometric mean and standard deviation 4.1 and 1.7 cm) for freshwater and 12.3 and 14.8 cm (geometric mean and standard deviation 5 and 2.6 cm) for estuarine systems, respectively.

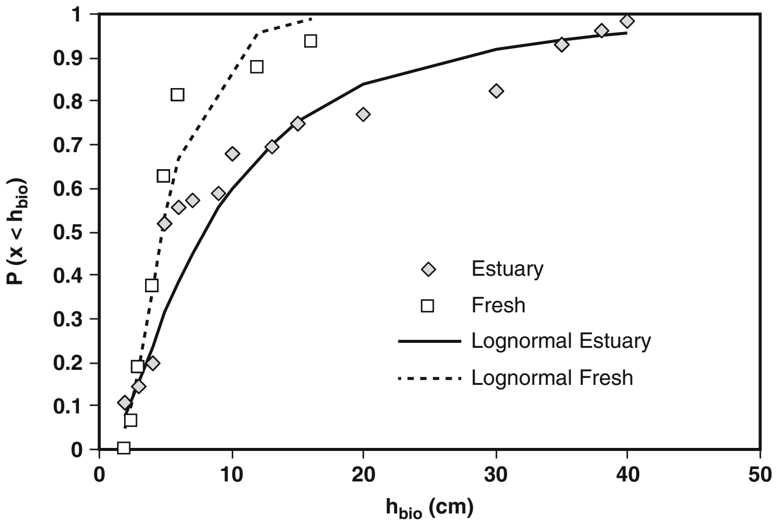

Figure 2.2. Probability distribution of bioturbation mixing depth.

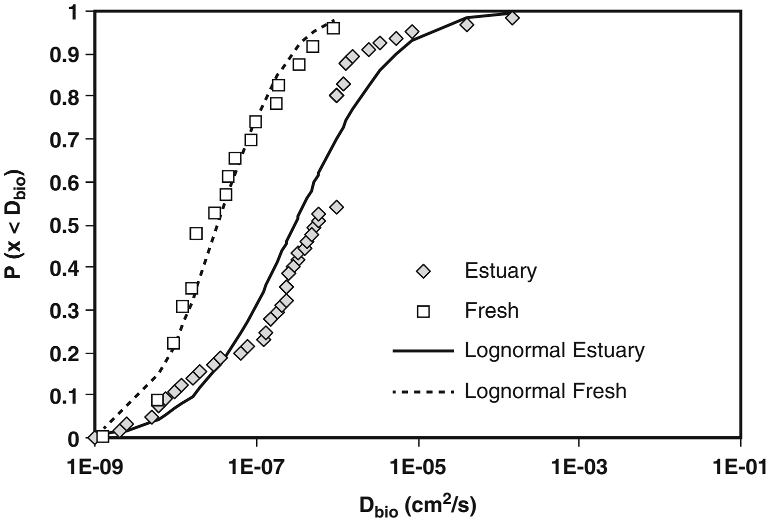

Figure 2.3. Effective particle biodiffusion coefficients.

The arithmetic mean and standard deviation for the biodiffusion coefficients are 1.23×10^{-7} and 4.31×10^{-7} cm^2/s for freshwater and 3.95×10^{-6} and 5.20×10^{-5} cm^2/s for estuarine systems, respectively.

Figure 2.2 indicates that the effectively mixed zone is relatively shallow despite the fact that some marine organisms may exhibit deep burrowing behavior of up to a meter (e.g., the geoduck organism in the Pacific Northwest). Occasional, low-density deep penetrations apparently do not give rise to substantial bioturbation of the sediments. The distribution of both depth of biological-induced mixing and the effective mixing rate (i.e., biodiffusion coefficients) are generally contained within relatively narrow bounds. There are low probability outliers but the depth and intensity of mixing are reasonably well estimated by the mean values with an uncertainty as characterized by the standard deviation (± 50% in the case of bioturbation depth and ± an order of magnitude in the intensity of mixing).

It should be emphasized that the effective bioturbation diffusion coefficient in Figure 2.3 is a *particle* diffusion coefficient. That is, it represents the rate of mixing associated with particle movement which causes mixing of both porewater contaminants and particle associated contaminants. Thus, the contaminant flux associated with bioturbation in the actively mixed zone is given by:

$$F_{bio} = -D_{bio}\frac{\partial[\varepsilon C + \rho_s(1-\epsilon)W_s]}{\partial z} = -D_{bio}\frac{\partial R_f C}{\partial z} \tag{Eq. 2.14}$$

This assumes that the porewater mixing is at the same rate as the particle mixing. As shown by the filter feeders, this could be considerably higher due to active pumping mechanisms of the organisms. For strongly hydrophobic contaminants, however, the dominant mechanism of contaminant transport is due to particle transport and the flux is relatively insensitive to porewater pumping.

Not taken into account in this analysis are site-specific variations associated with low or negligible density of organisms due to substrate deficiencies or toxicity. Also not included in the analysis is whether the particle flux is relevant to the flux at the surface. For example, contaminants are typically strongly sorbed to hard carbon (or activated carbon) and the particle flux in the bed likely does not lead to release of dissolved contaminants to the overlying water. In the absence of site-specific information, however, this model may provide a reasonable first estimate of the effect of bioturbation on contaminant fate and transport.

2.3.4 Hyporheic Exchange

A final mechanism that we will consider here is unique to the sediment-water interface and is the exchange between surface water and groundwater. The zone where groundwater and surface water meet is the hyporheic zone and the exchange processes are termed hyporheic exchange. There exist a variety of mechanisms that can encourage this exchange by the development of pressure variations in time or space along the sediment surface. The pressure variations combined with variations in surface roughness or permeability give rise to flow directed inward at portions of the sediment surface and outward at other locations and times Example mechanisms that can give rise to this pressure non-uniformity and hyporheic flow include:

- Flow over an uneven bottom,
- Flow around obstacles in the overlying water,
- Water depth fluctuations due to waves, tides, dam release flows and vessel traffic at the water surface, and
- Flow above organism burrows in the sediment.

Figure 2.1 includes an illustration of the effects of flow over an uneven bottom. The flow generates an elevated pressure on the upstream surface of sediment dunes and a negative pressure on the downstream face. This results in a flow within the dune that transports contaminants in porewater and also influences the distribution of oxygen and water borne nutrients in the system. This source of hyporheic exchange was evaluated by Savant et al. (1987).

A similar effect can be observed in sediment heterogeneities associated with organism burrows. Small pressure variations can be transmitted effectively through open burrows but are significantly dampened in surrounding low permeability sediments. This variation can lead to rapid movement of oxygen and soluble nutrients into the sediment bed although the effect on hydrophobic solids (whose motion may be significantly retarded by sorption) may be less important.

Sawyer et al. (2011) showed that obstacles in the overlying water could have a similar effect on in-bed flow. The creation of pressure variations by the obstacles translate to flow in the beds. Similarly, Sawyer et al. (2009) showed that other variations in water column level, in particular dam release flows, could lead to exchange with groundwaters in adjacent banks. Even if no significant net outflow is observed, the fluctuations in river levels give rise to alternate flows into the banks and then back out of the banks, which enhances exchange.

A similar but more transitory effect can result from short-term wave action or water depth variations associated with vessel passage. A similar transitory pressure variation can result from turbulence in the overlying water that is transmitted into the underlying sediments. The magnitude or significance of these sources of hyporheic exchange are not well understood and have received less study than the previously discussed mechanisms.

Regardless of the source of the in-bed flow, the contaminant migration by advection is subject to the same sorption and retardation processes discussed previously. The significance of hyporheic exchange is greatest in relatively permeable coarse grained sediments and for transport of soluble constituents such as oxygen and certain nutrients which exhibit negligible retardation due to sorption.

2.4 SUMMARY

An evaluation of the sediment and contaminant processes important in surficial sediment layers was presented in order to aid the understanding of the effect of these processes on assessing and managing contaminated sediments in the coming chapters.

Particular characteristics and processes of critical importance to contaminant behavior in sediments include:

- The low permeability and strong sorption characteristics of the fine-grained sediments that are likely to accumulate contaminants,
- The stable, non-erosive nature of sediments beds that are likely to accumulate contaminants,
- Diffusion, advection and dispersion in stable sediment beds, both driven by mean hydraulic gradients (e.g., groundwater upwelling) and spatially variable and dynamic processes such as hyporheic exchange, and
- The strong effect of bioturbation on surficial sediments due to the movement of both sediment particles and their associated contaminants.

The result of these different processes and the different character of most sediment environments make the assessment and management of contaminated sediments a difficult and challenging problem. We will examine those challenges in more detail in the subsequent chapters, building upon the introduction in this chapter.

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CHAPTER 3

FUNDAMENTALS OF SEDIMENT TRANSPORT

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3.1 INTRODUCTION

The goals of this chapter are to (1) describe the processes that govern the transport of sediment in surface waters, (2) provide guidance for use in assessing and/or quantifying sediment transport, and (3) describe the procedure to use in modeling sediment transport. A basic knowledge of these topics is requisite to understanding many of the contaminant transport processes important in sediments due to the strong particle associations of most contaminants of concern. This chapter starts with brief overviews of sediment transport – sedimentation related problems and how sediment in surface waters responds to the forces that cause water movement. Basic sediment transport processes are also defined. Section 3.2 describes pertinent properties of sediments, and transport processes for cohesive sediments. Section 3.3 provides guidance to use to assess and/or quantify sediment transport. It is often necessary for remedial project managers to conduct a Sediment Transport Assessment in support of a remedial alternatives evaluation for contaminated sediment Superfund sites. The assessment involves using a systematic approach to (1) identify the processes and mechanisms that might result in erosion, (2) determine the most appropriate methods to use to assess sediment resuspension and deposition, and (3) quantify sediment resuspension and deposition rates under varying flow conditions. Section 3.4 provides an overview of the procedures involved in performing a sediment transport modeling study. These procedures or steps include: (1) model selection and setup, (2) hydrodynamic modeling, (3) sediment transport modeling, (4) calibration and validation of the models and (5) analyzing model results.

3.1.1 Sediment-Related Engineering Problems

Managing sediment shoaling in marine ports and harbors, often located in estuaries, has been an ongoing challenge for several millennia. This sediment is transported to estuaries from inland sources by rivers and from marine sources by tidal currents. With the explosive growth of population and commerce over the past several 100 years (yr), particularly centered around estuaries and other water bodies, the need to manage water resources is increasing. Included in water resource management are maintenance of navigable waterways and control of water pollution, both of which are affected to varying degrees by the load of suspended and deposited sediment.

Under low-flow velocities, fine-grained cohesive sediments (clays and silts) in particular have a tendency to deposit in areas such as dredge cuts, navigation channels, basins (e.g., harbors and marinas), and behind pilings (Einstein and Krone, 1962; Ariathurai and Mehta, 1983). In addition, the estuarial mixing zone (referred to as the estuarine turbidity

D.D. Reible (ed.), *Processes, Assessment and Remediation of Contaminated Sediments*,
doi: 10.1007/978-1-4614-6726-7_3,

maximum [ETM] zone) between upland fresh water and sea water is a favorable site for sediment accumulation. The amounts and locations of sediment deposits are also affected by development projects such as construction of port facilities or dredging of navigation channels. Accurate estimates of the amount of dredging required to maintain navigable depths in commercial ports is required.

Contamination of surface waters caused by the dumping and subsequent transport of contaminants such as metals (zinc and copper), organic compounds (polychlorinated biphenyls [PCBs], polycyclic aromatic hydrocarbons [PAHs]) and pesticides is a critical problem in many estuaries, rivers and lakes. The potential impacts these contaminants have on aquatic environments and possible remediation alternatives can be assessed only if the transport and fate of such contaminants are known. To evaluate the transport of contaminants in surface waters it is necessary to know not only the biogeochemical processes that affect contaminants in aquatic environments (e.g., adsorption/desorption, volatilization), but also changes in the various factors (e.g., pH) that govern them. The latter requires an ability to predict hydrodynamics, water quality and sediment transport because the movement of surface waters, sediments and contaminants are highly coupled. For example, the role of sediments and organic matter in assimilating contaminants in depositional environments such as harbors and lakes has been revealed in many studies (e.g., Reese et al., 1978; Abernathy et al., 1984; Medine and McCutcheon, 1989; Brown et al., 1990). Therefore, an understanding of sediment transport is critical when evaluating various remedial alternatives (e.g., no-action, monitored natural recovery [MNR], capping, dredging) at contaminated sediment sites such as the Fox and Upper Hudson Rivers and New Bedford Harbor.

In many contaminated water bodies, contaminants in the sediment are a legacy of historical sources that may have been since controlled. As a result, more highly-contaminated historical sediments have often been buried by subsequent layers of cleaner sediment, and human and ecological risks have declined over time. In these situations there will normally be some indication of long-term sediment deposition. Often, simply by virtue of the fact that contaminated sediment deposits still exist today from historical sources decades ago, there is a basis to assume some degree of inherent long-term stability (lack of movement) of the sediment bed. In considering the effectiveness of an MNR remedy or the need for active remediation, it is important to determine the likelihood that buried contamination will stay buried and not be eroded as a result of extreme events such as a 100-yr flood.

It is important to differentiate between routine processes (e.g., baseflow in rivers) that tend to only affect the surface layer, and extreme events that may disrupt deeper sediments. Routine processes should be understood and quantified because they affect the rate of potential natural recovery of contaminant concentrations in fish, water, and sediment. However, sediment erodibility under extreme events is one of the primary considerations in evaluating the permanence of in-place management options, such as engineered capping and thin-layer capping of dredge residuals.

3.1.2 Sediment Transport Terminology

For completeness and consistency, the following sediment transport related terms that are used extensively throughout this chapter are defined below.

Aggradation is the process by which the bottoms of water bodies are raised due to deposition of sediment.

Bedload is sediment material moving on top of or near a channel bed by rolling, sliding, and saltating, i.e., jumping.

Bed shear strength is a direct measure of a sediment bed's resistance to a flow-induced shear stress at the surface of the bed. Another term that is commonly used for this parameter is *critical shear stress for erosion*.

Bed shear stress is a force per unit area of the bed surface that acts parallel to the surface of the sediment bed and is generated by a current flowing over a sediment bed.

Degradation is the process by which the bottom of a water body is lowered due to erosion of bed sediment.

Deposition is the process of suspended sediment settling and coming to rest on the bed/bottom of the water body.

Erosion is the removal or wearing away of soil particles from the bottom or sides, i.e., wetted perimeter, of a water body through the action of moving water, i.e., currents and/or waves.

Erodibility is a measure of a sediment bed's propensity to lose sediment particles due to the action of currents and/or waves.

Resuspension is normally defined as the erosion of deposited sediment. The resuspension rate is a function of the flow-induced bed shear stress and the shear strength of the deposited sediment.

Sedimentation is the deposition of sediment. It often refers to total deposition over a specified time period (a storm event, a single year, etc.).

Stability of a sediment bed refers to its ability to resist erosional forces acting on the bed surface due to the action of currents and/or waves.

Suspended load is the amount of sediment that is supported by the upward components of turbulence in a channel and that stays in suspension for an appreciable length of time.

Transport refers to the physical movement of sediment particles (some of which are suspended in the water column and others that are rolling and bouncing, i.e., saltating, along the bottom) due to the action of moving water. It is typically assumed that suspended material (i.e., inorganic sediment and organic matter) has the same velocity as the water. Sayre (1968) verified the reasonableness of this assumption for sediment particles less than about 100 micrometers (μm) in diameter.

3.1.3 Response of Sediment to Driving Forces

Sediment transport in surface waters is governed by the sum of natural and human impacts that impart mixing or erosive forces on the sediment bed, either through direct disturbance or by moving water. A list of possible natural and human impacts is presented in Table 3.1. When the erosive forces are sufficiently large, sediment is eroded. If currents and/or waves are present, the eroded sediment will be transported by the currents generated by the driving forces.

As defined in the previous section, a current flowing over a sediment bed generates a bed shear stress. Waves on the water surface can generate a vertical force on the surface of the sediment bed, and the force per unit bed area is called a normal stress since it acts normal to the bed surface. Physical processes that can generate a bed shear stress are currents and wave-induced water motion in the horizontal direction, and processes that can generate normal stresses are wave-induced water motion in the vertical direction. The appendix to this chapter contains a commonly used methodology for calculating the combined current- and wave-induced bed shear stress.

To further introduce the response of sediments to current-induced bed shear stresses, a brief qualitative description of sediment transport in rivers and the response of the sediment bed is given here. As rivers flow from mountains to coastal plains, noncohesive sediment such as sand tends to deposit because they have relatively high settling speeds, creating a sediment

Table 3.1. Potential Natural and Human Disturbances to the Sediment Bed

Natural Disturbances	Human Disturbances
Hydraulic Impacts	
• Currents, tides, wind waves, seiches • Storm events – high flows, waves, or surges • Breach of natural dams or reservoirs (e.g., beaver dam, ice jam) • Flow under ice cover	• Hydraulic structure operations (locks and dams, sewer outfalls, etc.) • Watershed development (altered runoff and sediment loading)
Direct Impacts	
• Activity of fish, waterfowl and mammals • Bioturbation and benthic activity (activity of organisms that dwell in or on the sediment bed) • Impact by debris or ice • Groundwater advection and gas ebullition	• Commercial fishing • Vessel activity (including propeller, bow wake, anchoring, etc.) • Construction • Placement of fill or structural stone • Dredging/excavation

bed with a decreasing slope in the downstream direction and a pattern of downstream fining of bed sediment. When the sediment transport capacity in a given reach of a river exceeds the total sediment load being transported from upstream reaches, the difference between the capacity and total load is supplied from the bed. This means that the river channel will undergo erosion, i.e., degradation. In a river with nonuniform bed material, the finer surficial bed sediment will be eroded more rapidly than the coarser sediment. By this process, the median diameter of the surficial bed sediment becomes coarser. If the degradation continues, the finer surficial bed sediment will eventually be depleted, leaving a surficial layer of coarser sediment. This process is called *armoring* and the surficial layer of coarser sediment is called the *armor layer*.

3.2 SEDIMENT TRANSPORT PROCESSES

3.2.1 Sediment Properties

Properties of sediments that affect their transport in surface waters – more specifically their rates of erosion and deposition – are defined in this section. A basic understanding of these properties is needed to understand the description of the transport processes presented in Section 3.2.3.

Sediment Definition: Sediments are weathered rock material that are transported, suspended or deposited by flowing water. All constituents of the parent rock material are usually found in the sediment. Quartz, because of its greater stability, is by far the most common material found in sediments. However, numerous other rocks and minerals (e.g., shale, carbonate particles, feldspar, igneous and metamorphic rocks, magnetite) also are usually present. Even when material other than quartz particles is present in sediment, the average particle density of sediment is usually very close to that of quartz – 2.65 grams per cubic centimeter (g/cm^3). The specific gravity of sediment is defined as the ratio of the sediment particle density to the density of water at 4 degrees Celsius (°C) (i.e., 1.0 g/cm^3), and thus has an average value of 2.65.

Size Classification: Sediment diameter is denoted as D, and has dimensions of length. Since sediment particles are rarely exactly spherical, the definition of diameter requires elaboration. For sufficiently coarse particles, D is often defined to be the dimension of the smallest square mesh opening through which the particle will pass. For finer particles, D usually

Table 3.2. Sediment Gradation Scale (adapted from ASCE, 1975)

Sediment Class Name	Size Range (millimeters [mm])	Size Range (μm)
Very large boulders	4,096–2,048	
Large boulders	2,048–1,024	
Medium boulders	1,024–512	
Small boulders	512–256	
Large cobbles	256–128	
Small cobbles	128–64	
Very coarse gravel	64–32	
Coarse gravel	32–16	
Medium gravel	16–8	
Fine gravel	8–4	
Very fine gravel	4–2	
Very coarse sand	2–1	2,000–1,000
Coarse sand	1–0.5	1,000–500
Medium sand	0.5–0.25	500–250
Fine sand	0.25–0.125	250–125
Very fine sand	0.125–0.063	125–63
Coarse silt	0.063–0.031	63–31
Medium silt	0.031–0.016	31–16
Fine silt	0.016–0.008	16–8
Very fine silt	0.008–0.004	8–4
Coarse clay	0.004–0.002	4–2
Medium clay	0.002–0.001	2–1
Fine clay	0.001–0.0005	1–0.5
Very fine clay	0.0005–0.00024	0.5–0.24

denotes the diameter of the equivalent sphere with the same fall (or settling) velocity as the actual particle. A sediment gradation scale (Table 3.2) has been established to classify sediment in size classes, ranging from very fine clays to very large boulders. Sediment particles with diameters less than 63 μm are classified as fine-grained sediment, and are cohesive in nature, with the cohesiveness increasing with decreasing particle size. It should be noted that fine-grained particles (e.g., in the medium to coarse silt size) that do not include strong physiochemical forces may behave in a cohesive manner (i.e., attraction between particles) because of naturally occurring coatings on the particles. Sediment particles with diameters >63 μm are classified as noncohesive sediment.

Grain size distributions (GSDs) are commonly calculated from analysis of grab samples collected throughout a water body to determine the spatial variation in the surficial distribution of sediment sizes. Cores are also often collected at chosen locations of interest to determine

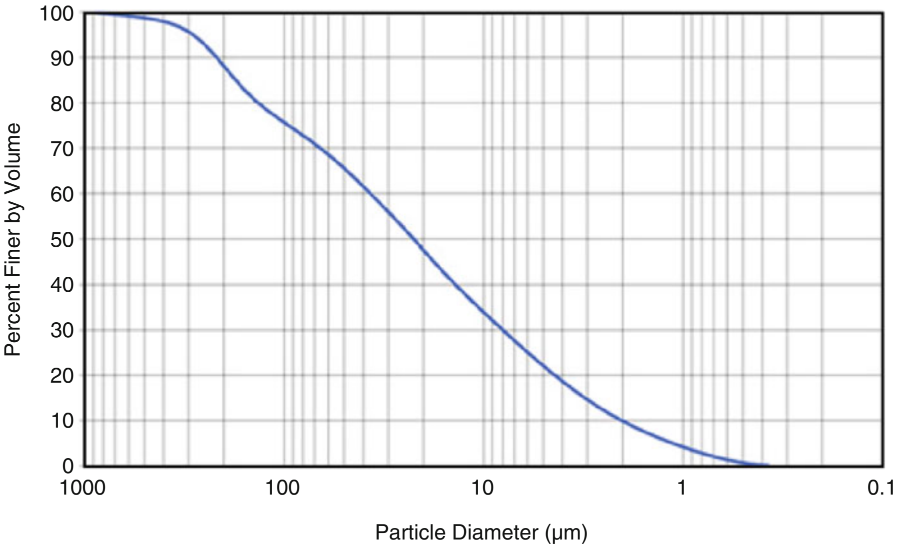


Figure 3.1. Example GSD.

how the GSD varies with depth below the bed surface. An example GSD is shown in Figure 3.1. Particle size (in units of microns) is plotted on the x-axis, and % finer by volume is plotted on the y-axis. It is seen in this plot that the median particle diameter, D50, is approximately 23 μm, approximately 70% of the sediment sample analyzed was in the cohesive sediment size range, and therefore approximately 30% of the sediment was in the noncohesive size range. Variations in the GSD throughout a water body typically indicate, among other things, areas that experience high flows and those that experience low flows. The former areas will typically have a larger D50 than the latter areas since coarser (i.e., larger) sediments are, in general, more resistant to eroding forces than finer (i.e., smaller) sediments. High flows often cause the erosion of the finer sediments from the surface layer, leaving a relatively thin layer of coarser sediment on the bed surface. This process is called *armoring*.

Cohesive Sediments: These sediments are composed of clay and non-clay mineral components, silt-sized particles, and organic material, including biochemicals (Grim, 1968). Clays are defined as particles with an equivalent diameter of <4 μm, and generally consist of one or more clay minerals such as kaolinite, bentonite, illite, chlorite, montmorillonite, vermiculite and halloysite. The non-clay minerals consist of, among others, quartz, calcium carbonate, feldspar and mica. The organic matter often present in clay materials can be discrete particles, adsorbed organic molecules or constituents inserted between clay layers (Grim, 1968). Additional possible components of clay materials are water-soluble salts and adsorbed exchangeable ions and contaminants. Clays possess the properties of plasticity, thixotropy and adsorption in water (van Olphen, 1963).

Cohesion: For clay-sized particles, surface physicochemical forces exert a distinct controlling influence on the behavior of the particles due to the large specific area, i.e., ratio of surface area to volume. In fact, the average surface force on one clay particle is several orders of magnitude greater than the gravitational force (Partheniades, 1962). The relationships between clay particles and water molecules are governed by interparticle electrochemical forces. Interparticle forces are both attractive and repulsive. The attractive forces present are the London-van der Waals and are due to the nearly instantaneous fluctuation of the dipoles that result from the electrostatic attraction of the nucleus of one atom for the electron cloud of a neighboring atom (Grimshaw, 1971). These electrical attractive forces are weak and are only significant when interacting atoms are very close together. However, the electrical attractive forces are strong enough to cause structural build-up since they are additive between pairs of atoms. The magnitude of these forces decreases with increasing temperature; they are only slightly dependent on the salt concentration (i.e., salinity) of the medium (van Olphen, 1963). The cohesiveness of clays, such as illite or bentonite, is due to these electrical attractive forces. Particle cohesion is promoted by an increased concentration of dissolved ions and/or an increased ratio of multivalent to monovalent ions present in saline waters. The salinity and ratio of multivalent to monovalent ions both serve to determine the net interparticle force and, thus, the potential for clay particles to become cohesive. Kaolinite becomes cohesive at a salinity of 0.6 practical salinity units (psu), illite at 1.1 psu, and montmorillonite at 2.4 psu. The rapid development of cohesion and the relatively low salinities at which clays become cohesive indicate that cohesion is primarily affected by salinity variations near the landward end of an estuary where salinities are often less than about 3 psu.

The magnitude of these net attractive electrochemical surface forces on the particles is significant in that they control the cohesiveness and therefore the bed shear strength of fine-grain sediments deposited on the bottom of a water body. Bed shear strength is usually quantified as the critical shear stress of erosion. As the attractive forces increase, the bed shear strength increases while their erosion rate decreases when the bed surface is subjected to bed shear stresses that are greater than the bed shear strength since the erosion rate of cohesive sediment beds have been found to be proportional to the difference between the bed shear stress and the bed shear strength.

Flocculation: In water with very low salinity (less than about 1 psu), individual cohesive sediment particles are often found in a dispersed state. Small amounts of salts, however, are sufficient to repress the electrochemical surface repulsive forces among the particles, with the result that the particles being transported in surface waters collide and then coagulate (due to their cohesiveness) to form flocs. This process is defined as *flocculation*. It is important to note that flocs can form even in freshwater. Each floc can contain thousands or even millions of particles. The transport properties of flocs are affected by the hydrodynamic conditions and by the chemical composition of the suspending fluid. An understanding of the transport properties of cohesive sediments requires knowledge of the process of flocculation.

As stated above, flocculation depends on the collision of suspended cohesive sediments. There are three principal mechanisms of interparticle collision in suspension, and these influence the rate at which individual sediment particles coagulate to form flocs. The first is Brownian motion that results from the thermal motions of the molecules of the suspending water. Generally, coagulation rates by this mechanism are too slow to be significant unless the suspended sediment concentration exceeds 5–10 grams per liter (g/L), and flocs formed by this mechanism are generally weak and are easily fractured by shearing, especially in high shears found near the bed in rivers or estuaries, or are crushed easily when deposited (Krone, 1962). The second mechanism is due to internal shearing produced by local velocity gradients in the fluid. Collision will occur if the paths of the particles' centers in the velocity gradient are displaced by a distance that is less than the sum of their radii. Flocs produced by this mechanism tend to be relatively dense and strong because only those bonds that are strong enough to resist internal shearing can survive. The third mechanism, differential sedimentation, results from particles of different sizes having different settling velocities. A larger particle, due to its higher settling velocity, will collide with smaller, more slowly settling particles and will have a tendency to pick up these particles. This mechanism produces relatively weak flocs and contributes to the observed rapid clarification of estuarial waters at slack tide.

Settling Speed: The settling velocity for individual noncohesive sediment particles, w_s, is given by van Rijn (1984b) as the following functions of D, g', and R_d (defined by Eq. 3.17):

$$\frac{w_s}{\sqrt{g'D}} = \begin{cases} \frac{R_d}{18} & for\ \ D \leq 100\ \mu m \\ \frac{10}{R_d}\left(\sqrt{1+0.01R_d^2}-1\right) & for\ 100\ \mu m < D \leq 1000\ \mu m \\ 1.1 & D > 1000\ \mu m \end{cases} \tag{Eq. 3.1}$$

Another commonly used formula for the settling velocity of natural noncohesive sediment particles is given by Cheng (1997) as the following function of D, v, and R_d:

$$\frac{w_s D}{v} = \left(\sqrt{25+1.2\left(\frac{R_d}{v}\right)^{2/3}}-5\right)^{1.5} \tag{Eq. 3.2}$$

The settling rate of coagulated cohesive sediment particles depends on, in part, the size and density of the flocs, and as such is a function of the processes of coagulation and flocculation (Owen, 1971). Therefore, the factors that govern these two processes also affect the settling rate of the resulting flocs. The settling velocities of flocs can be several orders of magnitude larger than those of individual clay particles (Bellessort, 1973). For flocs from 10 to 1,000 μm in size, settling velocities have been found to range from 10^{-5} to 10^{-1} meters per second (m/s) (Dyer, 1989).

The following four settling zones have been identified for flocs: free settling, flocculation settling, hindered settling and negligible settling. In the free settling zone, the settling velocities are independent of the suspension concentration. In the flocculation zone, the settling velocities increase with increasing suspension concentration due to increased interparticle collisions that result in the formation of larger and denser flocs. In the hindered settling zone, the upward transport of interstitial water is inhibited (or hindered) by the high suspension concentration. This, in turn, results in a decrease in the floc settling velocity with increasing suspension concentration. At the upper end of the hindered settling zone, the suspension concentration near the bed is so high that no settling of flocs occurs (i.e., negligible settling).

Hwang (1989) proposed the following expressions for the floc settling velocity:

$$w_{sf} = \begin{cases} w_{sf} & for\ C < C_1 \\ a_w \frac{C^{n_w}}{\left(C^2+b_w^2\right)^{m_w}} & for\ \ C_1 < C < C_3 \\ 0 & C > C_3 \end{cases} \tag{Eq. 3.3}$$

where w_{sf} = free settling velocity, a_w = velocity scaling coefficient, n_w = flocculation settling exponent, b_w = hindered settling coefficient, m_w = hindered settling exponent, C_1 = concentration between free settling and flocculation settling zones, C_3 = concentration at the upper limit of the hindered settling zone and C_2 = concentration between the flocculation and hindered settling zones (where w_{sf} is maximum). Ranges of values for C_1, C_2, and C_3 are 100–300 mg/L, 1–15 g/L, and on the order of 75 g/L, respectively (Odd and Cooper, 1989).

Shrestha and Orlob (1996) developed the following expression for the settling velocity of flocs that accounts for the effect of both the suspension concentration and flow shear:

$$w_{sf} = C^{\alpha}\exp(-4.21+0.147G) \tag{Eq. 3.4}$$

where $\alpha = 0.11 + 0.039G$, and $G = \sqrt{\left(\frac{\partial u}{\partial z}\right)^2 + \left(\frac{\partial v}{\partial z}\right)^2}$; i.e., G = magnitude of the vertical shear of the horizontal velocity.

Ziegler et al. (2000) found that settling velocity of flocs was related to the following power law function of the shear stress (τ) at which flocs are formed and the suspended sediment concentration (C):

$$w_{sf} = 2.5(C\,\tau)^{0.12} \tag{Eq. 3.5}$$

Ziegler et al. state that if this equation is used in a depth-averaged sediment transport model, the appropriate shear stress to use is the bed shear stress.

Sediment Bed Properties: Noncohesive sediment beds at a given location are characterized by vertical profiles in GSD and in porosity (or dry bed density). Since these beds do not undergo consolidation, their resistance to erosion only changes with time if the composition of the bed changes with time due to, for example, bed armoring. In contrast, the erosion rates for fine-grained sediment beds are highly dependent on porosity. Decreases in porosity enhance electrochemical interparticle bonds, resulting in increased resistance to erosive forces. Flow-deposited beds of cohesive sediment flocs typically possess vertical density and bed shear strength profiles. The average values of bed density and bed shear strength increase over time and their vertical profiles change with time, primarily due to consolidation and secondarily due to thixotropy and associated physicochemical changes affecting inter-particle forces. Consolidation is caused by the weight of overlying deposited flocs (overburden) that crushes, and thereby decreases the order of flocculation of the underlying sediment. Consolidation changes the erosive behavior of cohesive sediment beds in two ways: (1) as the shear strength of the bed increases due to consolidation, the susceptibility of the bed to erosion decreases, and (2) the vertical shear strength profile determines the depth into the bed that a bed will erode when subjected to excess shear, i.e., an applied bed shear stress in excess of the bed surface shear strength.

In rivers and other water bodies, sediment beds will often be composed of a mixture of cohesive and noncohesive sediments. Lick et al. (2004) found that percentages of fine-grained sediment as low as 2% in such beds can have a large effect on erosion rates, thus demonstrating the importance of determining the variation in GSDs, bed shear strengths and erosion rates of sediment beds throughout the water body.

3.2.2 Noncohesive Sediment Transport

Incipient motion of a noncohesive sediment particle occurs when the flow-induced forces are greater than the resistance forces and the particle begins to move across the surface of the sediment bed. Figure 3.2 is a diagram of the forces acting on a single, spherical sediment particle in the surface layer of a sediment bed. For simplicity, all the particles are assumed to have the same diameter and to be arranged in the orderly fashion seen in this figure. The dashed brown line in this figure represents the hypothetical bed surface where the mean flow velocity is zero. The angle between the horizontal black line (on the right side of the figure) and the bed surface is shown to be θ. The slope of the bed is equal to tanθ. The forces shown in this diagram are the following: Ws = submerged weight of the particle; F_D = flow-induced drag force; F_L = flow-induced lift force; and F_R = resistance force due to contact between adjacent particles.

Summing the forces in the direction perpendicular to the bed at the onset of incipient motion, i.e., when the particle has not yet started to move, gives:

$$F_L - W_s \cos\theta = 0 \tag{Eq. 3.6}$$

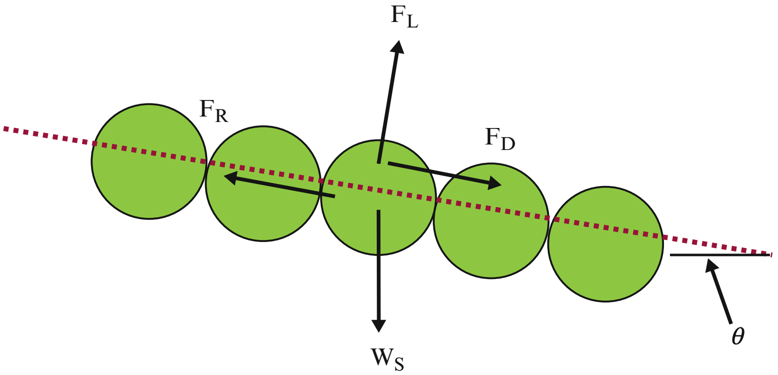


Figure 3.2. Diagram of forces acting on a sediment particle.

The lift force that acts on the particle is given by:

$$F_L = C_L \frac{\pi}{4} D^2 \frac{\rho}{2} V_D^2 \quad \text{(Eq. 3.7)}$$

where C_L = lift coefficient, D = particle diameter, ρ = water density and V_D = velocity at a distance D above the bed. The submerged weight of the particle is given by:

$$W_s = \frac{\pi D^3}{6} (\rho_s - \rho) g \quad \text{(Eq. 3.8)}$$

where g = gravitational acceleration and ρ_s = sediment particle density. Summing the forces in the direction parallel to the bed at the onset of incipient motion gives:

$$F_D - F_R + W_s \sin\theta = 0 \quad \text{(Eq. 3.9)}$$

The drag force that acts on the particle is given by:

$$F_D = C_D \frac{\pi}{4} D^2 \frac{\rho}{2} V_D^2 \quad \text{(Eq. 3.10)}$$

where C_D = drag coefficient. Yang (1973) gives the following expression for the resistance force:

$$F_R = \Psi (W_s - F_L) \quad \text{(Eq. 3.11)}$$

where Ψ = friction coefficient. V_D in Equations 3.7 and 3.10 can be determined using a logarithmic velocity distribution:

$$\frac{V_y}{u_*} = 5.75 \log \frac{y}{D} + B \quad \text{(Eq. 3.12)}$$

where V_y = velocity at a distance y above the bed, B = roughness function, and $u_* = (\tau_b/\rho)^{0.5}$ = shear velocity, with τ_b = bed shear stress. In the hydraulically smooth regime, as defined by the shear velocity Reynolds number < 5, B is given by:

$$B = 5.5 + 5.75 \log \frac{u_* D}{\nu} \quad \text{for} \quad 0 < \frac{u_* D}{\nu} < 5 \quad \text{(Eq. 3.13)}$$

In the hydraulically rough regime, $B = 8.5$ for $u_*D/\nu > 70$. Substituting y = D into Equations 3.12 and 3.13 gives $V_D = Bu_*$. The depth-averaged velocity, V, can be obtained by integrating Equation 3.12 over the flow depth d:

$$\frac{V}{u_*} = 5.75\left(\log\frac{d}{D} - 1\right) + B \tag{Eq. 3.14}$$

Three different approaches have been used to develop criteria for incipient motion. These are the shear stress, velocity and probabilistic approaches. The shear stress approach by Shields (1936) for determining the critical shear stress at the onset of incipient motion, τ_{cs}, is probably the most well-known of all the approaches. An example of a probabilistic approach is that developed by Gessler (1965, 1970). The Shield's shear stress approach, further developed by van Rijn (1984a) and the velocity approach used by Yang (1973) are summarized below.

The basis of the shear stress approach is that incipient motion of noncohesive sediment occurs when the bed shear stress exceeds a critical shear stress referred to as the Shield's shear stress, τ_{cs}. The latter can be defined by the following nondimensional relationship:

$$\theta_{cs} = \frac{\tau_{cs}}{g'D} = f(R_d) \tag{Eq. 3.15}$$

where g' = reduced gravitational acceleration, given by:

$$g' = g\left(\frac{\rho_s}{\rho} - 1\right) \tag{Eq. 3.16}$$

and R_d = sediment particle densimetric Reynolds number, given by:

$$R_d = \frac{D\sqrt{g'D}}{\nu} \tag{Eq. 3.17}$$

where ν = kinematic viscosity. van Rijn (1984b) gives the following expressions for $f(R_d)$ on the right hand side of Equation 3.15:

$$f(R_d) = \begin{cases} 0.24\left(R_d^{2/3}\right)^{-1} & \mathit{for}\ R_d^{2/3} < 4 \\ 0.14\left(R_d^{2/3}\right)^{-0.64} & \mathit{for}\ 4 \le R_d^{2/3} < 10 \\ 0.04(R_d^{2/3})^{-0.1} & \mathit{for}\ 10 \le R_d^{2/3} < 20 \\ 0.013\left(R_d^{2/3}\right)^{0.29} & \mathit{for}\ 20 \le R_d^{2/3} < 150 \\ 0.055 & \mathit{for}\ R_d^{2/3} \ge 150 \end{cases} \tag{Eq. 3.18}$$

In his velocity approach, Yang (1973) first assumed that the channel slope was small enough to neglect the component of the sediment particle's weight in the flow direction in Equation 3.9, i.e., $W_s \sin\theta = 0$. Assuming that incipient motion occurs when the two remaining terms in Equation 3.9 are equal, i.e., $F_D = F_R$, he then equated Equations 3.10 and 3.11, substituted Equation 3.14 into both sides of the resulting equation, and then solved for the dimensionless parameter V_{cr}/w_s, where V_{cr} = depth-averaged critical velocity at the onset of incipient motion, and w_s = particle settling velocity (i.e., terminal fall velocity). He also assumed that the drag coefficient was linearly proportional to the lift coefficient. Yang then used laboratory data sets collected by several researchers to determine the values of the friction coefficient in

Equation 3.11 and the proportionality coefficient between the drag and lift coefficients to obtain the following expressions:

$$\frac{V_{cr}}{w_s} = \frac{2.5}{\log(u_* D/\nu) - 0.06} + 0.66 \quad \text{for} \quad 1.2 < \frac{u_* D}{\nu} < 70 \qquad \text{(Eq. 3.19)}$$

$$\frac{V_{cr}}{w_s} = 2.05 \quad \text{for} \quad 70 \leq \frac{u_* D}{\nu} \qquad \text{(Eq. 3.20)}$$

The friction force exerted along the wetted perimeter of an open channel on the flow is usually quantified using a resistance formula that contains a roughness coefficient. The Manning's roughness coefficient is the one most commonly used for open channels with rigid boundaries. This coefficient is normally used as a calibration parameter in hydraulic models to achieve optimum agreement between measured and predicted stages (i.e., water surface elevations) or discharges. Once the model is calibrated, the Manning coefficient is treated as being temporally constant. For movable boundary problems, i.e., when sediment transport is involved, the resistance coefficient (1) will change with time due to changes in the movable bed that result from aggradation and degradation and (2) can be attributable to two resisting forces: one force is due to the roughness of the bed surface (this is called grain roughness or skin friction) and the other force is due to the presence of bed forms in alluvial (i.e., movable boundary) channels (this is called form roughness or form drag). Einstein and Barbarossa (1952) and other researchers have developed procedures for calculating both forms of movable boundary resistance.

The approach by Yang (1976) for estimating the grain- and form-related flow resistance in movable boundary open channels does not involve predicting what type of bed form occurs for a given flow regime (Yang, 1976). The basis for his formulation is the theory of minimum rate of energy dissipation that states that when a dynamic system (e.g., alluvial channel) reaches an equilibrium condition, its energy dissipation rate is minimum. This theory was derived from the second law of thermodynamics. The basic assumption made is that the rate of energy dissipation due to sediment transport can be neglected. For an open channel, the energy dissipation rate per unit weight of water is equal to the unit stream power VS, where V is the average flow velocity in the open channel and S is the slope of the energy grade line. Therefore, the theory of minimum energy dissipation rate requires that:

$$VS = V_m S_m \qquad \text{(Eq. 3.21)}$$

where the subscript m indicates the value of V and S when the unit stream power is minimized. Yang's approach involves using Equation 3.19 or 3.20 to determine the value of V_{cr}, and then using the following sediment transport equation developed by Yang (1973) to determine the total sediment transport:

$$\begin{aligned}\log C_{ts} &= 5.435 - 0.286 \log \frac{w_s D}{\nu} - 0.457 \log \frac{u_*}{w_s} \\ &+ \left(1.799 - 0.409 \log \frac{w_s D}{\nu} - 0.314 \log \frac{u_*}{w_s}\right) \log\left(\frac{VS}{w_s} - \frac{V_{cr} S}{w_s}\right) \qquad \text{(Eq. 3.22)}\end{aligned}$$

where C_{ts} = total sediment concentration being transported by the flow (in parts per million [ppm] by weight), D = median sieve diameter of the sediment and $V_{cr}S$ = critical unit stream power required at incipient motion. Yang (1976) describes an iterative procedure to determine the value of the Manning's coefficient in an alluvial open channel as a function of Q, D, w_s, C_{ts}, and $A(d)$, where the latter is the functional relationship between the open channel cross-sectional area, A, and the flow depth in which the Manning equation (given below) is used to calculate the value of the Manning's coefficient, n:

$$V = \frac{1}{n} R^{2/3} S^{1/2} \qquad \text{(Eq. 3.23)}$$

where R = hydraulic radius, which is equal to the ratio A/P, where P is the wetted perimeter. Equation 3.23 is the Manning's equation form to use with metric units. Using the theory of minimum unit stream power, Yang and Song (1979) found good agreement between the following measured and computed parameters: S, V, d, VS and n. Parker (1977) also found good agreement for flows where the sediment transport rate was not too high, thus justifying Yang's assumption, mentioned previously, under such conditions. However, the method by Yang (1976) should not be used for critical or supercritical flows, or when the sediment transport rate is high, since the assumption is invalid under these conditions.

Figure 3.3 shows the transport models for noncohesive sediment as a function of the particle Reynolds Number, $\mathrm{Re_p} = w_s D/v$ (v = kinematic viscosity of water), plotted on the x-axis, and the critical bed shear stress plotted on the y-axis. There is no sediment motion below the curved heavy line, which represents the conditions under which incipient motion occurs. As shown, sediment generally moves as bedload immediately after the onset of motion. Bedload transport occurs when noncohesive sediment rolls, slides or jumps (i.e., saltates) along the bed. If the flow continues to increase, then some of the sediment moving as bedload will usually be entrained by vertical turbulent velocity components into the water column and be transported for extended periods of time in suspension. Thus, it takes more energy for the flow to transport sediment in suspension than as bedload. The sediment that is transported in suspension is referred to as suspended load. The portion of Figure 3.3 in which suspended load transport occurs is above the curved thin line. The total load is the sum of the bedload and suspended load. Bedload is typically between 10% and 25% of the total load, though for beds with a high fraction of coarse sediment, the percentage will normally be higher.

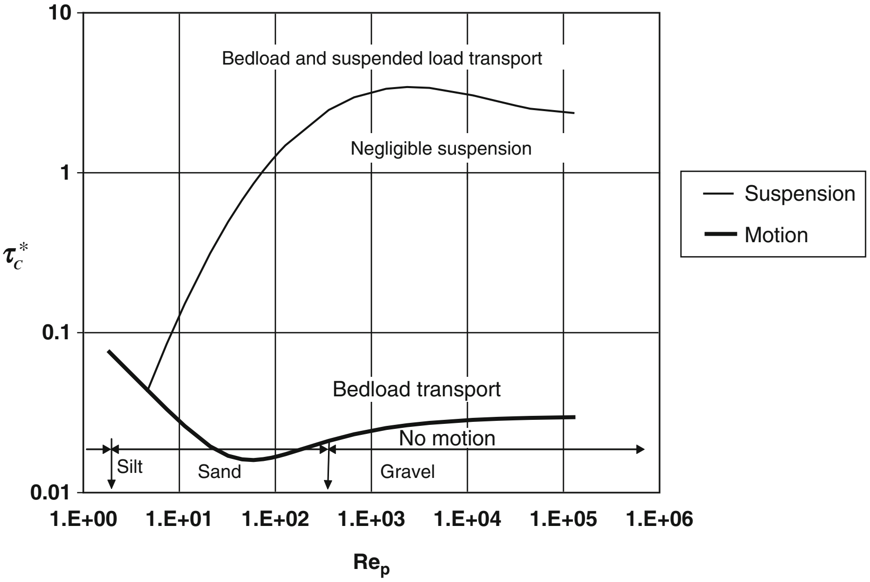


Figure 3.3. Transport modes for noncohesive sediment (after Parker, 2004; reprinted with author's permission).

Many different methods have been developed for calculating the bedload transport rate in open channels. Some of these methods (along with their references) are listed next. The specific shear stress approach of van Rijn (1984a) is also described in some detail in the following.

1. Shear Stress Method: Shields (1936), Chang et al. (1965) and van Rijn (1984a)
2. Energy Slope Method: Meyer-Peter and Muller (1948)
3. Probabilistic Method: Einstein (1950)

Utilizing a shear stress approach, the dimensionless form of the bedload transport rate is given by van Rijn (1984a) as:

$$\frac{q_b}{\rho_s D\sqrt{g'D}} = \frac{0.053}{R_d^{1/5}\theta_{cs}^{2.1}}(\theta - \theta_{cs})^{2.1} \quad \text{(Eq. 3.24)}$$

where $\theta = \frac{\tau_b}{\rho g' D}$, q_b = bedload transport rate (with units of mass per unit time per unit width) and θ_{cs} is defined in Equation 3.15. Sediment is transported as bedload in the direction of the mean flow.

To predict the noncohesive suspended sediment load in a water body, it is necessary to determine whether, for a given particle size and flow regime, the sediment is transported as bedload or as suspended load. van Rijn (1984a) presented the following approach for distinguishing between bedload and suspended load. When the bed shear velocity, u_*, is less than the critical shear velocity, u_{*cs}, no erosion is assumed to occur, and, therefore, no bedload transport occurs. Under this latter flow condition, any sediment in suspension whose critical shear velocity is greater than the bed shear velocity will deposit. When the bed shear velocity exceeds the critical shear velocity for a given particle size, erosion of that size (and smaller) sediment from the bed surface is assumed to occur. Therefore, if the following inequality is true, sediment will be transported as bedload (and not as suspended load):

$$u_{*cs} < u_* < w_s \quad \text{(Eq. 3.25)}$$

Under this inequality condition, any suspended sediment whose critical shear velocity is greater than the bed shear velocity is assumed to deposit. If the bed shear velocity exceeds both the critical shear velocity and settling velocity for a given particle size, then that size sediment (and any smaller) is assumed to be eroded from the bed and transported as suspended load, and any sediment of that particle size (and smaller) already moving as bedload is assumed to be subsequently transported in suspension.

The rate of suspended load transport can be calculated as:

$$q_s = g\,\rho_s \int_a^d \bar{u}\,\bar{c}\,dz \quad \text{(Eq. 3.26)}$$

where q_s = suspended load transport rate per unit width of the open channel (with units of kg/s), $\bar{u}$ = time-averaged velocity at a distance z above the bed, $\bar{c}$ = time-averaged suspended sediment concentration (by volume) at a distance z above the bed and a = thickness of the bedload transport zone. Though not described in this paper, Lane and Kalinske (1941), Einstein (1950), Brooks (1963), and Chang et al. (1965) developed alternative methods to calculate q_s.

The two general approaches used to calculate the total noncohesive sediment load in an open channel consist of: (1) adding the separately estimated bedload and suspended load and (2) using a total load function that directly estimates the total amount of bedload and suspended load transport. Various formulations of the latter are briefly reviewed in this section. The advantage of using a total load approach is that sediment particles can be transported in suspension in one reach of an open channel and as bedload in another reach. In this section, only the unit stream power methods developed by Yang (1973) for estimating the total load will be presented.

The total sediment load function given by Equation 3.26 is valid for total sand concentrations less than about 100 ppm by weight (approximately 100 mg/L). For higher sediment concentrations, Yang (1979) presented the following total load equation, again based on the unit stream power concept:

$$\log C_{ts} = 5.165 - 0.153\log\frac{w_s D}{v} - 0.297\log\frac{u_*}{w_s} + \left(1.780 - 0.360\log\frac{w_s D}{v} - 0.480\log\frac{u_*}{w_s}\right)\log\frac{VS}{w_s} \qquad \text{(Eq. 3.27)}$$

Yang (1984) also presented the following unit stream power based total load equation that is applicable for gravel sized sediment with median particle sizes between 2 and 10 mm:

$$\log C_{tg} = 6.681 - 0.633\ \log\frac{w_s D}{v} - 4.816\ \log\frac{u_*}{w_s} + \left(2.784 - 0.305\ \log\frac{w_s D}{v} - 0.282\ \log\frac{u_*}{w_s}\right)\log\left(\frac{VS}{w_s} - \frac{V_{cr}S}{w_s}\right) \qquad \text{(Eq. 3.28)}$$

For open channels that have bed sediments in the sand to medium gravel size range, i.e., between 0.063 and 10 mm, the total load would be the sum, depending on the value of C_{ts}, of either Equations 3.22 and 3.28 or Equations 3.27 and 3.28.

When the sediment transport capacity in a given reach of an open channel exceeds the total sediment load being transported from upstream reaches, the difference between the capacity and total load is supplied from the bed. This means that the channel will undergo erosion, i.e., degradation. In a natural open channel with nonuniform bed material, the finer surficial bed sediment will be eroded more rapidly than the coarser sediment. By this process, the median diameter of the surficial bed sediment becomes coarser. If the degradation continues, the finer surficial bed sediment will eventually be depleted, leaving a layer of coarser sediment on the bed surface. This process is called *armoring*, and the surficial layer of coarser sediment is called the *armor layer*.

Garcia and Parker (1991) developed the following approach that accounts for the effect of armoring to estimate the near-bed equilibrium concentration, C_{eq}, for bed material that consists of multiple, noncohesive sediment size classes:

$$C_{jeq} = \rho_s \frac{A(\lambda Z_j)^5}{\left(1 + 3.33A(\lambda Z_j)^5\right)} \qquad \text{(Eq. 3.29)}$$

where C_{jeq} = near-bed equilibrium concentration for the *j-th* sediment size class, $A = 1.3\times10^{-7}$, and

$$\lambda = 1 + \frac{\sigma_\phi}{\sigma_{\phi o}}\,(\lambda_o - 1) \qquad \text{(Eq. 3.30)}$$

$$Z_j = \frac{u_*}{w_{sj}} R_{dj}^{3/5}\, F_H \qquad \text{(Eq. 3.31)}$$

$$F_H = \left(\frac{D_j}{D_{50}}\right)^{1/5} \qquad \text{(Eq. 3.32)}$$

where D_{50} = median particle size of the noncohesive bed sediments, σ_{φ} = standard deviation on the sedimentological phi scale of the bed sediment size distribution, $\lambda_o = 0.81$ and $\sigma_{\varphi o} = 0.67$ (Garcia and Parker, 1991). F_H is referred to as a *hiding factor*.

The near-bed equilibrium concentration, which is equal to the sum of C_{jeq} for all sediment classes, is the suspended sediment concentration at a reference height, z_{eq}, above the bed surface. It represents the maximum suspended sediment concentration. Some researchers take z_{eq} to be equal to a, i.e., thickness of the bedload transport zone, in Equation 3.26. Einstein (1950) assumed that $z_{eq} = a = 2D_b$, where D_b was defined as the representative bed sediment grain size. van Rijn (1984b) assumed z_{eq} was equal to three grain diameters. DuBoys (1879) derived the following expression for the thickness of the bedload zone:

$$a = \frac{10(\tau - \tau_c)}{g\,(1-\lambda)(\rho - \rho_s)\,\tan\phi} \qquad \text{(Eq. 3.33)}$$

where λ = porosity of bed material and φ = angle of repose of the bed material.

In response to varying flow conditions, and hence the rate of sediment transport in an alluvial channel, the bed configuration of the water body will change. Simons and Sentürk (1992) defined bed configuration as any irregularity in the bed surface larger than the largest size sediment particle forming the bed. Bed form is one of several synonyms used in the literature for bed configuration. Ripples are one type of bed form that is created by a certain range of flow conditions. Other types of bed forms include: plane bed, dunes, washed out dunes, anti-dunes, and chutes and pools (Simons and Sentürk, 1992). A plane bed does not have any bed features. In other words, the bed is essentially flat or smooth. These will normally only be found in channels with very low flows. With an increase in flow, ripples form in plane bed alluvial channels. Ripples are small, asymmetric triangular shaped bed forms that are normally <5 centimeters (cm) in height and <30 cm in length. In general, ripples have long, gentle slopes on their upstream sides and short, steep slopes on their downstream sides. Dunes are typically larger than ripples but smaller than bars, and have similar longitudinal profiles as ripples. Dune formation occurs near the upper end of the subcritical flow regime, and as such, dunes are out of phase with the water surface; the water surface decreases slightly above the crest of the dune. Washed-out dunes (also referred to as a transitional bed form) consist of intermixed, low amplitude dunes and flat areas. These typically occur around the critical flow condition. Antidunes are usually more symmetrical (in their longitudinal profile) than dunes, and form under supercritical flows. Thus, antidunes are in phase with the water surface elevation and move in the upstream direction. Chutes and pools usually occur on relatively steep channel slopes, and as such, high velocities and sediment discharges occur in the chutes.

3.2.3 Cohesive Sediment Transport

The discussion in this section concentrates on cohesive sediment transport in estuaries. The difference between the description given here and that for cohesive sediment transport in rivers and lakes/reservoirs deals primarily with the hydrodynamics of the water bodies and the effect of salt water on the coagulation/flocculation process. The basic transport processes of erosion, advection, dispersion, settling, deposition and consolidation are essentially the same in all types of water bodies. Thus, this brief overview of cohesive sediment transport processes in estuaries is, for the most part, relevant to all water bodies, and will provide the reader with an expanded description of sediment transport processes.

Cohesive (fine-grained) sediment transport, especially in estuaries and coastal waters, is a complex process involving a strong coupling among tides, baroclinic circulation and the

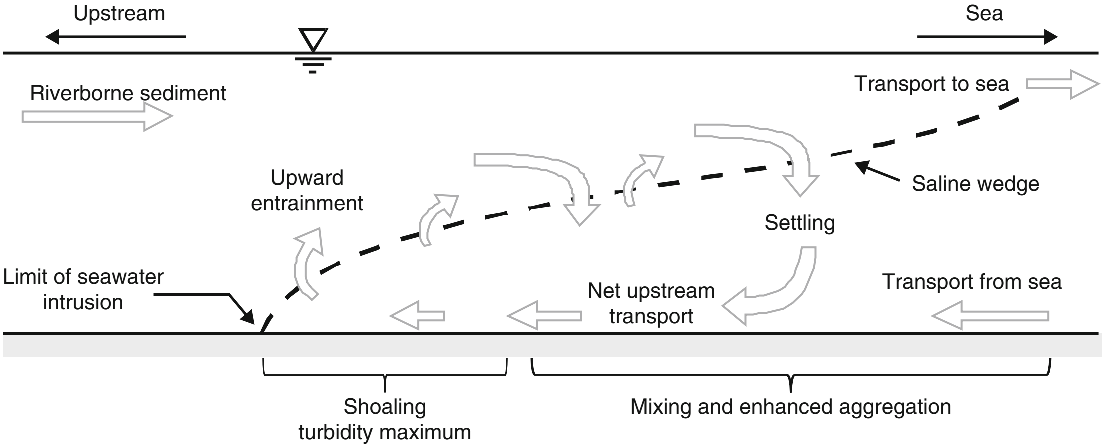


Figure 3.4. Schematic representation of transport and sedimentation processes in the mixing zone of a stratified estuary (after Mehta and Hayter, 1981).

coagulated/flocculated sediment. For an extensive description of this process, the reader is referred to Postma (1967), Partheniades (1971), Barnes and Green (1971), Krone (1972), Kirby and Parker (1977), Kranck (1980) and Dyer (1986). Figure 3.4 is a schematic depiction of the tidally-averaged sediment transport processes in a stratified (i.e., salt wedge) estuary, e.g., Lower Duwamish Waterway, Seattle. In the case of a partially mixed estuary (e.g., Chesapeake Bay), the description would have to be modified, i.e., there would not be a well-developed salt wedge, but since relatively steep vertical density gradients are sometimes present even in such a case, the sediment transport processes would generally remain qualitatively similar to that depicted.

As indicated in Figure 3.4, sediments from upstream fresh water sources arrive in the estuarial mixing zone. The high level of turbulence and the increasingly saline waters will cause flocs to form and grow in size as a result of frequent interparticle collisions and increased cohesion. Large flocs will settle to the lower portion of the water column because of their high settling velocities. Results from laboratory experiments show that floc settling velocities can be up to four orders of magnitude larger than the settling velocities of the individual particles (Bellessort, 1973). Some of the sediment will deposit; the remainder will be carried upstream near the bottom until periods close to slack water when the bed shear stresses decrease sufficiently to permit deposition in the ETM, after which the sediment starts to undergo self-weight consolidation. The depth to which the new deposit scours when the currents increase after slack will depend on the bed shear stresses imposed by the flow and the shear strength of the deposit. Net deposition will occur when the bed shear during flood, as well as during ebb, is insufficient to resuspend all of the material deposited during preceding slack periods. Some of the sediment that is resuspended may be re-entrained throughout most of the length of the mixing zone to levels above the seawater-fresh water interface, and subsequently transported downstream. At the seaward end, some material may be transported out of the estuary, a portion of which could ultimately return with the net upstream bottom current.

In the mixing zone of a typical estuary, the sediment transport rates often are an order of magnitude greater than the inflow rate of new sediment derived from upland or oceanic sources. The estuarial sedimentary regime is characterized by several periodic (or quasi-periodic) macro-time scales, the most important of which are the tidal period (diurnal, semi-diurnal, or mixed) and one-half the lunar month (spring-neap-spring cycle). The tidal period is the most important since it is the fundamental period that characterizes the basic mode of sediment transport in an estuary. The lunar month is often significant in determining net

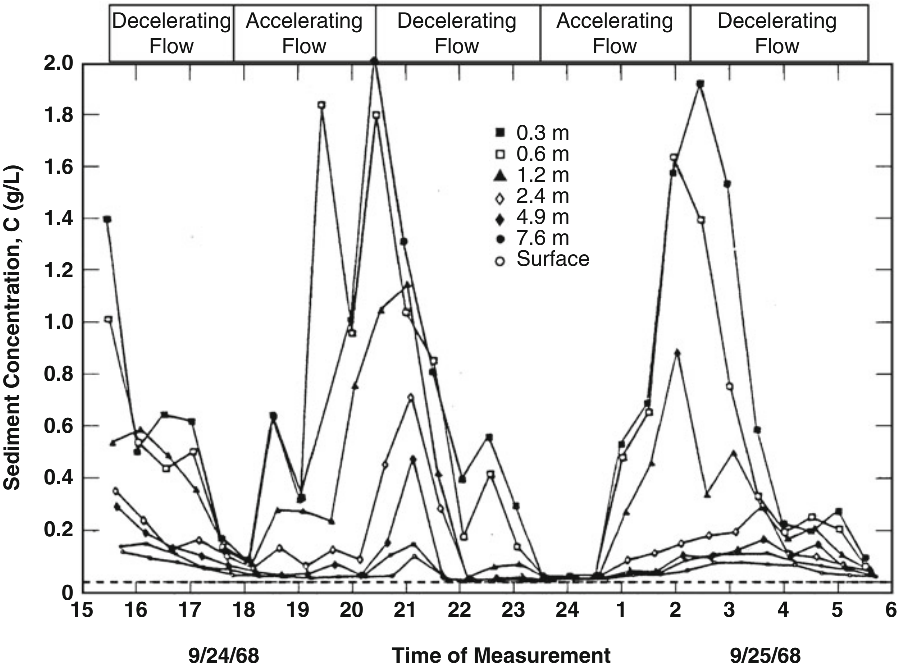


Figure 3.5. Time and depth variation of suspended sediment concentration in the Savannah River estuary (after Krone, 1972).

sedimentation rates. Episodic high energy events due to high precipitation-induced riverine flows or atmospheric forcings in the form of tropical storms or nor'easters can significantly alter the depicted flow regime and result in an increase in the sediment transport rate by two or more orders of magnitude.

From an Eulerian point of view, the superposition of oscillating tidal flows on the quasi-steady state transport phenomenon depicted in Figure 3.4 results in corresponding oscillations of the suspended sediment concentration with time as shown in Figure 3.5. Such a variation of the suspended load ultimately results from a combination of advective and dispersive transport, erosion and deposition. Because of the complexity of the phenomenon, more than one interpretation is possible as far as any schematic representation of these phenomena is concerned. One such representation is shown in Figure 3.5. According to this description, cohesive sediments can exist in four different physical states in an estuary: mobile suspension, stationary suspension, partially consolidated bed, and settled bed. The last two are formed as a result of consolidation of a stationary suspension. A stationary suspension, a partially consolidated bed, and a settled bed can erode if the shear stress exceeds a certain critical value. Erosion of a stationary suspension is referred to as redispersion or mass erosion, whereas erosion of a partially consolidated bed or a settled bed is termed resuspension or surface erosion.

To summarize, the sediment transport regime is controlled by the hydrodynamics, the chemical composition of the fluid and the physicochemical properties of the cohesive sediments. These factors affect the processes of erosion, advection, dispersion, flocculation, settling, deposition and consolidation. A brief description of these processes follows that of cohesive sediment beds.

A flow-deposited bed of cohesive sediment flocs possesses a vertical density and bed shear, i.e., yield, strength profile. The average values of bed density and bed shear strength increase

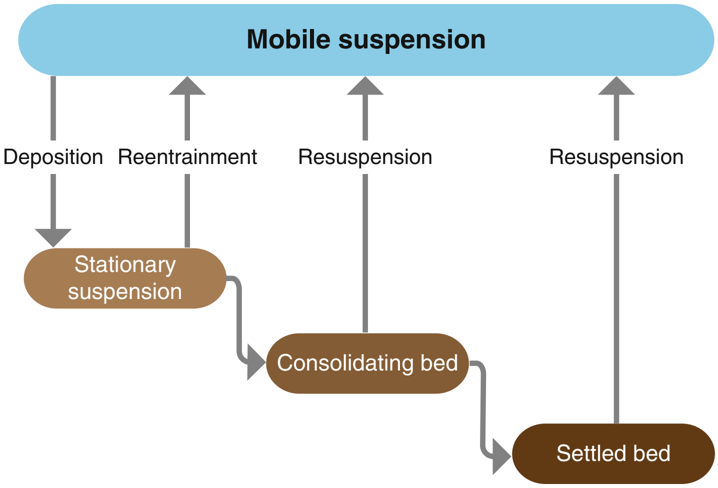


Figure 3.6. Schematic representation of the physical states of cohesive sediment in an estuarial mixing zone (after Mehta et al., 1982a).

and their vertical profiles change with time, primarily due to consolidation and secondarily due to thixotropy and associated physicochemical changes affecting inter-particle forces. Consolidation changes the erosive behavior of cohesive sediment beds in two ways: (1) as the shear strength of the bed increases due to consolidation, the susceptibility of the bed to erosion decreases and (2) the vertical shear strength profile determines the depth into the bed that a bed will erode when subjected to excess shear, i.e., a bed shear stress in excess of the bed shear strength.

Estuarial sediment beds, typically composed of flow-deposited cohesive sediments, can be assumed to occur in three different states: stationary suspensions, partially consolidated beds and settled (or fully consolidated) beds (see Figure 3.6). Stationary suspensions are defined by Parker and Lee (1979) as assemblages of high concentrations of sediment particles that are supported jointly by the water and developing skeletal soil framework and have no horizontal movement. These suspensions develop whenever the settling rate of concentrated mobile suspensions exceeds the rate of self-weight consolidation (Parker and Kirby, 1982). They tend to have a high water content and a very low shear strength that must be at least as high as the bed shear that existed during the deposition period (Mehta et al., 1982a). Thus, they exhibit a definite non-Newtonian rheology. Kirby and Parker (1977) found that the stationary suspensions they investigated had a surface bulk density of approximately 1,050 kilograms per cubic meter (kg/m^3) and a layered structure.

Whether redispersion of these suspensions occurs during periods of erosion depends upon the mechanical shear strength of the floc network. That portion of the flocs remaining on the bed undergoes: (1) self-weight consolidation and (2) thixotropic effects, defined as the slow rearrangement of deposited flocs attributed to internal energy and unbalanced internal stresses (Mitchell, 1961), both of which reduce the order of flocculation of sub-surface bed layers. This implies that the bed becomes stratified with respect to density and shear strength, with both properties typically increasing monotonically with depth, at least under laboratory conditions (Mehta et al., 1982a). Continued consolidation eventually results in the formation of settled mud, defined by Parker and Lee (1979) as “assemblages of particles predominantly supported by the effective contact stresses between particles as well as any excess porewater pressure.” This portion of the bed has a lower water content, lower order of flocculation and higher shear strength.

The settled mud in the Severn Estuary and Inner Bristol Channel, United Kingdom, was found to possess a bulk (i.e., wet) density ranging from 1,300 to 1,700 kg/m^3 (Kirby and Parker, 1983). The nature of the density and shear strength profiles typically found in cohesive sediment beds has been revealed in laboratory tests by, among others, Richards et al. (1974), Owen (1975), Thorn and Parsons (1980), Parchure (1980), Bain (1981), Dixit (1982) and Burt and Parker (1984).

Erosion of cohesive sediments occurs whenever the shear stress induced by water flowing over the sediment bed is great enough to break the electrochemical interparticle bonds (Partheniades, 1965; Paaswell, 1973). When this happens, erosion takes place by the removal of individual sediment particles and/or flocs. This type of erosion is time dependent and is defined as surface erosion or resuspension. In contrast, another type of erosion occurs more or less instantaneously by the removal of relatively large pieces of the bed. This process is referred to as mass erosion or redispersion, and occurs when the bed shear stress exceeds the bed bulk strength along some deep-seated plane and is much greater than the bed shear strength of the surficial sediment.

A number of laboratory investigations were carried out in the 1960s and 1970s in order to determine the rate of resuspension, ε, defined as the mass of sediment eroded per unit bed surface area per unit time as a function of bed shear in steady, turbulent flows. An important conclusion from those tests was that the usual soil indices, such as liquid and plastic limit, do not adequately describe the erosive behavior of these sediments (Mehta, 1981). For example, Partheniades (1962) concluded that the bed shear strength as measured by standard tests, e.g., the direct-shear test (Terzaghi and Peck, 1960), has no direct relationship to the sediment's resistance to erosion that is essentially governed by the strength of the interparticle and interfloc bonds.

The sediment composition, pore and eroding fluid compositions, and structure of the flow-deposited bed at the onset of erosion must be determined in order to properly define the erosion resistance of the bed. Sediment composition is specified by the GSD of the bed material (i.e., weight fraction of clays, silts), the type of clay minerals present and the amount and type of organic matter. The compositions of the pore and eroding fluids are specified by the temperature, pH, total amounts of salts and type and abundance of ions present, principally chloride (Cl^-), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). Cementing agents, such as iron oxide, can significantly increase the resistance of a sediment bed to erosion. Measurement of the electrical conductivity is used to determine the total salt concentration in the pore and eroding fluids. The effect of the bed structure, specifically the vertical sediment density and shear strength profiles, on the rate of erosion is discussed by Lambermont and Lebon (1978) and Mehta et al. (1982a).

The erosive forces, characterized by the flow-induced instantaneous bed shear stress, are determined by the flow characteristics and the surface roughness of the fluid-bed interface. Several different types of relationships between the rate of erosion, ε, and the time-mean value of the flow-induced bed shear stress, τ_b, have been reported for non-stratified beds. These include statistical-mechanical models (Partheniades, 1965; Christensen, 1965), a rate process model (Paaswell, 1973; Kelly and Gularte, 1981) and empirical relationships (Ariathurai and Arulanandan, 1978).

Ariathurai and Arulanandan (1978) found the following general relationship for the resuspension rate of consolidated beds:

$$\varepsilon = M'\left(\frac{\tau_b - \tau_c}{\tau_c}\right) \quad \text{(Eq. 3.34)}$$

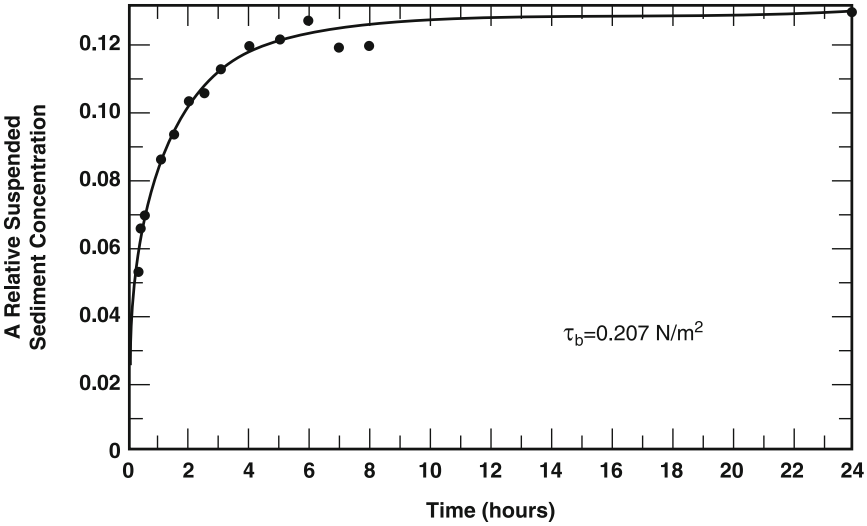


Figure 3.7. Relative suspended sediment concentration versus time for a stratified bed (after Mehta and Partheniades, 1979).

where $M' = M\tau_c$, where M is termed the erodibility constant, τ_b is the bed shear stress, and τ_c is the bed shear strength. The term inside the parentheses on the right-hand-side of Equation 3.34 is referred to as the normalized excess bed shear stress. Values for M and τ_c are normally determined using either laboratory tests (Parchure, 1984) or using a device such as the SEDFLUME (McNeil et al., 1996).

Gailani et al. (1991) found the following relationship between the resuspension potential, E, defined as the total mass of sediment that can be resuspended at a given shear stress, and the normalized excess shear stress:

$$\mathrm{E} = \frac{a_o}{t_d^n}\left[\frac{\tau_b - \tau_c}{\tau_c}\right]^m \qquad \text{(Eq. 3.35)}$$

where t_d = time after deposition of sediment in units of days; and a_o, n, m and τ_c are sediment-specific empirical coefficients, with n and m approximately equal to 2 and 3, respectively.

Figure 3.7 shows the measured variation of C, expressed as a relative concentration by dividing the measured suspended sediment concentration by the initial suspended sediment concentration, with time typically found by several investigators (Partheniades, 1962; Mehta and Partheniades, 1979; Mehta et al., 1982a) in laboratory resuspension tests with flow-deposited (i.e., stratified) beds under a constant τ_b. As observed, dC/dt is high initially, decreases monotonically with time, and appears to approach zero. The value of τ_c at the depth of erosion at which dC/dt, and therefore ε that is proportional to dC/dt, becomes essentially zero has been interpreted to be equal to τ_b (Mehta et al., 1982a). This interpretation is based on the hypothesis that erosion continues as long as $\tau_b > \tau_c$. Erosion is arrested at the bed level at which $\tau_b - \tau_c = 0$. This interpretation, coupled with measurement of $\rho_B(z_b)$, i.e., the dry bed density profile, and the variation of C with time resulted in an empirical relationship for the rate of erosion of stratified beds.

Utilizing this above approach, resuspension experiments with deposited beds were performed by Parchure (1980) in a rotating annular flume and by Dixit (1982) in a recirculating straight flume. The following empirical relationship between ε and $\tau_b - \tau_c(z_b)$ was derived from these experiments:

$$\varepsilon = \varepsilon_o \exp\left[\alpha \frac{\tau_b - \tau_c(z_b)}{\tau_c(z_b)}\right] \tag{Eq. 3.36}$$

where ε_o and α are empirical resuspension coefficients. This relationship is analogous to the rate expression that results from a heuristic interpretation of rate process theory for chemical reactions (Mehta et al., 1982a). Christensen and Das (1973), Paaswell (1973) and Kelly and Gularte (1981) have used rate process theory to explain erosional behavior of cohesive beds. By analogy, ε is a quantitative measure of the work done by τ_b on the system, i.e., the bed, and ε_o and $\alpha/\tau_c(z_b)$ are measures of the internal energy, i.e., bed resistance to an applied external force.

An important conclusion reached from these experiments was that new deposits should be treated differently from consolidated beds (Mehta et al., 1982a). The rate of surface erosion of new deposits is best evaluated using Equation 3.36, while the erosion rate for settled beds is best determined using Equation 3.34, in which ε varies linearly with the normalized excess bed shear stress. The reasons for this differentiation in determining ε are twofold. First, typical τ_c and ρ_B profiles in settled beds vary less significantly with depth than in new deposits, and may even be nearly invariant. Therefore, the value of $(\tau_b/\tau_c) - 1 = \Delta\tau_b^*$ will be relatively small. For $\Delta\tau_b^* \ll 1$ the exponential function in Equation 3.33 can be approximated by $\alpha \cdot \left(1 + \Delta\tau_b^*\right)$ that represents the first two terms in the Taylor series expansion of $\exp\left(\alpha \cdot \Delta\tau_b^*\right)$. Thus, for small values of $\Delta\tau_b^*$, both expressions for ε vary linearly with $\Delta\tau_b^*$ and, therefore, the variation of ε with depth in settled beds can be just as accurately and more simply determined using Equation 3.34. Second, the laboratory resuspension tests required to evaluate the coefficients ε_o and α for each partially consolidated bed layer cannot be practically or easily performed using vertical sections of an original settled bed (obtained from cores). A simpler laboratory test has been described by Ariathurai and Arulanandan (1978) to evaluate the variability of M with depth.

Parchure and Mehta (1985) developed the following relationship for ε that is applicable for soft, cohesive sediment deposits such as the top, active layer of sediment beds in estuaries:

$$\varepsilon = \varepsilon_f \exp\left[\alpha(\tau_b - \tau_s)^{1/2}\right] \tag{Eq. 3.37}$$

where $\varepsilon_f =$ floc erosion rate (gm/m^2-s), $\tau_s =$ bed shear strength (Pa) and $\alpha =$ a factor that can be shown to be inversely proportional to the absolute temperature (Parchure, 1984). ε_f is defined to be the erosion rate when the time-averaged bed shear stress is equal to the bed shear strength, i.e., $\tau_b = \tau_s$. Even under this condition, some erosion of particles or flocs will occur due to the stochastic nature of turbulence and therefore in the instantaneous value of τ_b.

Jepsen et al. (1997) studied the effect of sediment bulk density on erosion rates of three different types of sediment during which the bulk densities of the sediments were experimentally determined as a function of depth into the sediment core for consolidation times varying from 1 to 60 days. The experiments were performed in a SEDFLUME (McNeil et al., 1996) during which the gross erosion rates were measured as a function of bed shear stress and depth into the core (from which the bulk density could be determined). The gross erosion rate, E, was approximated as a function of the bulk density and bed shear stress by the following equation:

$$E = A\tau^n\rho^m \tag{Eq. 3.38}$$

For the three sediments tested, n varied from 1.89 to 2.23; m varied from -45 to -95; and A varied from 3.65×10^3 to 2.69×10^6. This equation implicitly accounted for the effect of consolidation by including the time and depth varying bulk density as one of the independent parameters.

Once eroded from the bed, cohesive sediment is transported mostly as suspended load, though clumps/aggregates of cohesive sediments have been observed rolling along the bottom of both laboratory flumes and shallow rivers. The latter form of transport cannot be predicted at present. The transport of cohesive sediments in suspension is the result of three processes: (1) advection – the sediment is assumed to be transported at the speed of the local mean flow; (2) turbulent diffusion – driven by spatial suspended sediment concentration gradients, the material is diffused laterally across the width of the flow channel, vertically over the depth of flow, and longitudinally in the direction of the transport; and (3) longitudinal dispersion – the suspended sediment is dispersed in the flow direction by spatial velocity gradients (Ippen, 1966).

The principle of conservation of mass with appropriate source and sink terms describes the advective and dispersive transport of suspended sediment in turbulent flows. This principle, expressed by the advection-dispersion equation, says that the time-rate of change of mass of sediment in a stationary control volume is equated to the spatial rate of change of mass due to advection plus the spatial rate of change of mass due to turbulent diffusion and dispersion processes. The three-dimensional form of the advection-dispersion transport equation is:

$$\begin{aligned}\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+(w-w_{sc})\frac{\partial C}{\partial z}&=\frac{\partial}{\partial x}\left[K_{xx}\frac{\partial C}{\partial x}+K_{xy}\frac{\partial C}{\partial y}+K_{xz}\frac{\partial C}{\partial z}\right]\\&+\frac{\partial}{\partial y}\left[K_{yx}\frac{\partial C}{\partial x}+K_{yy}\frac{\partial C}{\partial y}+K_{yz}\frac{\partial C}{\partial z}\right]+\frac{\partial}{\partial z}\left[K_{zx}\frac{\partial C}{\partial x}+K_{zy}\frac{\partial C}{\partial y}+K_{zz}\frac{\partial C}{\partial z}\right]+S_T \qquad \text{(Eq. 3.39)}\end{aligned}$$

where K_{ij} = effective sediment dispersivity tensor and S_T = the net source/sink term that accounts for source(s) (i.e., addition) of sediment to the water column due to erosion and other inputs, and sink(s) (i.e., loss) of sediment due to deposition and other removals. Implicit in this equation is the assumption that suspended material has the same velocity as the water. Sayre (1968) verified the reasonableness of this assumption for sediment particles less than about 100 μm in diameter. Rolling and saltation of sediment that occur during bed load transport can result in a significant difference between water and sediment velocities, so the assumption of equal velocity is not applicable to bed load. The net source/sink term in Equation 3.39 can be expressed as:

$$S_T=\left.\frac{dC}{dt}\right|_e+\left.\frac{dC}{dt}\right|_d+S_L \qquad \text{(Eq. 3.40)}$$

where $\left.\frac{dC}{dt}\right|_e$ is the rate of sediment addition (source) due to erosion from the bed, and $\left.\frac{dC}{dt}\right|_d$ is the rate of sediment removal (sink) due to deposition of sediment. S_L accounts for removal (sink) of a certain mass of sediment, for example, by dredging in one area (e.g., a navigational channel) of a water body, and/or dumping (source) of sediment as dredge spoil in another location.

The dispersive transport terms in Equation 3.39 include the effects of spatial velocity variations in bounded shear flows and turbulent diffusion. Thus, the effective sediment dispersivity tensor in Equation 3.39 must include the effect of all processes whose scale is less than the grid size of the model, or, in other words, what has been averaged over time and/or space (Fischer et al., 1979).

Turbulent diffusion is defined as “the transport in a given direction at a point in the flow due to the difference between the true advection in that direction and the time average of the advection in that direction,” and dispersion is defined as “the transport in a given direction due to the difference between the true advection in that direction and the spatial average of the advection in that direction" (Holley, 1969). Holley delineates the fact that turbulent diffusion and dispersion are both actually advective transport mechanisms, and that in a given flow field, the relative importance of one mechanism over the other depends on the magnitude of the concentration gradient. In Equation 3.39, the effective sediment dispersion coefficients are equal to the sum of the turbulent diffusion and dispersion coefficients. This approach follows the analysis of Aris (1956) that showed that the coefficients due to turbulent diffusion and shear flow (dispersion) were additive. Thus, analytical expressions used for the effective sediment dispersion tensor should represent both diffusion and dispersion. Analytical expressions for the sediment (mass) diffusion coefficients can be obtained by analogy with the kinematic eddy viscosity. The Reynolds analogy assumes that the processes of momentum and mass transfer are similar, and that the turbulent diffusion coefficient and the kinematic eddy viscosity are linearly proportional. Jobson and Sayre (1970) verified the Reynolds analogy for sediment particles in the Stokes range (less than about 100 μm in diameter). They found that the "portion of the turbulent mass transfer coefficient for sediment particles that is directly attributable to tangential components of turbulent velocity fluctuations: (a) is approximately proportional to the momentum transfer coefficient and the proportionality constant is less than or equal to 1; and (b) decreases with increasing particle size." Therefore, the effective sediment mass dispersion coefficients for cohesive sediments may be justifiably assumed to be equal to those for water.

Fischer et al. (1979) define four primary mechanisms of dispersion in estuaries: (1) gravitational circulation, (2) shear-flow dispersion, (3) bathymetry-induced dispersion and (4) wind-induced circulations. The last three mechanisms occur in freshwater water bodies as well. Gravitational or baroclinic circulation in estuaries is the flow induced by the density difference between freshwater at the landward end and sea water at the ocean end. Vertical gravitational circulation occurs with predominantly seaward flow in the upper part of the water column and landward flow in the lower part of the water column.

Deposition of flocs occurs relatively quickly during slack water. Settling and deposition also occurs in slowly moving and decelerating flows, as was observed in the Savannah River Estuary during the second half of flood and ebb flows (Krone, 1972). Under these flow conditions, only those flocs with shear strengths of sufficient magnitude to withstand the highly disruptive shear stresses in the near bed region will actually deposit and adhere to the bed. Thus, deposition is governed by bed shear stresses, turbulence structure above the bed, settling velocity, type of sediment, flow depth, suspension concentration, and ionic constitution of the suspending fluid (Mehta and Partheniades, 1973). Deposition has been defined to occur when τ_b is not high enough to resuspend sediment that settles onto and bonds with the bed surface. This process, therefore, involves two other processes: settling and bonding. Laboratory studies on the depositional behavior of cohesive sediment in steady turbulent flows have been conducted by, among others, Krone (1962), Rosillon and Volkenborn (1964), Partheniades (1965), Mehta and Partheniades (1975), Mehta et al. (1982b), Shrestha and Orlob (1996) and Teeter (2000).

The most commonly used expression for the sediment mass deposition rate, given initially by Einstein and Krone (1962), is:

$$\frac{dC}{dt} = -\frac{w_{sc}C}{d}\left(1 - \frac{\tau_b}{\tau_{cd}}\right) \qquad \text{(Eq. 3.41)}$$

where τ_{cd} = critical shear stress for deposition, above which no deposition occurs. The value of τ_{cd} was found to be equal to 0.06 pascals (Pa) for San Francisco Bay mud with C <300 mg/L (Krone, 1963), and values from 0.02 to 0.2 Pa have been reported in the literature. Mehta and Lott (1987) found Equation 3.41 to agree reasonably well with laboratory data for suspended sediment concentrations up to approximately 1 g/L.

Deposited cohesive sediments usually form at first a thin surface layer that is often called a fluff or benthic nepheloid layer that is often <1 cm in thickness. Cohesive sediments and organic material in this layer (that would be part of a stationary suspension when not in motion) are usually easily resuspended by tides, currents in rivers, vessels or other forces. These sediments re-deposit when the kinetic energy of the gravity-generated currents, tides, waves, winds, atmospheric pressure fronts, etc., acting on the water body is reduced. A cohesive sediment bed is formed when these deposited sediment particles comprising the fluff layer or stationary suspension begin to interact and form a soil that transmits an effective stress by virtue of particle-to-particle contacts. The self-weight of the particles, as well as deposition of additional material, brings the particles closer together by expulsion of porewater between the particles. A soil is formed when the water content of the sediment-water suspension decreases to the fluid limit. Unfortunately, there is not a unique water content value for cohesive soils at which the suspension changes into a soil (Been and Sills, 1981).

During the transition from suspension to soil, an extremely compressible soil framework or skeleton develops (Been and Sills, 1981). The strains involved in this first stage of consolidation are relatively large and can continue for several days or even months. The straining and upward expulsion of porewater gradually decreases as the soil skeleton continues to develop. Eventually, this skeleton reaches a state of equilibrium with the normal stress component of the overlying sediment (Parker and Lee, 1979).

During the early stages of consolidation, the self-weight of the soil mass near the bed surface is balanced by the seepage force induced by the upward flow of porewater from the underlying sediment. As the soil continues to undergo self-weight consolidation and the upward flux of porewater lessens, the self-weight of this near surface soil gradually turns into an effective stress. This stress will first crush the floc structure and then the flocs themselves. Primary consolidation is defined to end when the excessive porewater pressure has completely dissipated (Spangler and Handy, 1982). Secondary consolidation can continue for many weeks and is the result of plastic deformation of the soil under its overburden. The shear strength of clays is due to the frictional resistance and interlocking between particles (physical component), and interparticle forces (physicochemical component) (Karcz and Shanmugam, 1974; Parchure, 1980). Consolidation results in increasing bed density and shear strength (Hanzawa and Kishida, 1981). Figure 3.8 shows the increase in the shear strength profile with consolidation time and bed depth for flow-deposited kaolinite beds in tap water.

Wave-induced normal stresses applied to a cohesive sediment bed may lead to a decrease in the bulk density and bed shear strength, and ultimately could lead to liquefaction of the bed. *Liquefaction* is defined as an outcome of the loss of the yield strength of initially solid or intact sediment bed, and occurs when the bed surface is perturbed by wave-induced cyclical shear and normal stresses that exceed the yield strength up to some depth in the sediment bed. The portion of the sediment bed above this depth is liquefied. The yield strength, which is a bulk property of the soil, is characterized by the Bingham-plastic yield stress (Barnes et al., 1989).

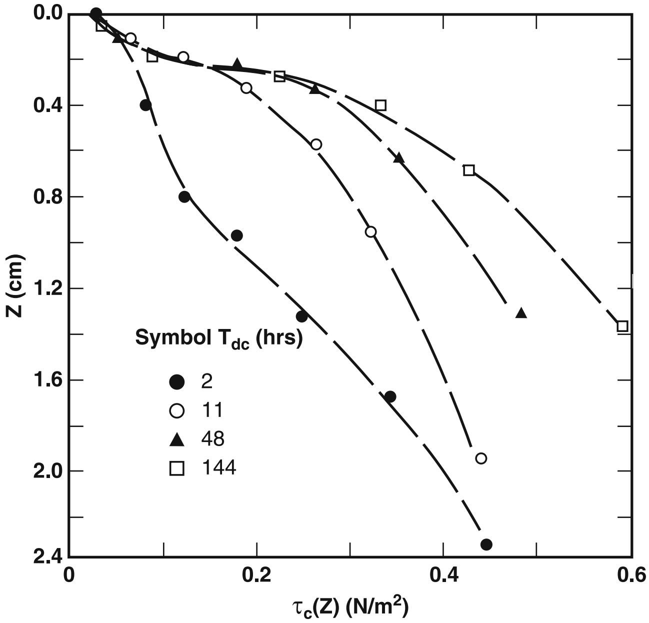


Figure 3.8. Bed shear strength versus distance below the initial bed surface for various consolidation periods, T_{dc} (after Dixit, 1982).

3.3 SEDIMENT TRANSPORT ASSESSMENT

This section provides guidance to use when it is necessary to assess and/or quantify sediment transport. The methodology described here is called a Sediment Transport Assessment (SEDTA). For example, it is often necessary for remedial project managers to conduct a SEDTA in support of a remedial alternatives evaluation for contaminated sediment sites. Site-specific information on sediment transport collected and evaluated using the approach presented here can be used to develop and refine the conceptual site model (CSM) for the site. A CSM describes, among other things, how the sediment became contaminated and the current and future pathways that could result in exposure.

A SEDTA is generally applicable to both freshwater and near-shore marine sediment sites, and involves using a systematic approach that (1) identifies the processes and mechanisms that might result in transport, (2) determines the most appropriate methods to use to assess sediment resuspension and deposition and (3) quantifies sediment resuspension and deposition rates under varying flow conditions.

3.3.1 Assessment Methodology

The recommended methodology for performing a SEDTA is described in this section. The order of the tasks given below might be modified for a particular site, though it is recommended that the first two tasks be performed first.

Table 3.3. Site-Specific Considerations in Project Scoping During the SEDTA

Site-Specific Considerations in Project Scoping During the SEDTA
• Availability of historical data • Understanding of site characteristics and sediment dynamics provided from existing information • Potential natural events of concern that may impact sediment stability (e.g., floods or wind waves, extreme sea level fluctuations, etc.) • Potential human activities that may impact sediment stability (e.g., marine navigation, construction or alternative site uses) • Historic and future use of hydraulic control structures such as dams, etc.

3.3.1.1 Project Scoping and Study Questions Formulation

This task should be performed first so that collection of needed data can be planned early in this process to insure that critical data needs are adequately met. Key site-specific questions should be identified; these will depend on the level of study expected. In defining study questions, the focus should be on questions that identify the most relevant information needs. Project scoping considerations for a specific site may include those shown in Table 3.3.

3.3.1.2 Current and Historical Site Review

Historical site review may include study of past events, or simply compilation of relevant, available historical site information such as that described in Table 3.3. All hydrologic, hydraulic, and contamination data collected/measured by the state and federal agencies should be thoroughly reviewed. In addition, previous environmental studies that have been performed at the site as well as other studies such as conventional water quality studies, flood insurance studies, bathymetric surveys, hydrodynamic measurements, and modeling must be identified and reviewed. Unless significant changes have occurred to the water body since the previous data collection, these data can generally be assumed to accurately reflect present conditions and be extremely valuable for the SEDTA.

Historic sediment bed data can normally be directly used in the SEDTA. However, the option of using existing sediment data needs to be assessed differently. These data may reflect existing conditions if the bed is in relative equilibrium, or if the bed evolves significantly only during relatively large events and no such event has occurred since the earlier sampling. Recent data are required to determine if the historic data reasonably represent present conditions.

Other recommended sources of information and data are described below. In addition to the information listed below, look for the timeline and description of system modifications, such as dams, revetments, bridges, dredged channels, or other structures that may have impacted the flow regime, and therefore the sediment transport in the water body.

Federal Government Agencies:

- U.S. Army Corps of Engineers (USACE): Check with the USACE District Office whose jurisdiction includes the contamination site. Often the best way to gather historic dredging and bathymetric data is to contact someone directly in the District Office. If maintenance dredging is or has been performed in this water body, ask for copies of dredging surveys. Also check the following website for information – http://www.ndc.iwr.usace.army.mil/dredge/dredge.htm; accessed August 30, 2012. Review of dredging records can be used to determine average sediment accumulation rates, areas of deposition, channel deepening, and areas of potential sediment column disturbance (for design of coring programs and interpretation of profiles).

- U.S. Geological Survey (USGS): The USGS maintains elevation maps for many navigable and non-navigable water bodies. Call the USGS Water Resources Division (WRD) office in the state in which the contaminated site is located and ask for a list of gaging stations in the site's watershed. Also check the WRD website (http://water.usgs.gov/; accessed August 30, 2012) for information. On that web page, select the state in which the contaminated water body is located, e.g., http://ms.water.usgs.gov/ (accessed August 30, 2012) for Mississippi, and look for stage, discharge, and water quality data for the contaminated water body on that website. The website http://www.usgs.gov/pubprod/ (accessed August 30, 2012) provides access to most online USGS maps and products.
- National Oceanic and Atmospheric Administration (NOAA): Go to http://www.noaa.gov (accessed August 30, 2012) and look for data on the contaminated water body. Nautical charts are available online for all coastal areas, including the Great Lakes.
- The federal government has a clearing house website for geospatial data (http://gos2.geodata.gov/wps/portal/gos; accessed August 30, 2012). This site is extremely valuable for collecting additional information/data about the area in which the contaminated water body is located.

State Agencies: Check with the state's natural resources and environmental regulation agencies for information and data on the contaminated water body. Also, if there are any bridge crossings in the area of contamination, check with the state's Department of Transportation for hydraulic information/data at the location of the bridge.

Local Governments (City, County, etc.): Check with extension agencies and water boards for information and data on the contaminated water body.

Local and State Universities: Check with the colleges of science and engineering at these universities to locate studies conducted by current or past faculty on the water body. Also, check the libraries at these universities. Some universities have all library holdings listed on their website. This allows searches to be made of all their holdings that contain the name of the contaminated water body or the name(s) of the potentially responsible party (PRP).

County/City Libraries and Newspapers: Search these entities for articles on the source(s) of contamination, and records of previous floods, tropical storms, nor'easters, etc., that impacted the area of contamination (often anecdotal or qualitative information).

Private Entities: There are also private entities that have reason to collect data, e.g., industrial plants near the water body, port authorities at water intakes, and sewage processing plants. In general, it is best to determine who is responsible for water quality issues and contact that person directly.

3.3.1.3 Bathymetric Analysis

Bathymetric data reflect water body evolution over time due to sediment accumulation, erosion, dredging, filling, or other actions. Bathymetric data exist for most U.S. waterways. The USGS, USACE, NOAA, as well as some state agencies collect bathymetric data in navigational channels and adjacent to shoreline or marine structures on large water bodies. The USACE collects data on navigable waterways. These surveys are generally at higher spatial and temporal frequency than NOAA charts, but are often (but not always) confined to the navigation channel. USACE data are not as readily available as NOAA nautical charts. However, historic bathymetric data are available through the USACE. The USACE generally surveys channels before and after dredging. This can provide high-frequency data going back 100 yr or more. On smaller water bodies and on rivers, state transportation departments may have bathymetric records at bridge crossings. All bathymetric surveys are referenced to some datum, which may differ among surveys and the datum may change over time. The user must know the datum for each bathymetric survey being used for historic analysis. When accounting for the factors mentioned in the next paragraph, bathymetric data can be used to evaluate long-term sedimentation or erosion rates by determining the differences between two or more bathymetric surveys. In addition, before-and-after comparisons of bathymetric data can be used to assess impacts of extreme events, e.g., out-of-bank floods, when surveys preceding and following events are available. These are valuable data for the SEDTA by locating areas that are subject to erosion during extreme events as well as areas that are net depositional.

When comparing bathymetric surveys, it is important to quantify the uncertainty in both horizontal and vertical measurements, particularly if the bathymetric surveys to be compared were performed at two different times (e.g., years apart), or by different surveying contractors, or used different vertical datums or different types of survey instruments (e.g., single beam versus multi-beam echo sounder), and take this uncertainty into account in performing the comparison. There is typically a +/− 15 cm uncertainty band associated with bathymetric surveys made from a moving boat, and this needs to be accounted for in calculations using repeated surveys. In addition, the +/− 15 cm uncertainty associated with each survey is compounded by the factors in the first sentence. A horizontal uncertainty of 1 meter (m) corresponds to a vertical uncertainty of 20 cm in a sediment surface with a 5:1 slope. In conclusion, it is recommended that differences in bathymetric surveys should only be used to calculate average deposition rates when the differences between the two surveys are substantial, e.g., >50 cm.

3.3.1.4 Hydrodynamic Assessment

Where possible, flow rate and water elevation data should be collected. Even if water elevation (river stage data) cannot be converted to flow rate, these data can provide a better understanding of the range of flow conditions expected at a location. This range of conditions will help define the potential for event-induced erosion. For rivers and estuaries, the maximum flow and/or water level elevation in the period of record is of particular interest, as is determination of the 100-yr flow event. The maximum event on record, or the 100-yr storm event, is often of particular importance and may be the "design event" for purposes of modeling the impact of an extreme event on the sediment bed.

The USGS maintains inland and coastal water elevation gages for coastal regions, tidally dominated river reaches, lakes (not including the Great Lakes), and reservoirs. These data are available at http://waterdata.usgs.gov/nwis/rt (accessed August 30, 2012). USGS gaging stations for tidally dominated areas include inland gages on coastal rivers while others are directly on the coast. The USGS website given previously is designed for obtaining historic water elevation and flow rate graphics. State, county, water district, and other local agencies also maintain flow or water elevation data for various streams and rivers. In addition, other federal agencies, such as NOAA and the USACE, maintain flow gages, particularly in rivers near the coast, offshore, and in navigable waterways.

For estuarine or coastal contaminated sediment sites, tidal forces, including water level fluctuations with storm events, must be considered. Tidal records are available from NOAA's website and others. In settings where river flow is not a dominant hydraulic influence, water velocities associated with extreme tides or storm surges will be required in performing the SEDTA. A review of historical tide gage records to evaluate what extreme events have occurred in the past should be conducted during the SEDTA for such sites. Real-time active current station data at several coastal and Great Lakes locations are available at the following NOAA website: http://tidesandcurrents.noaa.gov/cdata/StationList?type=Current+Data&filter=active (accessed August 30, 2012).

Wave records are also useful in assessing storm histories for coastal sites. Historic and current water level and wave data for coastal regions (including the Great lakes) are available from NOAA at http://www.ndbc.noaa.gov (accessed August 30, 2012). These data are excellent for assessing the impact of tide-induced flows as well as coastal storms, e.g., tropical storms and nor'easters. NOAA buoys are generally offshore but data can be extrapolated to near-shore conditions in many cases (although this requires careful analysis and appropriate expertise). NOAA performs this extrapolation for hundreds of coastal locations (benchmarks) and the data are available online. Many port authorities also maintain buoys at harbor entrances. The NOAA website given previously provides a link to some of these data, but it may be necessary to contact the port authorities directly to obtain additional data.

3.3.1.5 Geomorphology Assessment

Geomorphology is primarily concerned with the study of the characteristics, configuration, and factors influencing the long-term evolution of the sediment bed and surrounding landforms. Sedimentation patterns and sediment bed dynamics may be highly variable within a site, especially for river channels, estuaries, and near-shore sites with large variation in water depths. Geomorphology assessment performed during a SEDTA should consider local and watershed-scale processes governing the formation and ongoing morphological changes of the water body. Examples of local scale factors include (1) point bar formation at a river bend, (2) scour zone formation between bridge abutments, (3) tidal mudflat accretion or degradation and (4) bank erosion. Some local factors, such as dam removal, can have far-reaching effects on sediment transport at a site. Example watershed-scale factors include land-use changes, such as conversion of agricultural land to development, conversion of agricultural land to vegetated state, flood control projects, removal of upstream dams and changes in hydropower operations. Over time, sediment transport causes morphological changes in most water bodies due to sedimentation and erosion. Landslides and bank erosion can also cause significant changes. These morphological changes may be accelerated or slowed by changes in the watershed or shoreline conditions, including anthropogenic changes. Historical site review should include an inspection of available mapping information including historical maps and air photos. A site visit will also yield useful information on shoreline changes. This type of information can be very important in performing the SEDTA, especially when the problem of interest, e.g., contaminated sediment, resides in near-shore areas.

Several governmental agencies often record shoreline or river bank position over time. These historic records have become more readily available with the advent of geographic information systems (GIS). Historic shoreline or bank position data are invaluable in understanding past system evolution and in performing the SEDTA. This can be especially dramatic for meandering rivers where cutoffs and new meanders develop over time. Uncontrolled rivers embedded in unconsolidated materials can exhibit active channel meandering. In some cases, river bank profiles may actually be available from multiple surveys over time to assess bank succession. Where bank changes are of particular importance, such as when the banks contain contaminated sediment, various survey methods may be employed to monitoring bank changes. Erosion stakes are one such method, where stakes are placed and the elevations and changes in the bank profile monitored and resurveyed over time.

3.3.1.6 Evaluate Anthropogenic Impacts

At many contaminated sediment sites, the sediment bed is not in a completely natural state. For example, river and estuarine systems where contaminants are present as a result of industrial activity are typically altered due to construction of locks and dams, navigational channels, bridge abutments, dredged channels, and other structures. These structures may have localized impacts (e.g., depositional areas immediately downstream of large bridge piers), or large-scale impacts (e.g., dam control of water levels, or dredged navigational channels). In some cases, the trend is toward reversing prior construction. Efforts are underway to remove dams on some rivers. Elsewhere, construction is planned with new shipping terminals, bridges, etc. These historical or planned changes are of importance when using historic data to understand future behavior; a compilation of these changes over time will be helpful in the SEDTA in understanding the potential impacts of extreme events. Stratigraphic data may indicate past erosion or deposition events that are no longer possible at this site. As such, anthropogenic activity must be accounted for when analyzing stratigraphic records during the SEDTA.

3.3.1.7 Sediment Stratigraphy and Geochronology Analysis

Sediment stratigraphy refers to the characteristics and ordering of layers in the sediment bed, and can show useful information about the depositional record. Stratigraphy is especially useful when it can be compared to radio-dated sediment cores from which geochronology of the sediments can be inferred. High flow events that have had a significant impact on sediment transport may be revealed as distinct bands of sediment in the core that depend on the types of sediment in transport and the flow velocity during the event. A device that can be used at a sediment site to help characterize the stratigraphy of a sediment bed is the sediment profile imaging (SPI) camera. The specific purpose of using a SPI camera is to characterize the physical and biological condition of surface sediments (usually the top 10–15 cm) and assess the water body's benthic community by using the camera that is pushed into the sediment bed, thus providing an *in situ* view of the sediment structure, e.g., layers of sediment strata, and possibly benthic organisms, feeding tubes, etc.

A geochronology analysis uses depth profiles of radioisotope measurements to estimate sedimentation rates by radio-dating layers in the core. Geochronology analyses are generally conducted using three types of radioisotope data: Cesium-137 (^{137}Cs), lead-210 (^{210}Pb), and Beryllium-7 (^{7}Be). Each radioisotope provides a specific type of geochronologic information. For example, the peak level of detectable ^{137}Cs in sediments occurred in 1963. The best estimate of the long-term average sedimentation rate for a particular core is computed by dividing the depth of sediment between the sediment surface and the buried ^{137}Cs peak by the number of years between 1963 and the time of core collection. The structure of the ^{137}Cs profile may also provide insights about the sediment transport environment at the core location. The relative "sharpness" of the profile around the ^{137}Cs peak is indicative of the strength of mixing processes in the surface bed layer, e.g., a sharp, well-defined peak suggests a relatively low rate of surficial mixing, whereas a broad, poorly-defined peak suggests a relatively high rate of mixing.

3.3.2 Data Needs for Most Sites

Data needed to perform a SEDTA depend on the type of water body, the type of sediment present in the water body, and the forces that govern the motion of the water. Examples of different types of water bodies along with data (not listed in a particular order)

Table 3.4. Data Needed to Perform a Sediment Transport Assessment at Different Types of Water Bodies

Data	River	Reservoir/ Lake	Harbor	Estuary	Coastal Sea
Discharge	x	x		x	
Stage (water surface elevation)	x	x	x	x	x
Current velocity	x	x	x	x	x
Wind speed and direction		x	x	x	x
Bathymetry	x	x	x	x	x
Wave height, period, and direction		x	x	x	x
Sediment grain size distribution	x	x	x	x	x
Sediment bed density	x	x	x	x	x
Organic content in the sediment bed	x	x	x	x	x
Salinity			x	x	x
Water temperature		x		x	x
Settling speed of cohesive sediment	x	x	x	x	x
Sediment erodibility	x	x	x	x	x
Suspended sediment concentration	x	x	x	x	x

that might be needed to perform a SEDTA are given in Table 3.4. One example of each of the types of water bodies are the following: River – Upper Hudson; Reservoir/Lake – Lake Hartwell, South Carolina; Estuary – Lower Duwamish Waterway, Washington; and Coastal Seas – Palos Verdes Shelf, California. A lot of the data given in this table would be needed at multiple locations over time, i.e., not a single measurement. Other considerations related to data needs are the data that would be needed for addressing specific sediment management issues or questions.

Common to all water bodies and therefore not included in Table 3.4 is the need to quantify the erodibility of the sediment – not only the sediment at the surface of the sediment bed, but with depth into the bed as well. Different instruments that can be used to measure sediment erodibility at sediment sites are presented in Section 3.3.3.

3.3.3 Determination of Sediment Erodibility

As mentioned previously, quantification of sediment erodibility at several locations where fine-grained and/or mixed cohesive and noncohesive sediments occur is usually recommended at Superfund Sites with contaminated sediments. This recommendation especially applies at sites where the contaminated sediments are not in an isolated, low energy environment, such as a protected harbor. Table 3.5 summarizes some of the more common research and commercially available methods that can be used to measure sediment erodibility parameters. All of the devices measure critical shear stress of erosion of cohesive sediments and erosion rate; the primary differences between them are related to whether they can be used *in situ* and whether they can measure sediment erodibility below the surficial sediment layer.

The erosion rate column in this table is interpreted in this manner: ‘yes’ indicates that the erosion rate of the sediment bed is explicitly measured, whereas ‘no’ indicates that erosion rate is calculated as a function of the measured suspended sediment concentration.

Table 3.5. Comparison of Various Sediment Stability Measurement Devices (adapted from Blake et al., 2007)

Device	Flow Conditions (Over Sediment Surface)	*In Situ*	*Ex Situ*	Transport Measured	τ_c	Erosion Rate	Sediment Type	Depth Measured	Shear Stress Range
Straight Flume	Linear/oscillatory	Yes	Yes	Total load	Yes	Yes	Clay/silt/sand	Surficial layer	0–4 Pa
Annular Flume/Sea Carousel	Linear	Yes	Yes	Suspended load only	Yes	No	Clay/silt/sand	Surficial layer	0–1 Pa
Shaker	Unknown	No	Yes	Suspended load only	Yes	No	Clay/silt/sand	Surficial layer	0–1 Pa
SEDFLUME	Linear	No	Yes	Total load	Yes	Yes	Clay/silt/sand	0–1 m	0–10+ Pa
ASSET flume	Linear	No	Yes	Suspended and bedload	Yes	Yes	Clay/silt/sand	0–1 m	0–10+ Pa
SEAWOLF flume	Linear/oscillatory	No	Yes	Total load	Yes	Yes	Clay/silt/sand	0–1 m	0–10+ Pa

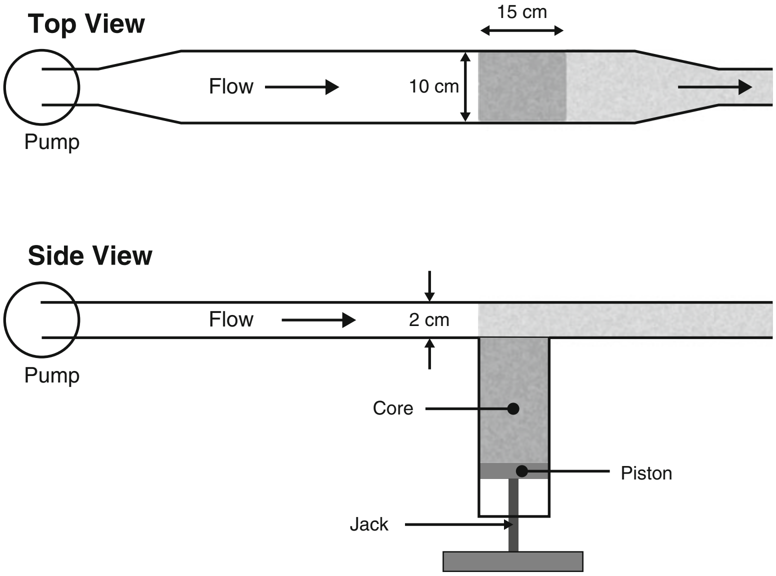
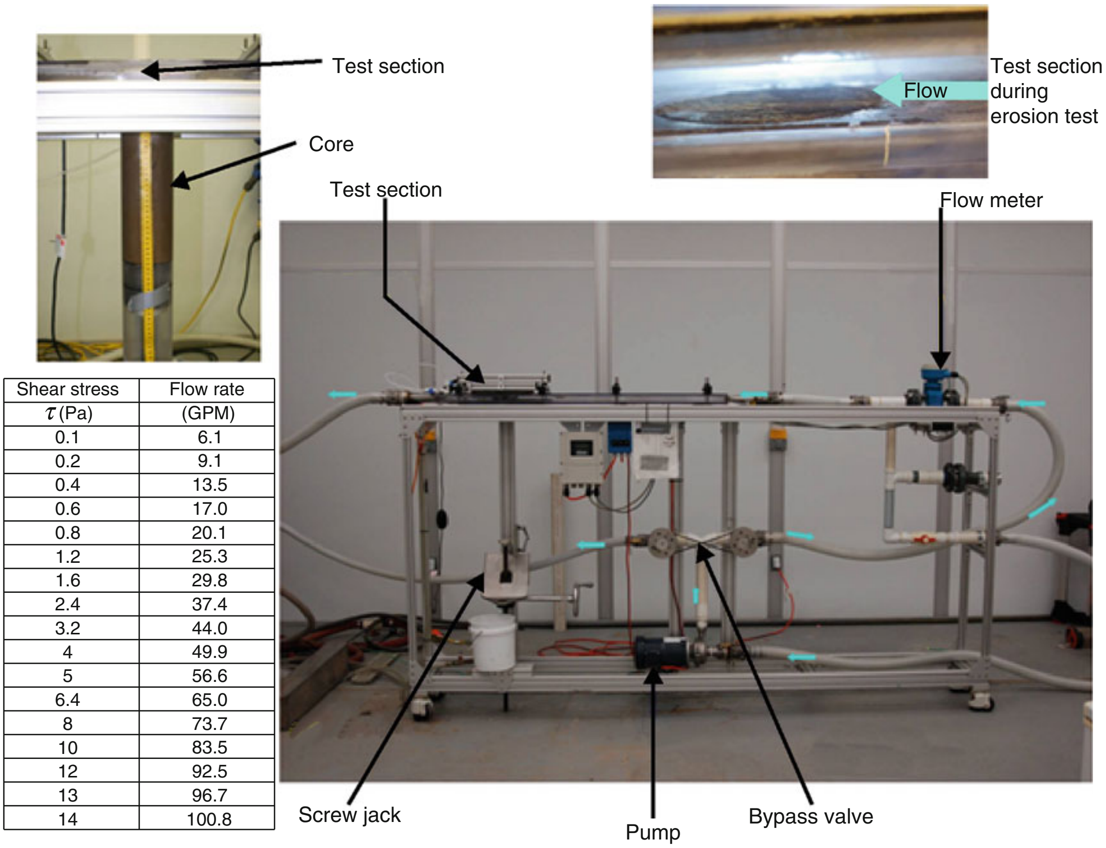


Figure 3.9. Schematic illustrating operating principles of SEDFLUME. Pictured are SEDFLUME channel, flow development region, testing section and sediment core.

The advantages of SEDFLUME (McNeil and Lick, 2004), ASSET, and SEA WOLF over other devices, such as Sea CAROUSEL (Maa et al., 1993) and FLUME (Ravens, 2007), are that the erosion rates, critical shear stresses for erosion, and bulk densities can be determined with depth into the sediment bed. The other devices are only capable of determining these parameters at the bed surface.

SEDFLUME is a field- or laboratory-deployable flume for quantifying cohesive sediment erosion. SEDFLUME is a flume developed by researchers at the University of California at Santa Barbara (McNeil et al., 1996). The flume includes an 80-cm-long inlet section (Figure 3.9) with cross-sectional area of 2 × 10 cm for uniform, fully developed, smooth-turbulent flow. The inlet section is followed by a 15-cm-long test section with a 10 × 15 cm open bottom (the open bottom can accept cores with rectangular cross-section 10 × 15 cm] or circular cross-section [10-cm diameter]). Coring tubes and flume test section, inlet section, and exit sections are constructed of clear polycarbonate materials to permit observation of sediment-water interactions during the course of erosion experiments. The flume includes a port over the test section to provide access to the core surface for physical sampling. The flume accepts sediment cores up to 80 cm in length. An exit section for removal of water and eroded sediment follows the test section. Plungers inserted into the bottom of the coring tube provide two functions: (1) to seal the bottom of the core to prevent pore-water drainage during storage and erosion experiments and (2) to provide a means of advancing the core surface within the flume during erosion experiments. During experiment preparation, cores are measured and visual observations noted prior to the erosion experiment. Cores are inserted into the testing section of SEDFLUME and a screw jack is used to advance the plunger such that the core surface remains flush with the bottom wall of the flume. Flow is directed over the sample by diverting flow from a 1-horsepower (hp) pump, through a 5-cm diameter stiff hose, into the flume. The flow through the flume produces shear stress on the surface of the core. Erosion of the surface sediment is initiated as the shear stress is increased beyond the critical stress for erosion. As sediment erodes from the core surface, the operator advances the screw jack to maintain the sediment surface flush with the bottom wall of the erosion flume. Figure 3.10 includes a



Shear stress τ (Pa)	Flow rate (GPM)
0.1	6.1
0.2	9.1
0.4	13.5
0.6	17.0
0.8	20.1
1.2	25.3
1.6	29.8
2.4	37.4
3.2	44.0
4	49.9
5	56.6
6.4	65.0
8	73.7
10	83.5
12	92.5
13	96.7
14	100.8

Figure 3.10. SEDFLUME.

photograph of the flume, a close-up photograph of the test section, and a table of flow rate/ shear stress relationships.

The ASSET and SEA WOLF flumes listed in Table 3.5 are specialized versions of SEDFLUME. The ASSET flume can be used to measure sediment core resuspension rates and the ratios of bedload to suspended load transport (Roberts et al., 2003; Jepsen et al., 2010). The SEA WOLF flume is capable of measuring resuspension rates of sediment cores under the action of both a unidirectional current and waves (Jepsen et al., 2004). Thus, a SEAWOLF flume should be considered for use in relative shallow water bodies when wind-generated waves are identified as one of the processes that could cause resuspension of the sediment bed.

3.4 SEDIMENT TRANSPORT MODELING

3.4.1 Overview of Modeling

Models are generally used to quantify processes (hydrodynamic and sediment transport) for conditions (such as storm events) for which no data exist. Sufficient data rarely exist to quantify critical sediment transport processes for all relevant hydrodynamic conditions required to assess fate and transport at a site. Models are used to address these data gaps by providing predicted solutions based on best available data and process understanding for conditions that require assessment, e.g., site remediation. Models use existing understanding of the physics of hydrodynamics and water column transport, coupled with site-specific hydrodynamic, morphology, and sediment process data, to perform these predictions. These predictions are estimates, meant to reasonably represent the hydrodynamic and sediment conditions; they are not exact solutions. The solutions represent first order processes influencing hydrodynamics and transport, but they may not include some second order processes. The user must always be aware of the limitation of numerical models.

This chapter has reviewed various methods used to describe, measure, and assess sediment transport processes and properties. Project managers often require the ability to confidently predict future transport. The CSM uses available data to develop working hypotheses of transport in a system, and provides managers with a better understanding of how sediments move through the system. However, some type of predictive model is sometimes required to quantify future erosion, deposition, and transport. The term ‘predictive model’ is broad. Some predictive models perform simple calculations to describe only one process (such as sedimentation) or identify sediment pathways or sources/sinks. On the other end of the spectrum, fully three-dimensional, coupled hydrodynamic/sediment transport models are used to quantify all relevant processes on resolution of a few meters. These complex models are often used to simulate large water bodies and are computationally intensive.

Discussion in this section will briefly review hydrodynamic modeling, and then describe sediment transport modeling in more detail. Hydrodynamic models are relatively mature compared to sediment transport models. However, hydrodynamic model validation is still required for each site application. Sediment transport models are sometimes coupled (i.e., dynamically linked) with a hydrodynamic model. In these models, the forces that drive sediment (currents and waves) are coupled with the actual transport predictions.

3.4.2 Hydrodynamic Modeling

Hydrodynamics deals with the movement of water when external forces, such as wind and gravity, act on a water body. The water movement can be calculated using the fundamental principles of Newtonian physics: conservation of mass, linear momentum, and energy, and an equation of state (used to calculate the water density as a function of temperature, salinity, and pressure). These governing equations are given later in this section, while the forces that cause water to move are discussed next.

3.4.2.1 Driving Forces

Contained in the equations governing the motion of waters are the forces that cause water to move (referred to as *driving forces*) as well as other forces that act to decrease the water’s acceleration (referred to as *retarding forces*). Friction is the main retarding force. Common driving forces in different types of water bodies are listed below.

- Freshwater stream/river with uni-directional flow
  - Gravitational force (proportional to gradient)
  - Tributary inflows
  - Direct runoff into water body during runoff events
  - Wind
- Lake/reservoir
  - Wind
  - Tributary inflows
  - Discharge from dam

  - Thermal stratification
  - Direct runoff into water body during runoff events
- Stream/river with oscillatory flow
  - Gravitational force (proportional to gradient)
  - Astronomical tides
  - Tributary inflows
  - Spatial (horizontal and vertical) salinity gradients
  - Direct runoff into water body during runoff events
  - Wind
- Estuary/Bay/Coastal Sea
  - Astronomical tides
  - Freshwater discharge
  - Spatial (horizontal and vertical) salinity gradients
  - Wind
  - Coriolis force
  - Atmospheric pressure gradients
  - Direct runoff into water body during runoff events

3.4.2.2 Governing Equations of Hydrodynamics

The hydrodynamics of a water body are described by the continuity equation (conservation of water mass), the equations of motion (conservation of linear momentum), an equation of state, $\rho = \mathrm{F}(p,S,T)$, and transport equations for temperature (T) and salinity (S). These governing equations are:

Continuity equation:

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) + \frac{\partial}{\partial z}(\rho w) = -\frac{\partial \rho}{\partial t} \qquad \text{(Eq. 3.42)}$$

where u, v, w = velocity components in the x, y, z coordinate directions.

Equations of motion in the x-, y- and z-directions, respectively:

$$\begin{aligned}&\frac{\partial}{\partial t}(u) + u\frac{\partial}{\partial x}(u) + v\frac{\partial}{\partial y}(u) + w\frac{\partial}{\partial z}(u)\\ &\quad = \frac{\partial}{\partial x}\left(\left(v + \frac{A_x}{\rho}\right)\frac{\partial u}{\partial x}\right) + \frac{\partial}{\partial y}\left(\left(v + \frac{A_y}{\rho}\right)\frac{\partial u}{\partial y}\right) + \frac{\partial}{\partial z}\left(\left(v + \frac{A_z}{\rho}\right)\frac{\partial u}{\partial z}\right)\end{aligned} \qquad \text{(Eq. 3.43)}$$

$$\begin{aligned}&\frac{\partial}{\partial t}(v) + u\frac{\partial}{\partial x}(v) + v\frac{\partial}{\partial y}(v) + w\frac{\partial}{\partial z}(v)\\ &\quad = \frac{\partial}{\partial x}\left(\left(v + \frac{A_x}{\rho}\right)\frac{\partial v}{\partial x}\right) + \frac{\partial}{\partial y}\left(\left(v + \frac{A_y}{\rho}\right)\frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial z}\left(\left(v + \frac{A_z}{\rho}\right)\frac{\partial v}{\partial z}\right)\end{aligned} \qquad \text{(Eq. 3.44)}$$

$$\begin{aligned}&\frac{\partial}{\partial t}(w) + u\frac{\partial}{\partial x}(w) + v\frac{\partial}{\partial y}(w) + w\frac{\partial}{\partial z}(w)\\ &\quad = \frac{\partial}{\partial x}\left(\left(v + \frac{A_x}{\rho}\right)\frac{\partial w}{\partial x}\right) + \frac{\partial}{\partial y}\left(\left(v + \frac{A_y}{\rho}\right)\frac{\partial w}{\partial y}\right) + \frac{\partial}{\partial z}\left(\left(v + \frac{A_z}{\rho}\right)\frac{\partial w}{\partial z}\right) + g\end{aligned} \qquad \text{(Eq. 3.45)}$$

where A_x, A_y and A_z = coefficients of turbulent viscosity. Ranges of values for A_x and A_y are 10^{-2}–10^{2}, and for A_z are 10^{-6}–10^{-2}. These equations incorporate the following Boussinesq-type relationship between the turbulent (Reynolds) shear stress and a spatial velocity gradient:

$$\tau_{zx} = -\rho\overline{u'w'} = -A_z\frac{\partial u}{\partial z} \tag{Eq. 3.46}$$

Transport equations for temperature (T) and salinity (S), respectively:

$$\frac{\partial}{\partial t}T + \frac{\partial}{\partial x}uT + \frac{\partial}{\partial y}vT + \frac{\partial}{\partial z}wT = \frac{\partial}{\partial x}\left(K_X\frac{\partial}{\partial x}T\right) + \frac{\partial}{\partial y}\left(K_Y\frac{\partial}{\partial y}T\right) + \frac{\partial}{\partial z}\left(K_Z\frac{\partial}{\partial z}T\right) + Q_T \tag{Eq. 3.47}$$

$$\frac{\partial}{\partial t}S + \frac{\partial}{\partial x}uS + \frac{\partial}{\partial y}vS + \frac{\partial}{\partial z}wS = \frac{\partial}{\partial x}\left(K_X\frac{\partial}{\partial x}S\right) + \frac{\partial}{\partial y}\left(K_Y\frac{\partial}{\partial y}S\right) + \frac{\partial}{\partial z}\left(K_Z\frac{\partial}{\partial z}S\right) \tag{Eq. 3.48}$$

where K_i = coefficients of turbulent diffusion and Q_T = thermal sources/sinks.

The system of equations described above provides a closed system for the variables u, v, w, p, ζ, ρ, S and T, provided that the vertical turbulent viscosity and diffusivity and the source and sink terms are specified. To determine values for the vertical turbulent viscosity and diffusivity, a turbulence closure model is typically used.

3.4.2.3 Basic Principles of Hydrodynamic Modeling

The basic principles of modeling the hydrodynamics in a water body are listed below.

- Identify and quantify driving forces – these are given in Section 3.4.2.1.
- Identify and quantify sources and sinks of water mass. Typical sources of water include input from tributary flows, non-point source runoff into water bodies during runoff events. Precipitation, discharge of groundwater to surface waters, and hydraulic connections to larger water bodies such as coastal seas. Usual sinks include evaporation, infiltration into the bottom of the water body, and outflows of water into both natural and man-made discharge rivers/channels.
- Choose an appropriate modeling domain. Two guidelines for doing this are the following:
  1. Open water boundaries should be sufficiently far removed from the area of interest in the water body and
  2. Open water boundaries should be chosen where boundary values are known or can be measured.
- Decide what type of hydrodynamic model should be applied to the modeling domain. The different types of models are described in the next section.
- Decide what level of spatial discretization is needed to adequately represent the geometry and bathymetry of the water body as well as the driving forces and the significant physical processes that determine the movement of water.
- Where any type of numerical model is used, model calibration and validation should be performed to yield a scientifically defensible modeling study. Definitions of these terms are provided below.

- *Model calibration*: Consists of using site-specific information from a historical period of time to adjust model parameters in the governing equations (e.g., bottom friction coefficient in hydrodynamic models) to obtain an optimal agreement between a measured data set and model calculations for the simulated state variables.
- *Model validation*: Consists of demonstrating that the calibrated model accurately reproduces known conditions over a different period of time than that used for model calibration. The parameters adjusted during the calibration process should not be adjusted during validation. Model simulations during the validation period should be compared to the measured data set. If an acceptable level of agreement is achieved, then the model can be considered validated as an effective tool, at least for the range of conditions defined by the calibration and validation data sets. If an acceptable level of agreement is not achieved, then further analysis should be carried out to determine possible reasons for the differences between the model simulations and data. The latter sometimes leads to refinement of the model (e.g., using a finer model grid) or to the addition of one or more physical processes in the model.

It is important that both calibration and validation be conducted at the space and time scales associated with the questions the model must answer. For example, if the model will be used to make decade-scale predictions, then model simulations should be compared to decade-scale data sets. Even when data exist for a much shorter time period than will be used for prediction, it is recommended that the long-term behavior of the model be examined as a part of the calibration process. It is not unusual for a model to perform well for a short-term period, e.g., a few months, but produce unreasonable results when run for a much longer duration, e.g., 1 or more years.

3.4.2.4 Types of Hydrodynamic Models

The four commonly used types of hydrodynamic models are described below. These models are classified based on the number of spatial dimensions in the equation(s) of motion solved in the model.

1. One-dimensional (1D) model – solves the cross-sectionally averaged conservation of mass and momentum equations for the water surface elevation (i.e., stage) and discharge (i.e., flow) at discrete locations along the modeled water body. A 1D hydrodynamic model is an appropriate representation for water bodies in which the most significant constituent gradient is along the longitudinal axis in the direction of flow of the stream or river. The vertical and lateral dimensions are assumed to be well-mixed since the gradients of constituents in these directions are considered to be negligible in relation to the dominant longitudinal gradient. A stream of up to a third order river is usually modeled using a 1D model. An example of a public domain 1D model is HEC-RAS.
2. Two-dimensional depth-averaged (2D-H) model – solves the depth-averaged conservation of mass and momentum equations for the water surface elevation (i.e., stage) and horizontal flow velocity at discrete locations (called nodes or cells) throughout the modeled water body. A 2D-H hydrodynamic model is an appropriate representation for water bodies in which the most significant gradients are in the horizontal direction. The vertical dimension is assumed to be well-mixed since the gradients of constituents in

this direction are considered to be negligible in relation to the dominant horizontal gradients. A well-mixed freshwater lake, or an embayment of a large lake, is typically modeled using a 2D-H model. An example of a public domain 2D-H model is RMA2.

3. Two-dimensional laterally-averaged (2D-V) model – solves the laterally-averaged conservation of mass and momentum equations for the water surface elevation (i.e., stage) and the x- and z-components of the velocity at discrete locations throughout the modeled water body. A 2D-V hydrodynamic model is an appropriate representation for vertically stratified water bodies in which the most significant gradients are in the longitudinal and vertical directions. The lateral dimension is assumed to be well-mixed since the gradients of constituents in this direction are considered to be negligible in relation to the dominant longitudinal and vertical gradients. A stratified, relatively narrow estuary, reservoir, or river maybe modeled using a 2D-V model.
4. Three-dimensional (3D) model – solves the 3D conservation of mass and momentum equations for the water surface elevation and the x-, y-, and z-components of the velocity at discrete locations throughout the modeled water body. A 3D hydrodynamic model is an appropriate representation for vertically stratified estuaries, reservoirs, and coastal seas water bodies, however, 3D models are computationally intense. Additional validation is required to demonstrate appropriate representation of the stratification. Using the 3D equations is probably always the best choice if nothing is known about the geometrical constraints or physical simplifications that are applicable to the water body being modeled. In this case, all terms in the governing equations might be important, and no a priori scale analysis can be performed. A typical example is a deep lake where stratification can develop. The lake is large enough so that no direction can be identified with the main axis, or, if there is a main axis, the dynamics in the direction perpendicular to it cannot be neglected. Stratification will prevent treating the whole water column as vertically mixed, and, therefore, vertical and horizontal internal pressure gradients, due to density differences between different water masses, will be important for the acceleration of the fluid body. An example of a public domain 3D model is EFDC.

3.4.3 Sediment Transport Modeling

3.4.3.1 Modeling Objectives

The purpose of a model is to provide transport predictions under hydrodynamic conditions for which data do not exist. The model can be used to predict how transport has modified the sediment bed from a previous state to its present condition (forensic modeling) or to estimate how transport will effect suspension and sediment bed morphology in the future (predictive modeling). Within a specific study, often both types of modeling are performed. The forensic modeling is used to demonstrate that the model can replicate what has happened (model validation). The model is then used to support remediation decision making by predicting how the sediment bed and suspended load will evolve in the future. Rigorous model validation provides confidence that the model can predict future behavior.

A sediment transport model is a numerical description of physical processes that drive transport. The model predicts the fate of sediments within the model domain. Therefore, the model must include a numerical description of the hydrodynamics and other forcing mechanisms (waves, ship passage, dredging) that move the sediment. The model must also include numerical representation of the sediment physics. It is well known how to represent transport in the water column within a numerical model. However, sediment behavior that effects transport is more complex and less well understood. This is particularly true for cohesive sediments where electro-chemical interactions can greatly influence transport processes. As described in previous sections within this chapter, site-specific parameterization is often used to quantify cohesive processes. This parameterization must be appropriately implemented within the sediment transport model. Model resolution (spatial and temporal) and required process representations are dependent on the issues to be addressed using the model.

3.4.3.2 Model Dimensions and Resolution

As stated previously, this section will discuss models that simulate all transport within a specified domain (a water body or segment of a water body). These models can have various dimensions: 1D, 2D, quasi 3D and fully 3D models. It may appear, at first, that a fully 3D model would be "best" for any application because it best represents the physics of hydrodynamics and transport. However, the benefits of fully 3D models must be weighed against the computational costs. Each dimension added to the model restricts the number of simulations and duration of each simulation performed. Therefore, the finer resolution of 3D models comes at a cost by limiting model data output to a few scenarios. In general, it is considered best to develop a model that is of sufficient complexity to appropriately address the issues of concern, but not to exceed the required complexity. For example, the value to remediation decision support of modeling efforts can be compromised by model complexity/computational intensity that does not permit simulation of multiple scenarios.

1D models are often used to estimate wash load in flashy streams and rivers. There is no cross-shore variation in flow rate or velocity. Therefore, these models provide poor resolution of local scour. Local scour is one of the important factors in contaminant transport. Therefore, these models are not frequently used for contaminant transport studies.

2D models generally include two planar directions. All hydrodynamic and transport processes are presumed to be well mixed in the vertical direction. The models can include both bed and suspended load. This scale of model is often applied in riverine or open water conditions. However, they are not appropriate in stratified water columns, such as estuaries. Quasi 3D models are an extension of 2D models. In these cases, a 2D hydrodynamic model is coupled with a sediment transport model that does not represent a well-mixed water column. Instead, suspended sediment stratification is assumed based on the energy in the water column and the ability of this energy to mix sediment within the water column. Quasi 3D modeling is of particular benefit when modeling sand transport in a regime where hydrodynamics can be reasonably represented using a 2D model.

Although the water column is treated in two dimensions in these models, the sediment bed can be represented in three-dimensions. The vertical dimension to the sediment bed sub-model is required to represent stratification or consolidation of the sediment column. Unless the CSM indicates that stratification is a significant contributor to transport dynamics, a 2D model may be sufficient. Many Superfund site models and other high-resolution contaminant transport model applications are performed using a 2D model.

3D models include 3D representation of both the water column and sediment bed. These models are used in areas where there is significant stratification of the water column and the hydrodynamics cannot be described adequately in two dimensions. Stratified environments may include estuaries, navigation channels, thermal stratification, etc. 3D models are also used in scenarios where quasi 3D models cannot adequately describe the transport. These scenarios may include environments where vertical stratification of sediment in the water column is not the product of energy in the water column. These models are often used at Superfund and other contaminated sediment sites, but should only be used if there is significant doubt pertaining to the capability of 2D simulations to provide accurate solutions.

Once the model dimension is chosen, the user can select the appropriate model. There are multiple, robust, free-ware, or commercially available 2D and 3D models. These include EFDC (Hamrick, 2007) and ECOMSED (HydroQual, 2007). Each of these models can be used in 2D or 3D. Each model requires the user to perform site-specific parameterization of cohesive sediment transport processes, such as erosion and settling. Each model permits 3D representation of the sediment bed.

Numerical models require the use of either a grid or mesh to represent the chosen model domain. A grid is a series of interconnected quadrilaterals that cover the entire domain being modeled. A mesh is a matrix of nodes that cover the entire domain, and either triangular or quadrilateral elements are formed by connecting three or four nodes, respectively. Node spacing and grid size can vary over the domain. In a model mesh, state variables (e.g., suspended sediment concentration) are calculated at the nodal points in the mesh. In a model grid, state variables are usually calculated at the center of the grid, but the value is representative of the entire area within a grid cell.

The grid or mesh is either 2D or 3D. Each model variable is calculated at each cell within the grid or mesh. Parameters calculated include current velocity, water depth, suspended solids concentration (SSC), settling and erosion. Grid/mesh resolution is dependent on accuracy required from the resulting data. For many models, resolution can vary within a single grid or mesh. Therefore, fine-scale resolution (a few meters) can be used in areas of specific interest while larger grid elements or node spacing is typically used further from the location of interest. Resolution must be developed to accurately represent the hydrodynamic and transport processes of interest. Required resolution is dependent on the spatial variability of processes. For example, larger grid cells can be used in the open ocean where hydrodynamic processes vary slowly. Finer resolution will be required in ports or harbors or in proximity to jetties where there are complex interactions between structures and water. For contaminated sediment sites, cell size or node spacing is often on the order of 10–100 m. 3D models also have cells or nodes in the vertical direction. These cells or nodes are typically stacked; the planer locations are the same for each layer of cells or nodes in the vertical direction. The number of vertical cells is dependent on the processes to be replicated. At a minimum, the number of vertical cells must be able to accurately represent hydrodynamic and sediment processes that have a first order effect on transport. Examples of these processes include turbidity maxima, salt wedge, and thermal stratification.

For a dynamically linked hydrodynamic-transport model such as EFDC, the model progresses through time as follows: calculate hydrodynamic variables at each node or cell in the domain for time step n, calculate sediment transport variables at each node or cell for time step n, calculate hydrodynamic variables at time step n + 1 (using conditions from time step n), calculate sediment transport variables at time step n + 1 (using conditions from time step n). The advantage of using a dynamically linked hydrodynamic-transport model is that changes in the morphology (i.e., bottom elevations) resulting from simulated erosion and deposition processes are used to update the hydrodynamics at the next time step. The disadvantage of using a dynamically linked model is that the hydrodynamics have to be re-run every time the sediment transport model is run. Many modeling studies have used decoupled hydrodynamic and transport models. In this case, the hydrodynamic model is run, and the results are written to an output binary file. The latter is then read by the transport model and used in solving the advective-dispersive transport equation for the simulated constituent, e.g., sediment or contaminant. It is the author's opinion that the decoupled modeling strategy should only be used in water bodies in which the simulated changes in morphology are $<10\%$ of the water depth.

3.4.3.3 Processes Modeled

Hydrodynamic models and wave models provide current, water depth, and wave conditions at each grid cell or node within the model domain. The sediment transport model uses these data to determine sediment transport for suspended solids. Sediment transport models generally have multiple constituents, each representing a different size class of sediment (e.g., clay, silt, fine sand, and coarse sand). An initial SSC is provided for each grid cell and for each water column layer for 3D models. The SSC represents the concentration at the previous time step. The model then uses the transport equation to advect sediment between cells or nodes in the domain. The transport equation is solved separately for each sediment size class. The 3D sediment transport equation was given previously (Equation 3.39).

For 2D and quasi 3D modeling, Equation 3.39 can be simplified by vertically integrating:

$$\frac{\partial(hC)}{\partial t}+\frac{\partial(UC)}{\partial t}+\frac{\partial(VC)}{\partial t}=K_H\left[\frac{\partial}{\partial x}\left(h\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(h\frac{\partial C}{\partial y}\right)\right]+Q \qquad \text{(Eq. 3.49)}$$

where C is the vertically averaged SSC, h is the total water depth at the cell or node, U and V are the vertically integrated velocities in the planar directions (Lick, 2009), K_H is the horizontal eddy diffusivity (which is assumed to have the same value in the x- and y-directions), and Q is the net flux of sediment at the sediment bed/water interface. Q is defined as the difference between erosion flux and sedimentation (mass per unit area) (Lick, 2009). As noted earlier in this chapter, settling velocity, deposition rate, and erosion rates are site-specific for cohesive sediments and are quantified through site-specific sediment testing.

The above equations are used for sediments in suspension. As previously stated in this section, some noncohesive sediments move as bedload. van Rijn (1993) provides a thorough review of bedload transport modeling. For the purposes of this text, it is sufficient to state that any sediment transport model that includes a sand fraction must have a bedload component to the model. It should be noted that sand may be transported both in suspension and as bedload. The fraction that transports within each regime is dependent on GSD and energy in the water column. The reader is referred to van Rijn (1993) for further detail on modeling of both suspended and bedload simultaneously.

For suspended load, the value of Q for each sediment class is quantified from (Lick, 2009):

$$Q=E-pw_sC \qquad \text{(Eq. 3.50)}$$

where E is the erosion flux for each sediment class, p is the probability of deposition for the sediment class (based on energy in the water column), and C represents either the vertically integrated concentration (for 2D modeling) or the concentration in the bottom cell (node) for 3D modeling. The second term on the right hand side of Equation 3.50 is total deposition, D (mass per unit area). Although there is an interaction between erosion and deposition, most models treat the two processes as separate and each occurs independent of the other. Critical shear stress for deposition or erosion, described earlier in this chapter, often dictates that only one process occurs for a given hydrodynamic condition. Under some conditions, both processes can occur simultaneously.

3.4.3.4 Sediment Bed Model

Both 2D and 3D hydrodynamic/sediment transport models generally include a 3D representation of the sediment bed. This is done by using sediment bed layers. At a minimum, the sediment bed includes an active (surface) layer and an underlying parent layer. Erosion and sedimentation fluxes (E and D, respectively) from the water column (Equation 3.50) are

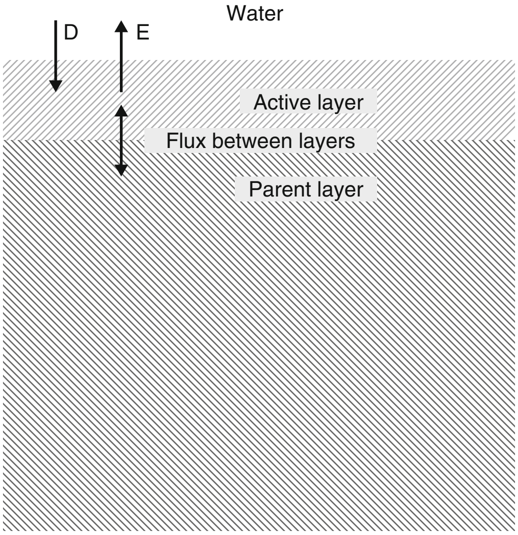


Figure 3.11. Active layer model configuration.

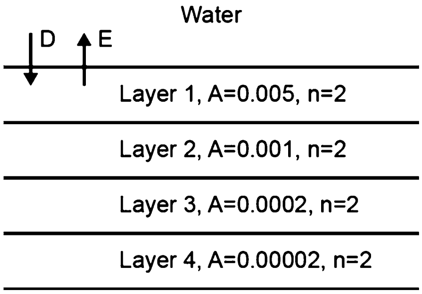


Figure 3.12. Multiple layer cohesive sediment bed with erosion parameterization.

handled in the active layer. Sediment from the active layer is moved down to the parent layer if the active layer accumulates too much sediment. Conversely, sediment is moved from the parent bed to the active layer if erosion reduces the thickness of the active layer. Figure 3.11 provides a schematic of fluxes between layers for this sediment bed model.

For cohesive sediments, erosion potential is a function of bed bulk density. This process is simulated by generating a bed with multiple layers. Each layer has an erosion potential that is reflective of the sediment density in that layer. Multiple layers may exist in the bed at any given time, dependent on the evolution of the bed. Each layer will have specific erosion parameterization, as described earlier in this text. Figure 3.12 provides a schematic of a layered sediment bed with vertically varying erosion parameterization. It can be seen that the value of A in Equation 3.38 decreases with layers further below the sediment/water interface. This parameterization may represent a consolidating bed. These values can also change with time as the bed further consolidates. Values of A, n and time for consolidation are obtained from site-specific parameterization. If Layer 1 erodes completely, erosion of Layer 2 will begin. However, Layer 2 will erode at a slower rate because of the smaller value of A. If sedimentation is greater than erosion, Layer 1 will be re-generated. For this example, Layer 1 represents freshly deposited sediment.

3.4.3.5 Model Setup

Hydrodynamic model setup has already been described. For sediment transport modeling, the user must provide input for sediment process parameterization and initialization. Sediment boundary conditions must also be provided. Most sediment transport models for cohesive sediment will require input that parameterize processes (erosion, settling speed, and consolidation for each class of sediment) and initialize the sediment bed (composition of each layer, thickness, and erosion parameterization). Model grid and bathymetry are input as part of the hydrodynamic model. Most sediment transport models run on the same grid or mesh as the hydrodynamic model. Sediment transport models typically assume an initial SSC of zero. Concentration increases as sediment sources (boundary conditions) introduce sediment and as sediment is eroded from the bed. At each boundary that includes a sediment load, the user is expected to provide a time series of suspended solids load for each class of sediment. For 3D models, this load can be vertically stratified, i.e., a time series of SSC has to be provided for each water column layer. Setup is site- and model-specific. Most sediment transport models include guidance that steps the user through model setup.

3.4.3.6 Model Calibration and Validation

The general principles of calibration and validation are discussed in Section 3.4.2.3. With regard to calibrating and validating a sediment transport model, one additional recommendation is to use, when possible, different types of data for performing these two procedures. For example, the model could be calibrated against a time series of measured suspended sediment concentration profiles at different locations throughout the model domain and then validated by comparing predicted long-term (e.g., multiple years) changes in morphology with measured changes as determined by repeat bathymetric surveys.

3.4.3.7 Sensitivity and Uncertainty Analyses

Another important tool for understanding model results that is typically used in modeling studies is a sensitivity analysis. This process consists of varying each of the input parameters by a fixed percent (while holding the other parameters constant) to quantify how the model predictions vary. The resulting variations in the state variables are a measure of the sensitivity of the model predictions to the parameter whose value was varied. This can be very informative, especially in understanding how the various processes being modeled affect sediment transport. This analysis is frequently used to identify the model parameters having the most impact on model results, so that the modeling team can ensure these parameters are well constrained by site data.

Uncertainty in models usually results from the following three causes:

1. Models use equations that are simplified approximations of complex processes, which results in uncertainty in just how well these equations represent the actual processes;
2. The unknown accuracy of the values used to parameterize the equations (i.e., uncertainty in how well the input data represent site conditions); and
3. Uncertainty in the physical conditions (e.g., future hydrologic and meteorologic conditions, changes in land use) used in models for evaluating remedial alternatives.

Typically, uncertainty analyses focus on only the second source – the accuracy of the input parameters. While quantitative uncertainty analyses are possible and practical to perform with watershed loading models and food web models, they are computationally not so at present for fate and transport models. An issue intrinsic to conducting uncertainty analyses is that the uncertainty bounds for each parameter are also estimates, with their own associated uncertainty. One commonly used method to assess uncertainty is to use bounding calculations to produce a conservative model outcome to compare to the model's best estimate outcome. The model outcome can be developed using parameter values that result in a conservative outcome, but at the same time do not result in degraded model performance, as measured by comparison to the calibration and validation data sets. A second method of assessing uncertainty involves quantification of "model error" by comparing model results to the data used for model calibration and validation and applying that error to model predictions, as described in Connolly and Tonelli (1985).

3.4.3.8 Analyzing Model Results

The main outputs from the sediment transport models are (1) evolution of the sediment bed and (2) time series of total suspended solids at one or more locations. The user specifies output frequency within the input file of the sediment transport model. All sediment output files are saved at this frequency. In addition, many sediment transport models permit the user to output variables at higher frequencies for individual cells or nodes specified by the user. Typical frequency for output is on the order of 1–2 hours for a 1-week simulation. Output files can become extremely large if output for all cells/nodes is too frequent. The higher frequency output at specified nodes can be on the order of every 10–30 min.

The following figures show examples of model output from sediment transport models. Figure 3.13 shows spatial variation in deposition thicknesses over a portion of a model domain as predicted by a sediment transport model. Figure 3.14 shows a high frequency time series of suspended solids (vertically averaged) saved at a specific location. Figure 3.15 shows a high

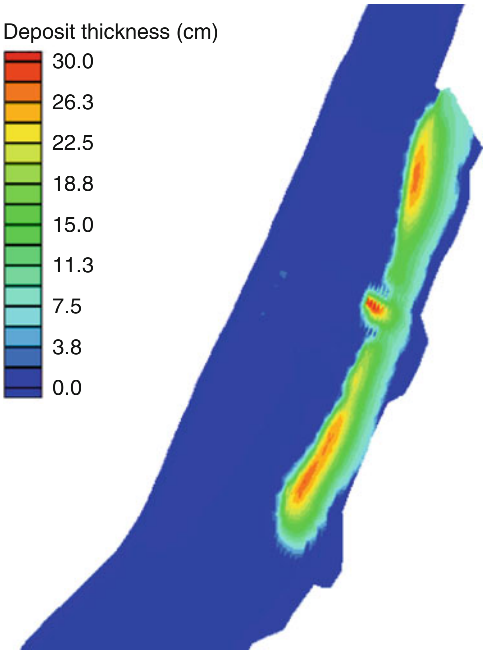


Figure 3.13. Spatial variation of deposition rates in proximity of a port. *Color legend bar* indicates deposition rates in cm/month.

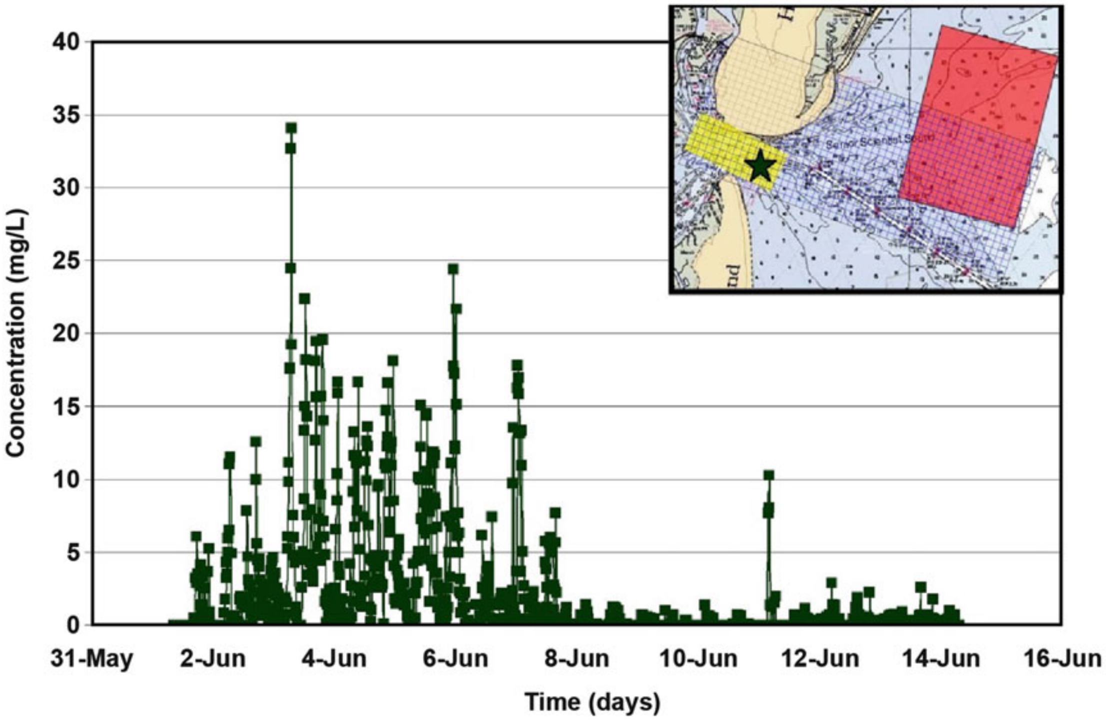


Figure 3.14. High frequency time series of suspended solids at a specific location (*star* in *inlet*).

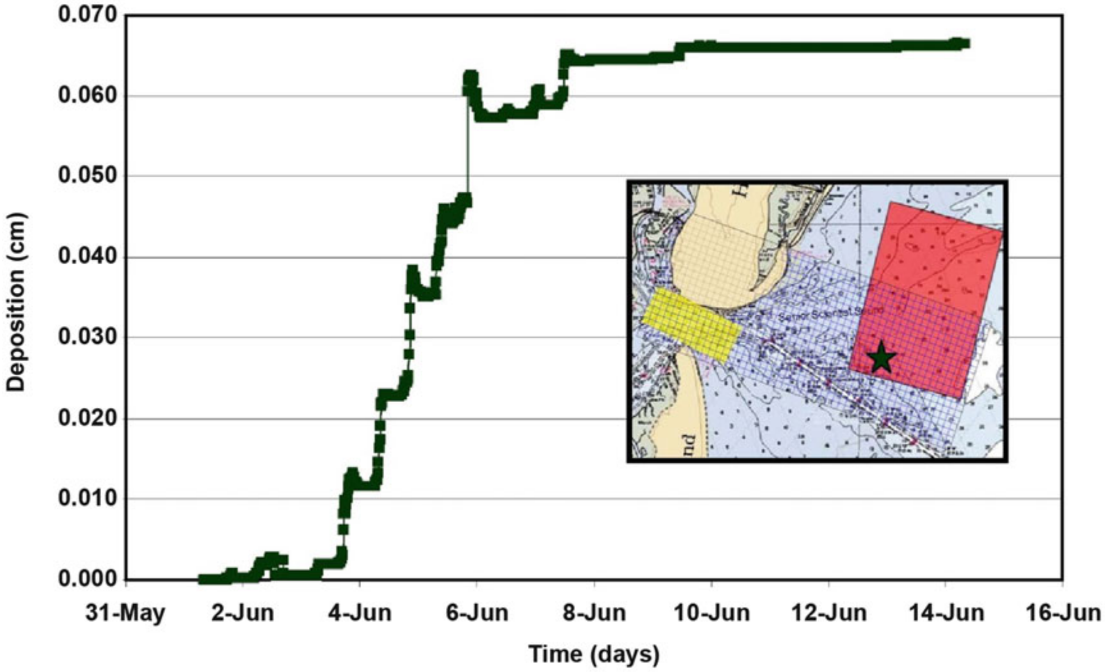


Figure 3.15. High frequency time series of sedimentation at a specific location (*star*).

Figure 3.16. Cross-section of sediment plume in a river.

frequency sedimentation time series. Figure 3.16 shows a channel cross-section of suspended solids for a plume moving downstream in a 3D sediment transport model.

Results from sediment transport models are often analyzed to determine specific, project-related output. Examples include the following:

- Deposition rates in navigation channels, ports, etc.
- Erosion rates in areas of the model domain where concentrations of a particular contaminant of concern are high.
- Erosion rates at offshore dredged material placement sites.
- Locations where sediment eroded from placement sites deposit.

3.5 SUMMARY

This chapter provided (1) an overview of the transport of both cohesive and noncohesive sediments in surface waters, (2) guidance for use in assessing and/or quantifying sediment transport and (3) procedures for use in modeling sediment transport. As discussed, the basic knowledge of these topics provided in this chapter is requisite to understanding many of the contaminant transport processes important in sediments due to the strong particle associations of most contaminants of concern. The assessment methodology involves (1) identifying the processes and mechanisms that might result in erosion, (2) determining the most appropriate methods to use to assess sediment resuspension and deposition and (3) quantifying sediment resuspension and deposition rates under varying flow conditions. Such a methodology could be used by remedial project managers in evaluating remedial alternatives for contaminated sediment Superfund sites.

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APPENDIX 3A

CALCULATION OF COMBINED CURRENT-WAVE BED SHEAR STRESS

The combined current-wave bed shear stress τ_{cw} formulation by Soulsby et al. (1993) is described in this appendix. The current-induced bed shear stress is calculated as:

$$\tau_c = \rho C_D u_{mean}^2 \qquad \text{(Eq. 3A.1)}$$

where ρ is the fluid density, C_D is the drag coefficient and u_{mean} is the mean current velocity. The drag coefficient is obtained from:

$$C_D = \left[\frac{0.4}{\ln(h/z_o) - 1}\right]^2 \qquad \text{(Eq. 3A.2)}$$

where h is the boundary layer height and z_0 is the virtual origin of the logarithmic velocity profile for turbulent flows. The shear velocity, u_*, is calculated as:

$$u_* = \sqrt{\tau_c/\rho} \qquad \text{(Eq. 3A.3)}$$

The wave-induced bed shear stress is calculated as:

$$\tau_w = 0.5\rho f_w u_b^2 \qquad \text{(Eq. 3A.4)}$$

Table 3A.1. Coefficients for Equations 3A.7 and 3A.8 by Soulsby et al. (1993)

a1	−0.06
a2	1.7
a3	−0.29
a4	0.29
m1	0.67
m2	−0.29
m3	0.09
m4	0.42
n1	0.75
n2	−0.27
n3	0.11
n4	−0.02
I	0.8

where f_w is the wave friction factor and u_b is the bottom orbital velocity amplitude. This amplitude is calculated using the linear wave equation:

$$u_b = \frac{H\sigma}{2\sinh kh} \qquad \text{(Eq. 3A.5)}$$

where H is the wave height, $\sigma = 2\pi/T$ is the wave angular frequency, $k = 2\pi/L$ is the wave number, T is the wave period and L is the wavelength. Given $A = u_b/\sigma$, the wave friction factor is given by:

$$f_w = 0.00251\exp\left[5.21\left(\frac{A}{k_s}\right)^{-0.19}\right]; \quad \frac{A}{k_s} > 1.57 \qquad \text{(Eq. 3A.6a)}$$

$$f_w = 0.3; \quad \frac{A}{k_s} \leq 1.57 \qquad \text{(Eq. 3A.6b)}$$

where k_s is the Nikuradse bed roughness, equal to $30z_0$.

The current and wave shear stresses are superimposed using the following equations:

$$\begin{aligned} Y &= 1 + aX^m(1-X)^n \\ Y &= \frac{\tau_{cw}}{\tau_c + \tau_w} \\ X &= \frac{\tau_c}{\tau_c + \tau_w} \end{aligned} \qquad \text{(Eq. 3A.7)}$$

where

$$a = \left(a_1 + a_2|\cos\phi|^I\right) + \left(a_3 + a_4|\cos\phi|^I\right)\log(f_w/C_D) \qquad \text{(Eq. 3A.8)}$$

with analogous expressions for m and n. The quantity ϕ is the angle between the current stress vector and the wave stress vector. These coefficients are given in Table 3A.1.

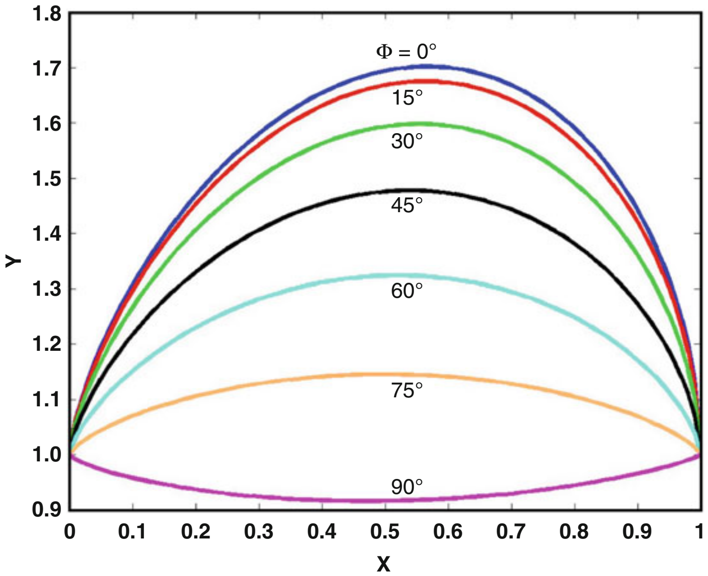

Figure 3A.1. An example of the Soulsby et al. (1993) current-wave bed shear stress function.

In Figure 3A.1, Equation 3A.7 is plotted in terms of Y against X for values of ranging from 0° to 90°. Additionally, the following ratios are assumed: $A/z_0 = 10^4$ and $z_0/h = 10^{-4}$. This plot indicates that the combined bed shear stress can be as much as 1.5 times the sum of the current and wave shear stresses.

CHAPTER 4

THE MECHANICS OF SOFT COHESIVE SEDIMENTS DURING EARLY DIAGENESIS

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4.1 INTRODUCTION

Natural, surficial, cohesive[1] (clay-bearing), aquatic sediments are subject to a variety of phenomena in which physics, rather than say chemistry, plays an essential role; this includes, but is not limited to, bioturbation, self-weight compaction and phase growth. Scientific monographs (e.g., Berner, 1971, 1980; Boudreau, 1997; DiToro, 2001; Burdige, 2006; Schultz and Zabel, 2006) that focus on early diagenesis, i.e., those changes occurring in the top 1–10 meters (m) of aqueous sediments, make only passing reference to the physics of early diagenetic phenomena. In contrast, civil engineers, soil physicists and geophysicists have afforded great attention to the physics/mechanics of compaction, particularly in soils, anthropogenic sediments and basin-scale studies (e.g., Yong and Warkentin, 1966; Giles, 1997; Wang, 2000; Craig, 2004; Mitchell and Soga, 2005; Das, 2008); yet, this knowledge has not been effectively transferred to obtain a better understanding of early diagenesis.

To place this gap in context, consider the following two questions. Firstly, could one hope to make sense of the flight of a bird without an understanding of the properties of the air it flies in? Likewise, would one be able to predict currents in a stream or the sea without knowledge of the properties and physics of water? Presumptions aside, we would say no in both cases. Yet, most scientists, and even some engineers, who study early diagenetic phenomena have been surprisingly content to ignore the physics of surficial, cohesive sediments.

This chapter addresses the physics of surficial, aqueous, cohesive (clay-bearing) sediments and how these physics play into a number of natural diagenetic phenomena. These phenomena occur in both pristine and contaminated sediments. This chapter is neither extensive nor comprehensive; it simply states a simple version of the three-dimensional, mathematical theory of stresses and strains common to books on mechanics (fluid or solid). Instead, its emphasis centers on some final results from theory and certain applications. As such, while this chapter may appear mathematically unsophisticated to those with a background in mechanics, the aim is to illustrate the application of theory to early diagenesis in natural, cohesive, surficial, soft sediments. Other more mathematical treatments of this topic for surficial sediments are available in Verreet and Berlamont (1988) and Winterwerp and van Kesteren (2004).

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[1] We use "cohesive" in the physics sense of "the sticking together of particles," without the geological restriction that these sediments be muds. Thus, we have found that clay-bearing sands are often cohesive, and are treated that way.

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The chapter begins with a review of the conceptual framework for describing the physical behavior of materials subject to stress(es). This review introduces names for certain end-member behaviors and the parameters found in their mathematical descriptions. Obtaining values of these constants for soft clay-bearing sediments is not a trivial task and a subsequent section reviews progress in that direction. Finally, these behavioral concepts are used to explain self-weight compaction, animal motion and bioturbation, and bubble formation – all early diagenetic phenomena that occur in pristine and contaminated sediments. Such phenomena are relevant to the study and understanding of contaminated sediments because compaction can concentrate pollutants, bioturbation can spread the contaminant to pristine zone and areas, and bubbles can release volatiles chemicals to the overlying waters.

4.2 PHYSICAL MODELS (RHEOLOGY) OF MATERIALS

4.2.1 Conceptual Models

If a stress (force per unit area), σ, is applied to a homogeneous material, a number of outcomes are possible. The application of stress usually engenders strains (deformations), ε, in the material. Stress and strain are inherently three-dimensional quantities (i.e., tensors), and they are defined mathematically in a subsequent Section 4.2.5. For the moment, however, they can be treated as uni-dimensional, which can then be simply extended to three dimensions.

Common classic responses to stress include (Long, 1961; Shames, 1964; Jaeger, 1969; Davis and Selvadurai, 1996, 2002; Giles, 1997; Winterwerp and van Kesteren, 2004; Bird et al., 2007):

- Continuous deformation of the material with time ($\dot{\boldsymbol{\varepsilon}} = \boldsymbol{d\varepsilon/dt \neq 0}$) as long as the force is applied (Figure 4.1a).[2] This type of response characterizes what is known as a fluid; hence the common adage thrown at generations of first year physics students that "a fluid does not support a stress." If the rate of strain (deformation) is constant with time, the fluid is termed Newtonian. Non-Newtonian fluids include power-law fluids and Bingham plastics.
- A material can adopt a new stable (time-independent) configuration upon application of a stress. If this deformation is entirely reversible when the stress is removed, then this material is said to be elastic (Figure 4.1b). If the new configuration is stable, but not reversible, the stress has passed the Yield or Elastic Limit and has deformed plastically. Plastic deformation can involve a flow. Strain hardening describes stable, increasing deformation that is significantly irreversible.
- Some materials will exhibit fluid-like behavior in response to some stresses and stress rates, while elastic or even plastic behavior for others. These are visco-elastic and visco-elasto-plastic materials. Sediments fall within this category, but idealization to an end-member is often possible.

The above classification is not exhaustive, and it is primarily based on tensional (pulling) stresses on solids. Geological processes are often compressive and that is considered below.

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[2] Many papers in the literature plot strain, ε, or strain rate (velocity), $\dot{\varepsilon}$, on the x-axis, probably for historic reasons, i.e., you could see the strains or strain rates, but stresses were hard to measure. Figure 4.1 plots the stress, σ, on the x-axis to be consistent with the scientific tradition of placing the independent variable (cause) on the abscissa. There will be an advantage to this when we consider compaction.

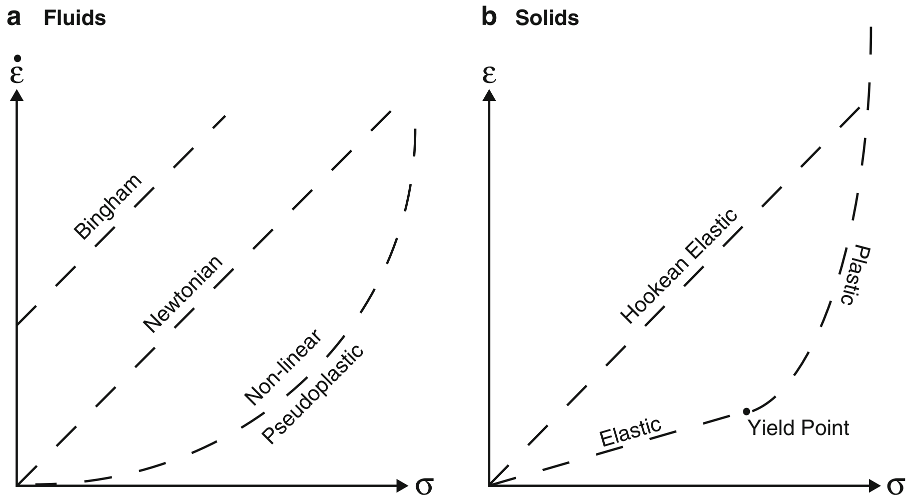

Figure 4.1. Figures illustrating classic behavior of fluids (a) and solids (b) to applied stress (σ). (a) True fluids do not support stresses and flow as a result of applied stress, i.e., their strain changes continuously with time, $\dot{\varepsilon}$. The flow response may be linear (Newtonian) or nonlinear (e.g., pseudoplastic). A Bingham fluid acts like a solid at low stresses, but as a Newtonian fluid above a threshold. (b) Elastic solids will reach a new equilibrium configuration, characterized by the strain ε, under applied (tensile) stress. If the deformation is completely reversible and linear, then the solid is Hookean. At some stress the material deformation will cease to be reversible (yield point), and further deformation is termed plastic Note that a solid may deform linearly with applied stress, but fail to be reversible; plasticity does not necessitate nonlinearity.

4.2.2 Phenomenological Formulas and Constants

The behaviors described above can be encapsulated into simple behavioral formulas, so-called constitutive equations, e.g., Jaeger (1969) and Davis and Selvadurai (1996, 2002). In general, stress applied even in a single direction will create strains in all directions; nevertheless, it is possible to discuss constitutive equations by considering only tensile/compressive stress applied in a single direction, σ, and the resulting deformation in that direction, ε (see Appendix 4A).

A fluid deforms continuously with applied stress (e.g., a pressure gradient), and a Newtonian fluid does so linearly; thus, the latter is characterized by the formula

$$\sigma = \eta\dot{\varepsilon} \qquad \text{(Eq. 4.1)}$$

where η is the dynamic viscosity. By equating $\dot{\varepsilon}$ to the spatial gradient of the velocity, one obtains the more familiar form of Newton's law of viscosity (Bird et al., 2007).

A linear elastic (Hookean) substance responds reversibly to stresses to attain a new equilibrium configuration, i.e.,

$$\sigma = k\varepsilon \qquad \text{(Eq. 4.2)}$$

where k is formally the "spring constant," but it is identical to Young's modulus, E, for the purposes in this chapter, i.e., $E = k$. The models advanced by Johnson et al. (2002), Gardiner et al. (2003) and Algar and Boudreau (2009) to explain methane bubble formation in muddy sediments are Hookean (see below).

There are a variety of idealized materials that exhibit elastic behavior at low strains and fluid behavior above a strain threshold. When a solid behavior is Hookean below such a limit and the subsequent fluid behavior is Newtonian, then the substance is termed a Bingham plastic. Bingham models have been applied to many sediments (see the review by Verreet and Berlamont (1988)).

A Kelvin or Voigt material, which is one form of a linear visco-elastic substance, is approximated by assuming that viscous and elastic behaviors act in parallel, i.e.,

$$\eta\dot{\varepsilon} + E\varepsilon = \sigma \tag{Eq. 4.3}$$

and this has been employed by Maa and Mehta (1988) and Jiang and Mehta (1995) to describe the transport behavior of some muds, and by Algar (2009) to explain gas bubble rise in cohesive sediments. Conversely, a Maxwell substance assumes that these responses act in series, i.e.,

$$\dot{\varepsilon} = \left(\frac{\dot{\sigma}}{E}\right) + \left(\frac{\sigma}{\eta}\right) \tag{Eq. 4.4}$$

and this has been employed in modeling fluidized muds (Maa, 1986; Williams and Williams, 1989). Many other types of behavior can be captured by these types of simple constitutive equations.

As noted above, a solid may exhibit plastic behavior, during which the solid will deform as in elastic deformation, but the deformation is not reversible; in other words, plastic deformations permanently alter the shape and relative positions of all the “particles” that make up the solid. Release of the stress can lead to some relaxation of the strain, but not to the original undeformed positions. The simplest models of plasticity are unidirectional in terms of the strain obtained for a stress level and can be simple algebraic equations, including linear forms like Equation 4.2. Plasticity is sometimes used to describe compaction of sediments, as discussed below.

4.2.3 Phenomenological Constants for Sediments

While the models described above were originally intended for relatively homogeneous materials, soft, cohesive (clay bearing) sediments, as well as other geological media, have been described using these equations (Jaeger, 1969). Aqueous sediments are patently heterogeneous and composite, made of an immiscible mixture of pore fluid and solid grains. When subject to a stress, sediments can and do behave in a more complex manner than homogeneous substances, and this in turn complicates not only their classification, but the values and meanings of their phenomenological constants.

Applying a stress can cause pore fluid to move relative to the solid grains, i.e., Darcy flow. If flow does occur, the solids and fluids are usually displaced relative to each other; therefore, this separation would characterize an irreversible deformation. As a consequence, scientists and engineers who make measurements of the geo-mechanical properties of sediments and the resulting phenomenological constants are careful to specify if the measurement permitted or did not permit pore fluid flow, regardless of whether or not such a relative displacement/flow, in fact, did occur. Thus, if the excess porewater pressure can be dissipated by flow, the measurement is termed drained; conversely, if pore fluid flow is prevented, e.g., by confinement in an encompassing, impermeable sample container, then the measurement is called undrained. Sediments in nature are usually in a drained state with respect to natural processes, so that drained-state elastic and plastic constants would normally be employed.

Values for the viscosity (η) and the true/reversible Young’s modulus (E) have been obtained experimentally for a number of sediment sites; these values, as well as some

Table 4.1. Selected Experimentally Determined Viscosities of Some (Non-resuspended) Muds and Other Reference Materials

Source Location	Porosity	Viscosity (Pa·s)	Source
Kerala, India	0.88	2.76×10^4	Jiang and Mehta, 1995
Okeechobee, USA	0.89	9.56×10^2	Ibid
Mobile Bay, USA	0.87–0.93	$0.0215–2.24 \times 10^2$	Ibid
Synthetic mud	0.89–0.97	1.15×10^4	Ibid
Gulf of Mexico	n/a	5.0×10^4	Hsiao and Shemdin, 1980
Pure water (20°C)	–	1.0×10^{-3}	http://en.wikipedia.org/wiki/Viscosity
Molasses (25°C)	–	5.0–10	Ibid
Peanut butter (25°C)	–	250	Ibid

environmental information, are provided in Tables 4.1 and 4.2. It is not known if these values are representative of all cohesive sediments, nor is the dependence of these values on sediment properties, i.e., depth, grain size, porosity, temperature, organic matter content, etc., quantitatively established at this time. The few sediment viscosities in Table 4.1 are for non-fluidized conditions. The values show that clay-bearing sediment is indeed "slower than molasses in winter"[3] and peanut butter on cold toast! This small viscosity explains why clays removed from core barrels retain their shape under their own weight (load) for long periods of time; nevertheless, under suitable stress conditions sediments can and do flow, to which turbidite flows attest.

Reversible (elastic) Young's moduli are reported in Table 4.2 and require one caveat. Finite-strain E values from reversible compression/release tests, e.g., Figure 4.2, are on the order of 10^5 Newtons/square meter (Nm^{-2}), or up to five orders of magnitude lower than what is recorded by acoustical measurements. This apparent discrepancy is not a problem, but rather it is related to the length and time scales of the applied stress and the measurements (Clayton and Heymann, 2001; L'Esperance, 2009). The two methods measure different parameters; consequently, one should use finite strain values for finite strain phenomena.

The reversible (elastic) E values in Table 4.2 are again from a limited data set from only a few sites, and they can hardly be called representative. In addition, the dependence of the reversible E on sediment properties and depth is not well known, but it does appear to increase with depth (Barry, 2010). See as an example Figure 4.3, i.e., the sediment becomes increasingly stiff with depth, undoubtedly due to the effects of compaction. More determinations from a wide variety of cohesive sediment environments are needed.

Another mechanical parameter that will appear in subsequent formulas is Poisson's Ratio, ν; this parameter is the ratio of the deformation in the direction of an applied uni-axial stress to the resulting deformation in the other directions (assuming isotropy). For an incompressible solid, $\nu = 0.5$. Since both water and most solids that make up sediments are incompressible, one would expect a ν near 0.5, at least if the sediment is fully saturated. Table 4.3 contains Poisson's Ratios for various sediments (including some sands), and the expectation is generally met. Even acoustically determined ν values are near 0.5. However, the presence of significant

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[3] Old North American proverb, indicating very slow to the eye.

Table 4.2. Young's Modulus Values (Drained) for Various Sediments and for Selected Reference Materials

Source Location	Sediment Type	E (Pa)[a]	Method	Source
Cole Habour, NS	Silty sand	$2.4–5.0 \times 10^4$	Uniaxial compression	L'Esperance, 2009
Cole Harbour, NS	Silty sand	1.4×10^5	Uniaxial compression	Johnson et al., 2002
Windsor and Canard, NS	Clay-bearing silty sands	$0–9 \times 10^5$ (0–25 cm)	*In situ* dilatometer	Barry, 2010
Continental shelf	Fine sand to silty sand	$8.13–15.11 \times 10^8$	Acoustic (calculated)	Hamilton, 1971
Windsor, NS	Silt to clay	7.5×10^5	Uniaxial compression	L'Esperance, 2009
Continental shelf	Silt to clay	4×10^8	Acoustic (calculated)	Hamilton, 1971
Deep sea	Clays	$1.45–4.3 \times 10^8$	Acoustic (calculated)	Hamilton, 1971
London clay (terrestrial)	Clay	$1.1–1.2 \times 10^8$	Bender element-triaxial	Gasparre et al., 2007
Margin sediment, India	?	$2.5–2.9 \times 10^9$	Acoustics	Raju and Ramana, 1986
Synthetic	Gelatin[b]	$0.6–1.3 \times 10^3$	Uniaxial compression	Takada, 1990
Synthetic	Gelatin[b]	$2.5–50 \times 10^3$	Uniaxial compression	Hall et al., 1997
Synthetic	Gelatin[b]	$1.5–10 \times 10^3$	Uniaxial compression	Johnson et al., 2002
Synthetic	Gelatin[b]	$31–81 \times 10^3$	1-D tensile tester	Sato et al., 2001
Synthetic	Gelatin[b]	$9.7–17 \times 10^3$	Uniaxial compression	L'Esperance, 2009
Synthetic	Polyethylene	$0.8–2.7 \times 10^9$	Compression	Johnson et al., 2002
Synthetic	Nylon	$2–4 \times 10^9$	Compression	Johnson et al., 2002
Synthetic	Rubber	$0.01–0.1 \times 10^9$	Compression	http://www.engineeringtoolbox.com/young-modulus-d_417.html
Synthetic	Aluminum	69×10^9	Compression	http://www.engineeringtoolbox.com/young-modulus-d_417.html

[a] $1\ \mathrm{N\ m^{-2}} = 1\ \mathrm{Pa}$

[b] Varies considerably with mixture strength and temperature

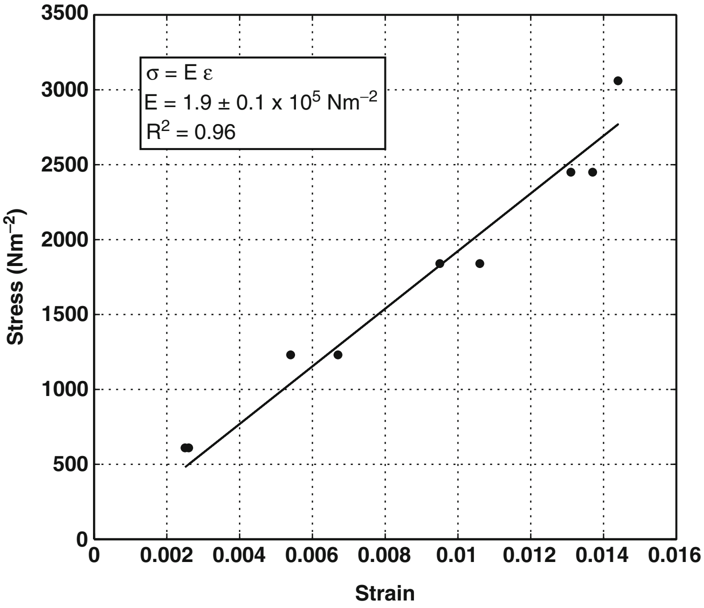

Figure 4.2. An example of a linear and reversible stress-strain diagram for a cohesive sediment from Nova Scotia, Canada. This is true Hookean elasticity with a Young's modulus of 1.9 × 10^5 Nm^{-2} (from Barry, 2010).

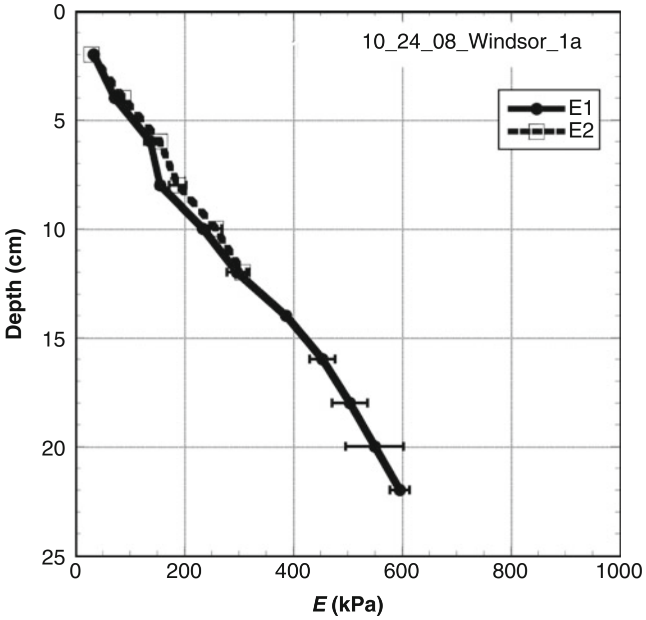

Figure 4.3. Typical depth profile of (reversible) Young's modulus, *E*, at a field site (Windsor) in coastal sediment of the Bay of Fundy, Nova Scotia, Canada. There is an essentially linear increase in modulus with depth from values near zero at the surface to values of 600 kPa at 22 cm depth. Profiles were run in two adjacent locations only 30 cm apart (*solid* and *dashed lines*) and show good homogeneity over short, lateral distances. One standard deviation error shown for average of three measurements (from Barry, 2010, but also see similar plots in Barry et al., 2012).

Table 4.3. Poisson's Ratio (Drained) for Various Sediments

Source Location	Sediment Type	ν (dimensionless)	Source
Various	Sand, fine sand, silty sand	0.453–0.491	Hamilton, 1971
San Diego	Medium sand	0.494	Hamilton et al., 1970 as cited in Hamilton, 1979
Shallow to deep sea	Silt clays, turbidites and mudstones	0.420–0.497	Hamilton, 1979
North sea	Sand	0.487–0.499	Hamilton, 1979
Cole Harbour, NS	Fine sand	0.49956 ± 0.003	L'Esperance, 2009
Deep sea to continental terrace	Silty clay	0.478–0.487	Hamilton, 1971
–	Clays	0.4982–0.4997	Davis and Schulteiss, 1980 as cited in Salem, 2000
Windsor, NS	Silt/clay	0.4989 ± 0.0008	L'Esperance, 2009
–	"Typical" silt and clay	0.25	Breitzke, 2006
Various	Soils (including undersaturated)	−1.0 to 0.5	Pickering, 1970 as quoted by Salem, 2000
Synthetic	Gelatin	0.5	Markidou et al., 2005

free gas can drive ν down to smaller values, even negative values. Some geophysicists employ ν values between 0.2 and 0.3 for some acoustical calculations, but measurements tend to support values near 0.5 when gas is not present.

Given Young's modulus and Poisson's Ratio, it is possible to calculate two other common elastic constants, the shear modulus, G, (Davis and Selvadurai, 1996, 2002)

$$G = \frac{E}{2(1+\nu)} \qquad \text{(Eq. 4.5)}$$

and the Lamé constant, λ,

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)} \qquad \text{(Eq. 4.6)}$$

If sediment is essentially incompressible, as indicated by the values in Table 4.3, then the shear modulus is E/3 and the Lamé constant is infinite. Finite-strain bending plate measurements (e.g., Lavoie et al., 1996) produce G values of 3–4 × 10^5 Nm^{-2} going from a depth of 20 centimeters (cm) to 200 cm in a muddy sediment of Ekernfjorde Bay (Germany). If Windsor-Canard sediments (Table 4.3) are indicative of E values for similar sediments, then one would indeed predict G values in this range, if these sediments are incompressible; therefore, the existing database of non-acoustic shear moduli may represent a significant resource for obtaining values of (reversible) Young's moduli for aqueous sediments.

If sediment can act as a solid, at least under some stress conditions, then it can fail, i.e., fracture, rather than simply flow or plastically deform. For example, fracture of sediments occurs when bubbles form as a result of gas injection (Johnson et al., 2002) or when various organisms (worms, clams, etc.) move through soft cohesive sediments (Dorgan et al., 2005).

Table 4.4. Fracture Toughness (K_{1C}) of Some Cohesive Sediments

Source Location	Sediment Type	K_{1C} ($N\ m^{-3/2}$)	Source
Cole Harbour, NS	Clay-bearing silty sand	410–550	Johnson et al., 2002
Canard, NS	Clayey silt	80–1,300	Johnson et al., 2012
Various	Agricultural soils	1,503–6,036	Aluko and Chandler, 2006
Synthetic	Gelatin	45–110[a]	Menard and Tait, 2002
Synthetic	Gelatin	28–60[a]	Rivalta and Dahm, 2006

[a] Dependent on concentration and temperature

The simplest theory of solids, i.e., linear elastic fracture mechanics (LEFM), e.g., Broek (1982) or Gross and Seelig (2006), characterizes the fracture strength of a solid by a parameter K_{1C}, known as the fracture toughness or the critical stress intensity factor – a real mouthful. K_{1C} is a material property and it has been measured in a few soft cohesive sediments, as well as in the analogue material, gelatin (see Table 4.4). Fracture of real solids is related to K_{1C}, rather than tensile strength, because real solids contain flaws, and it is the opening of these flaws that permits initiation of fracture. In an ordered solid, such as a perfect crystal that contains no flaws, fracture must break the underlying bonds of the structure, and that takes far more energy, characterized as the tensile strength.

That cohesive sediments have a fracture toughness should come as no surprise, as they have long been credited with possessing shear strength (e.g., Mehta and Partheniades, 1982; Partheniades, 1991), which is simply fracture by applied shear, rather than tensional, forces. (Note that while such measurements are reported as shear strength, they are, in fact, measurements of shear toughness.) Measurements of shear strength have long been made in cohesive sediments, and the literature on that topic is so large that it cannot be even superficially reviewed here. Shear strength is employed as a critical parameter in modelling the erosion of mud beds. The relationship between shear strength and K_{1C} has not been established for sediments.

The parameter K_{1C} appears generally to increase with depth due to compaction (Johnson et al., 2012), as does the shear strength (Partheniades, 1991), but K_{1C} is also dependent on grain size of the sediment, and probably on other sediment properties and may thus change with an alteration in lithology (Figure 4.4). Sands have no, or little, cohesion, while clays do; thus, sandier sediment layers show up as drops in K_{1C} values in profiles that otherwise increase with depth, again due to compaction.

4.2.4 The Origin of Sediment Mechanical Properties

The value of the mechanical constants for a cohesive sediment must be related to the way this material is put and held together. Early views of cohesive sediment fabric (e.g., Englehardt and Gaida, 1963; Rieke and Chilingarian, 1974) centered on the idea of the presence a “house of cards” structure of fine clay platelets, held together by the attraction of positively charged edges to negatively charged basal plates. TEM photomicrographs of real cohesive sediments (see Bennett et al., 1991, 1996) show a more complicated fabric, with mixtures of particles of different shape and sizes, clays both stacked and in house of cards and with admixed organic matter. In fact, while electrostatics plays a role in aggregation of sediments, these sediments seem to be primarily held together by long polymer organic molecules (e.g., Hunter, 2001; Winterwerp and van Kestern, 2004). An indication of the truth of that hypothesis is contained in

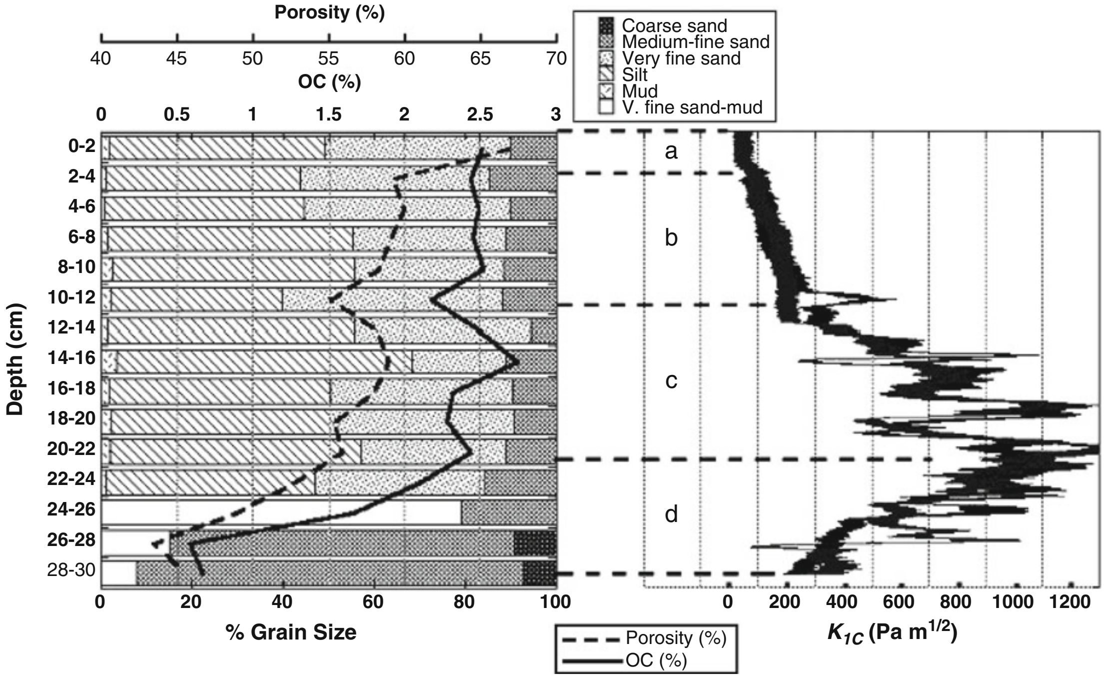

Figure 4.4. The *in situ* fracture toughness (K_{1C}) of a sediment from the Bay of Fundy, Nova Scotia, Canada, as a function of depth and correlated to grain size of the sediment with depth. Generally, K_{1C} increases with depth due to compaction, but the appearance of sand below 22 cm causes a drop in K_{1C} (data in this figure are reported in Johnson et al., 2012).

Table 4.2, which shows that gelatin, made of long chain polymeric proteins, has a Young's modulus similar to that of sediments. Similarly, the fracture strength of sediments and gelatin are comparable (Table 4.4), which suggests the breaking of similar bonds.

4.2.5 The Mechanical Equations for a Deforming Body

Now that we have the mechanical models and constants relevant to sediments, how are they employed? These constitutive equations and their associated constants form part of a system of equations that govern the deformation of any material. An example set of such equations is given below for an elastic Hookean substance, which is the most commonly assumed form. In this example, we generalize to a three-dimensional Cartesian coordinate system.

The following equations govern the interplay between the applied stresses and the observed deformations. There are nine possible stress components, but isotropic symmetry requirements reduce this to six independent components, σ_x, σ_y, σ_z, τ_x, τ_y and τ_z, where σ indicates a normally directed stress and τ represents a tangential (shear) stress. The subscripts on σ correspond to the direction in which the normal stress is applied and the subscripts on τ indicate the direction normal (perpendicular) to the plane on which the tangential stress is applied.

For a homogeneous solid, these stresses must satisfy the so-called static equilibrium conditions (e.g., Timoshenko and Goodier, 1934; Biot, 1941; Davis and Selvadurai, 1996)

$$\frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_z}{\partial y} + \frac{\partial \tau_y}{\partial z} - b_x = 0 \qquad \text{(Eq. 4.7)}$$

$$\frac{\partial \tau_z}{\partial x} + \frac{\partial \sigma_z}{\partial y} + \frac{\partial \tau_x}{\partial z} - b_y = 0 \qquad \text{(Eq. 4.8)}$$

$$\frac{\partial \tau_y}{\partial x} + \frac{\partial \tau_x}{\partial y} + \frac{\partial \sigma_z}{\partial z} - b_z = 0 \tag{Eq. 4.9}$$

where the b_i ($i = x,y,z$) are the components of any relevant body force (e.g., gravity).

The other observable is the amount of displacement of any arbitrary point in the solid due to the application of the stress(es), denoted u, v and w for the components in the x, y, and z directions. The strains in the constitutive equations are defined from the displacements as (e.g., Timoshenko and Goodier, 1934; Biot, 1941; Davis and Selvadurai, 1996)

$$\varepsilon_x = \frac{\partial \mathrm{u}}{\partial x} \tag{Eq. 4.10}$$

$$\varepsilon_y = \frac{\partial \mathrm{v}}{\partial y} \tag{Eq. 4.11}$$

$$\varepsilon_z = \frac{\partial \mathrm{w}}{\partial z} \tag{Eq. 4.12}$$

$$\gamma_x = \frac{\partial \mathrm{w}}{\partial y} + \frac{\partial \mathrm{v}}{\partial z} \tag{Eq. 4.13}$$

$$\gamma_y = \frac{\partial \mathrm{u}}{\partial z} + \frac{\partial \mathrm{w}}{\partial x} \tag{Eq. 4.14}$$

$$\gamma_z = \frac{\partial \mathrm{v}}{\partial x} + \frac{\partial \mathrm{u}}{\partial y} \tag{Eq. 4.15}$$

where ε_i is the normal strain (compression or dilation) and γ_i is the tangential or shear strain (for $i = x,y,z$).

Finally, the stresses and strains are related through so-called compatibility equations, which implement the constitutive equations. For a Hookean solid, these read (e.g., Timoshenko and Goodier, 1934; Biot, 1941; Davis and Selvadurai, 1996; Wang, 2000)

$$\varepsilon_x = \frac{\sigma_x}{E} - \frac{v}{E}(\sigma_y + \sigma_z) \tag{Eq. 4.16}$$

$$\varepsilon_y = \frac{\sigma_y}{E} - \frac{v}{E}(\sigma_x + \sigma_z) \tag{Eq. 4.17}$$

$$\varepsilon_z = \frac{\sigma_z}{E} - \frac{v}{E}(\sigma_x + \sigma_y) \tag{Eq. 4.18}$$

$$\gamma_x = \frac{\tau_x}{G} \tag{Eq. 4.19}$$

$$\gamma_y = \frac{\tau_y}{G} \tag{Eq. 4.20}$$

$$\gamma_z = \frac{\tau_z}{G} \tag{Eq. 4.21}$$

where E is Young's modulus (Table 4.2), G is the shear modulus, and ν is Poison's ratio (Table 4.3), as defined above. Equations 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.15, 4.16, 4.17, 4.18, 4.19, 4.20, and 4.21 define a system of 15 equations in 15 unknowns; these equations have been solved analytically for some cases, but are readily solved numerically, including by commercial packages, such as COMSOL. Plasticity may sometimes be described using a Hookean model, as long as one does not attempt to unload the solid using the same constitutive equation(s).

Biot (1941, 1956) extended these equations to a composite porous medium, such as sediment, in which the pore fluid may separate from the solid matrix of particles. Equations 4.16, 4.17, and 4.18 gain in that case a new term each that accounts for the "increment of water pressure"; this term disappears in drained situations. In addition, as the porosity or "variation in water content" becomes a variable in this case, another equation for changing water content must then be added and its constitutive equation is Darcy's law. Biot (1973), and many authors thereafter, have extended these equations for porous solids with non-linear constitutive equations and even plasticity (e.g., Small et al., 1976). A short historical review of this topic is available in de Boer (1992).

4.3 MECHANICAL PROCESSES IN NATURAL AQUATIC SEDIMENTS

We now summarize the results of applying mechanical theories to three common diagenetic processes where physics are central to understanding the phenomenon: compaction, bubble growth and bioturbation.

4.3.1 One-Dimensional Compaction with Sedimentation

The quintessential mechanical process during diagenesis is self-weight compaction, or consolidation, with sedimentation of new materials. The accumulating weight of a sediment will cause the porewater, held between sediment grains, to be expelled, creating a decrease in porosity with depth and time.

Models of compaction have a long history in the soils and sediments literature (see the summaries in Giles, 1997; Winterwerp and van Kesteren, 2004). In particular, Terzaghi (1943) produced the first systematic model of compaction by introducing the concept of consolidation/excess pressure that drives the compaction process; this was followed by classic papers from Gibson (1958), McNabb (1960), Been and Sills (1981), Lee and Sills (1981), Koppula and Morgenstern (1982), Znidarcic and Shiffman (1982) and Gibson et al. (1989). Oddly enough, reference to such work is virtually absent in the early diagenetic literature. This absence is in part the result of the unfortunate age-old problem of isolation of fields, but also due to the different perspectives of scientists studying early diagenesis versus those considering soils, or the entire sediment column, or man-produced lumps of sediment.

In this respect, engineers, geophysicists, geotechnical scientists and soil scientists use reference frames that are either fixed to a datum, e.g., the surface of the underlying bedrock, or a selected mass of sediment. The first is a fixed Eulerian frame, while the second is a moving Lagrangian frame. One can, of course, mathematically convert from one to the other, but one choice or the other may be preferred for convenience. Diagenetic studies traditionally do neither; because the focus is on the sediment-water interface, the reference frame is anchored instead at the moving sediment-water interface, i.e., a moving Eulerian coordinate system (e.g., Berner (1980); Boudreau (1997) and Burdige (2006)). This is technically a moving-boundary problem, but by anchoring the coordinate system to the moving sediment-water interface, that problem is transformed into a uni-dimensional problem with a fixed boundary and an apparent velocity (component) of the solids and fluid away from the interface (Berner, 1980; Boudreau, 1997).

Toorman (1996) and Boudreau and Bennett (1999) have formulated the equations of elastic–plastic compaction in this moving diagenetic Eulerian frame. That development will not be presented here. Instead we present solely the distillation and end-result of those studies.

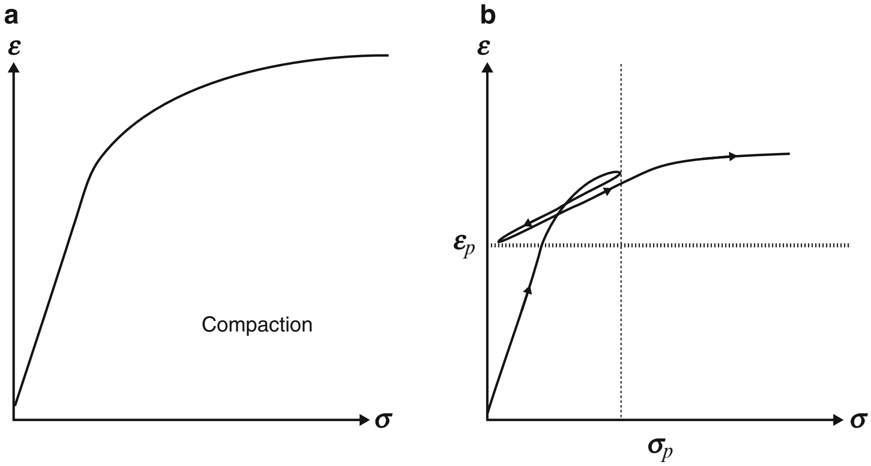

Figure 4.5. (a) An idealized stress-strain curve for a solid under compactive stress. The smaller and smaller effect of stress is due to the increasing difficulty of forcing water out of the sediment structure, and is termed compactive hardening here. (b) This figure illustrates the type of irreversibility expected during compaction, if the load is removed.

If one considers the one-dimensional, steady state compaction of a muddy sediment, an appropriate measure of strain in this case is the relative change in porosity, $\varphi(x)$:

$$\varepsilon_x = \frac{\varphi(x) - \varphi_o}{\varphi_o} = \frac{\varphi_{so} - \varphi_s(x)}{\varphi_o} \qquad \text{(Eq. 4.22)}$$

where x is the depth from the sediment-water interface (positive), $\varphi_s(x)$ is the solid volume fraction, i.e., $1 - \varphi(x)$, and the subscript o indicates an initial value at $x = 0$.

Next, we need to consider the constitutive behavior of sediments. Compaction is an essentially irreversible process by which porewater is "squeezed" out of sediments (permanently) due to self weight. This means that the process is not truly elastic, and the stress-strain relationship for compaction must reflect this irreversibility. This does not mean that there is not a small truly elastic component to the process, but overall it is a permanent deformation, i.e., plastic. Figure 4.5a illustrates the strain (relative porosity change) as stress (weight) is applied continuously to a sediment sample. There is a linear portion, which may or may not be truly elastic, and a nonlinear portion, which indicates definite plastic behavior. In the non-linear region, it takes progressively more and more weight to produce a constant increment of strain (compaction). The literature does not seem to contain a term for this increasing difficulty to compact (compactive hardening?).

If during non-linear plastic compaction the load is removed at some stress σ_p, then the sample does not return to zero strain, but to a finite level of strain ε_p, which reflects the permanent deformation of the porosity, caused by the removal of water (Figure 4.5b). Recommencing the compaction essentially returns the stress-strain relation to the theoretical curve for that material.

Figure 4.6 illustrates the stress-strain relation in sediments from a core taken on the California Margin (Bennett et al., 1999); these data follow the trend indicated in Figure 4.5a. Boudreau and Bennett (1999) offer a non-linear (irreversible/plastic) stress-strain relation for sediment compaction that is consistent with the above principles, i.e.,

$$\varphi_s = s[1 - e^{-r\sigma}] + \varphi_{so} \qquad \text{(Eq. 4.23)}$$

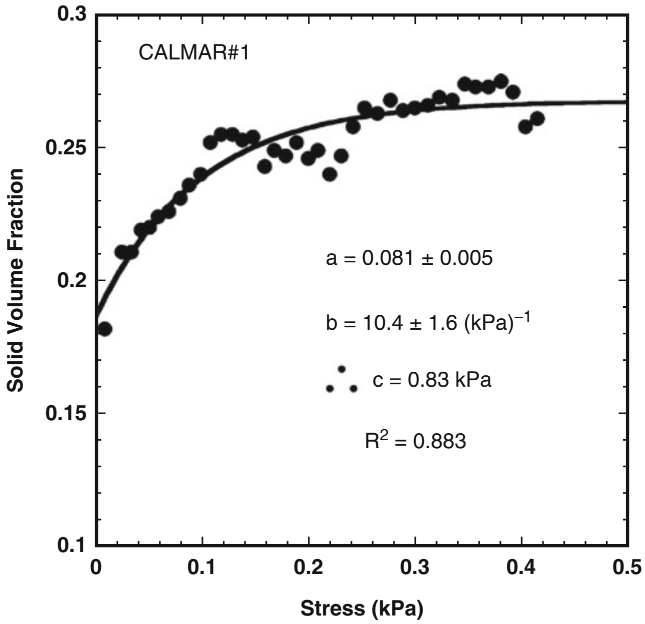

Figure 4.6. A measured solid volume-stress profile from a sediment off the California coast (data taken from Bennett et al., 1999).

where r and s are (empirical) parameters that account for the initial compressibility of the sediment and the attenuation of stress, respectively; a fit of Equation 4.23 is illustrated in Figure 4.6. For small stresses, one can expand the exponential in Equation 4.23 and ignore nonlinear terms; then using Equation 4.22, one can obtain a linear stress-strain relation:

$$\frac{\varphi_{so} - \varphi_s(x)}{\varphi_o} = -c\sigma \qquad \text{(Eq. 4.24)}$$

where $c = r \cdot s$, which is an apparent Young's modulus for compaction; however, this compaction is irreversible and c is not a true elastic constant.

The calculated value of c for this sediment is 0.83 kilopascal (kPa), which is one to two orders of magnitude smaller than the measured reversible Young's moduli for cohesive sediments in Table 4.2. One should not be shocked by this result; again, time scale of application of the force is the key to the separation of water and solids. Compaction c values are smaller than elastic E values because the forces applied over decades to millennia during *in situ* compaction cause the sediment to adjust (strain) more by expelling water, i.e., plastic deformation.

Porosity and its change with depth affect the chemistry of sediments in at least two ways. Compaction engenders a flow of porewater and that can move solutes; however, during early diagenesis, this flow is often small compared to transport by molecular diffusion, and it is this latter process that feels the effects of compaction. Specifically, diffusion is hindered by the presence of the solids, both because the area for diffusion is reduced and because the path the solutes must traverse is longer (see Berner, 1980; Boudreau, 1997). The longer path-length effect is characterized by the tortuosity, θ, which is the ratio of the length of the mean path that is actually followed to the direct distance. Thus, $D_e = D/\theta^2$, where D_e is the effective diffusion coefficient and D is the diffusion coefficient in the absence of the solid particles.

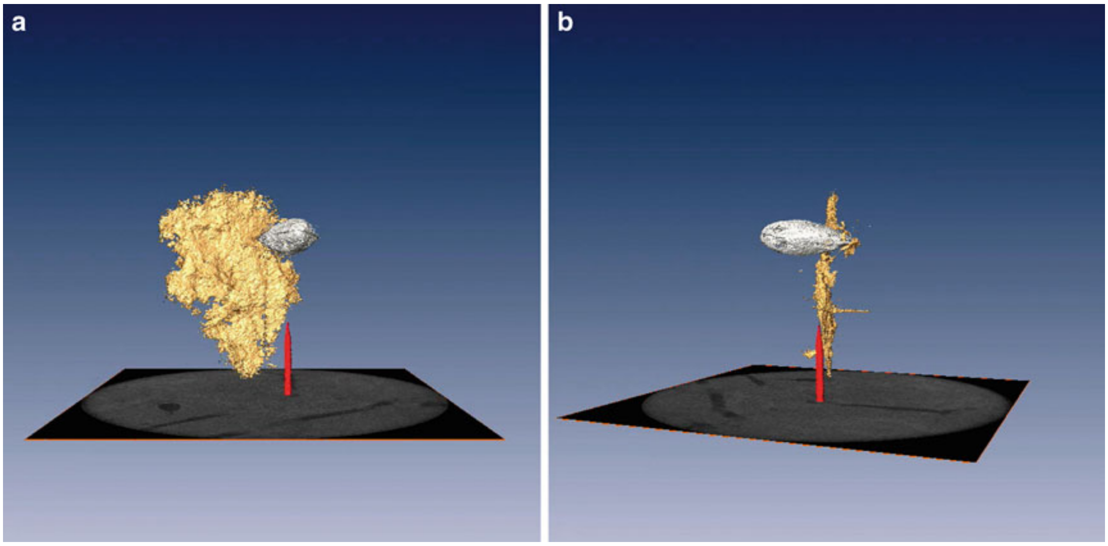

Figure 4.7. Two CT-scans (false color) of a bubble injected into natural sediment. The bubble (gas) is *gold*, the injector needle is *red*, and a small mussel shell, in contact with the bubble, is in *gray*. The sediment itself has been "removed" digitally. The *left-hand* diagram (a) shows a plane view and the *right-hand* (b) a cross section. The bubble is a flat, somewhat irregular mass that is reminiscent of a "corn flake"; for modeling purposes, it is adequately approximated as an eccentric oblate spheroid (from Best et al., 2006, reproduced with the kind permission of the American Geophysical Union).

Amongst others, Boudreau (1996) and Boudreau and Meysman (2006) have analyzed the existing data and presented models of cohesive sediment structure to argue that $\theta^2 = 1 - ln(\varphi^2)$. Therefore, as compaction reduces φ, this feeds back strongly into the effective solute diffusivity. This effect is part of all models of diagenetic processes for solutes in sediments.

4.3.2 The Growth of Methane Bubbles

When a new phase, e.g., free gas or an authigenic mineral, grows in sediments, the phase must make room for itself by displacing the sediment or incorporating the sediment. Gas bubbles, usually methane, in muddy sediments present an archetypal example of a new phase that does not incorporate the sediment and grows by displacing it. Investigations by Johnson et al. (2002), Winterwerp and van Kesteren (2004) and Boudreau et al. (2005) have established that the displacement of the sediment by the free gas is accomplished both by elastic expansion and by fracture, and not by fluid flow of the sediment. The result is a bubble best described as a "corn flake" (Bjorn Sundby, personal communication, McGill University, 2004), as illustrated by the computerized tomography (CT) scans in Figure 4.7, as opposed to the familiar spherical (or near-spherical) bubbles in fluids. Similar bubbles of eccentric shape can be obtained by injecting gas with a needle into gelatin, another soft solid (see Figure 4.8).

The idea that the bubbles in Figures 4.7 and 4.8 result from elasticity and fracture is supported by the application of linear elastic fracture mechanics (LEFM). Specifically, LEFM first assumes a linear Hookean constitutive equation for sediments, i.e., Equations 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.15, 4.16, 4.17, 4.18, 4.19, 4.20, and 4.21, for which we have values of E (Table 4.2) and ν (Table 4.3). Next, LEFM treats a bubble as a "coin shaped" or oblate spheroidal

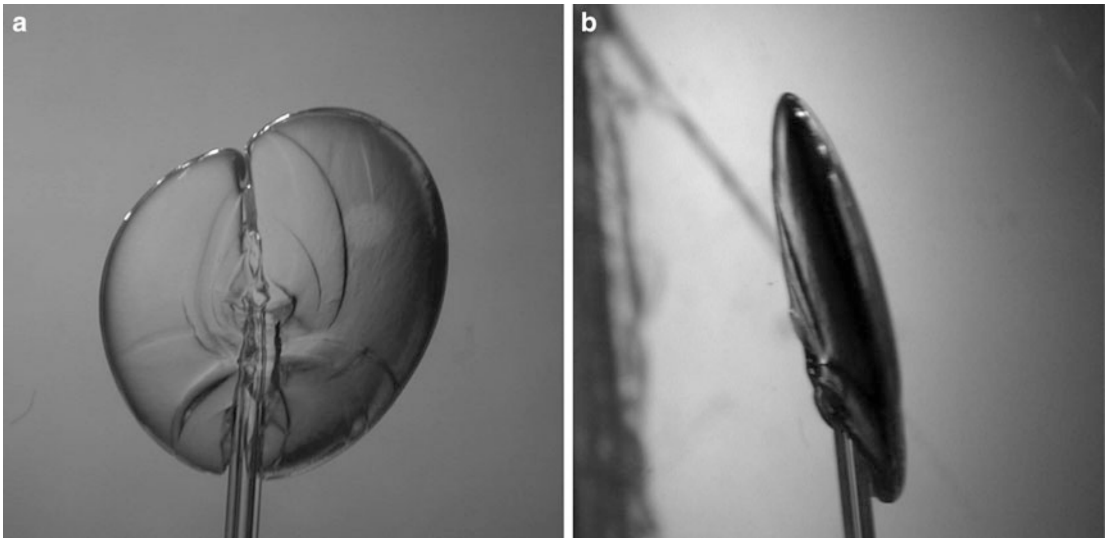

Figure 4.8. Photographs of a bubble injected into gelatin, *left* plane view (a) and *right* (b) cross section. This bubble is a thin oblate spheroid (from Johnson et al., 2002, reproduced with the kind permission of Elsevier B.V).

flaw in a thick (plane strain) medium. Given these reasonable assumptions, then the inverse of the aspect ratio, b/a, of the bubble should be given by the formula (Barry et al., 2010).

$$\frac{b}{a} = \frac{4P(1 - \nu^2)}{\pi E} \qquad \text{(Eq. 4.25)}$$

where b is half the length of the minor axis of the oblate spheroid, a is half the length of the major axis, and P is the internal gas pressure in excess of the surrounding ambient pressure, i.e., the stress that creates the deformation. Equation 4.25 is a similarity relation in that the aspect ratio is fixed for given combinations of ν, E and P. Figure 4.9 compares the observed inverse aspect ratio (IAR) of real bubbles in cohesive sediments and gelatin of various strengths with the predicted ratios from Equation 4.25; the agreement between observation and theory is solid, considering the errors in these measurements and the approximate nature of the theory.

Gardiner et al. (2003) and Algar and Boudreau (2009, 2010) have coupled the mechanical model for a bubble given above with a reaction-transport model for methane in porewaters to obtain predictions of the initial rate of growth of natural bubbles. Figure 4.10 illustrates the predicted initial growth rates for the conditions at Cape Lookout Bight, South Carolina, USA (see Martens and Klump, 1980; Martens and Albert, 1995). Bubbles at that site are about 100–200 cubic millimeters (mm^3) in volume and Figure 4.10 predicts about 4 days to grow bubbles to this initial size. Bubbles can grow much faster than this if they exploit pre-existing flaws/fractures in sediments that have lower K_{1C} values than the bulk sediment (Algar and Boudreau, 2010).

4.3.3 Methane Bubble Rise

If a bubble grows to a critical size in sediments, it will begin to rise due to a (pseudo-) buoyant force (Weertman, 1971a, b) from the difference in overall pressure between the top and the bottom of the bubble. While the formation and growth of a bubble in sediments can be treated as entirely an elastic process, rise must take into account more of the full dynamics of the sediment (Algar, 2009); in particular, the control of bubble rise should include a time

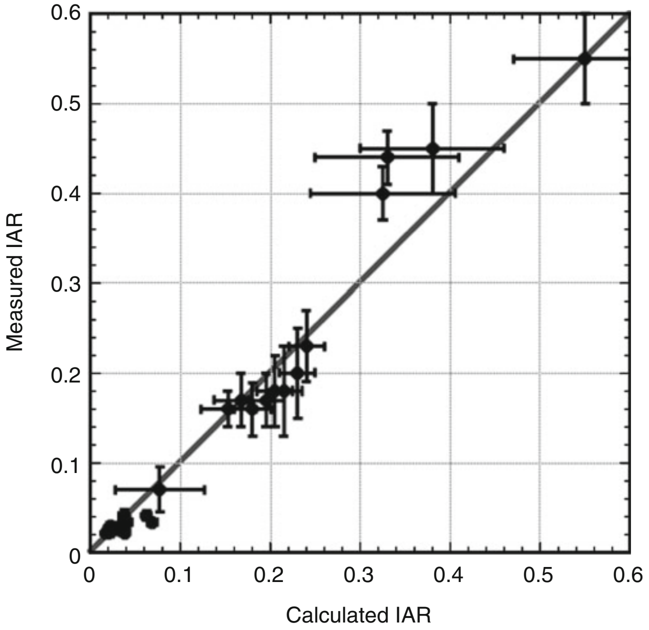

Figure 4.9. A plot of the predicted, Equation 4.10, and observed IAR of bubbles in gelatin of various strengths and in sediments. The *black line* is a 1:1 relationship (from Barry et al., 2010, reproduced with the kind permission of the American Geophysical Union).

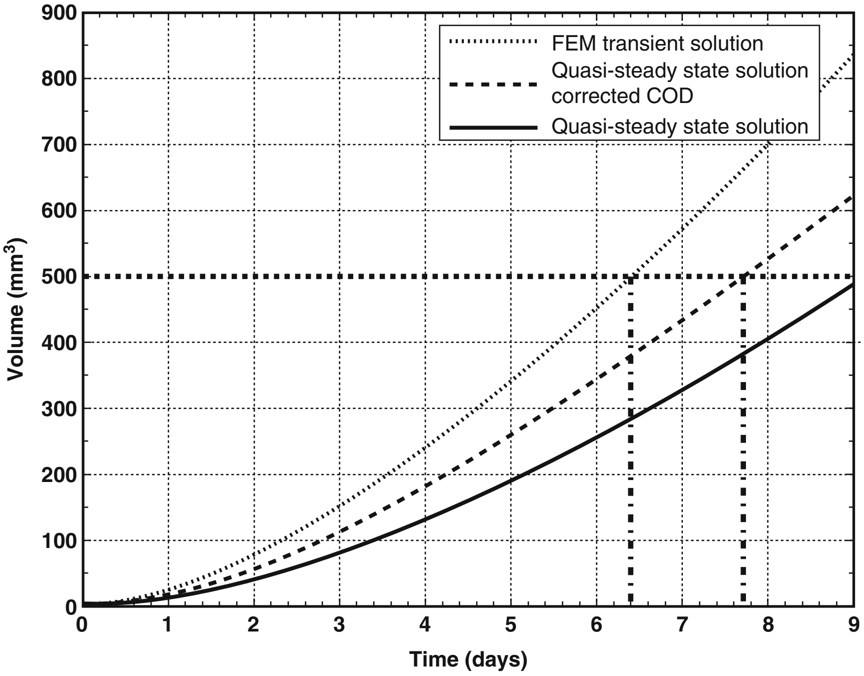

Figure 4.10. The predicted initial growth rate of a bubble in sediments from Cape Lookout Bight, North Carolina, USA. The curve labeled "FEM transient solution" is the best prediction for a sediment without a previous bubble-created flaw (from Algar and Boudreau, 2009, reproduced with the kind permission of Elsevier B.V).

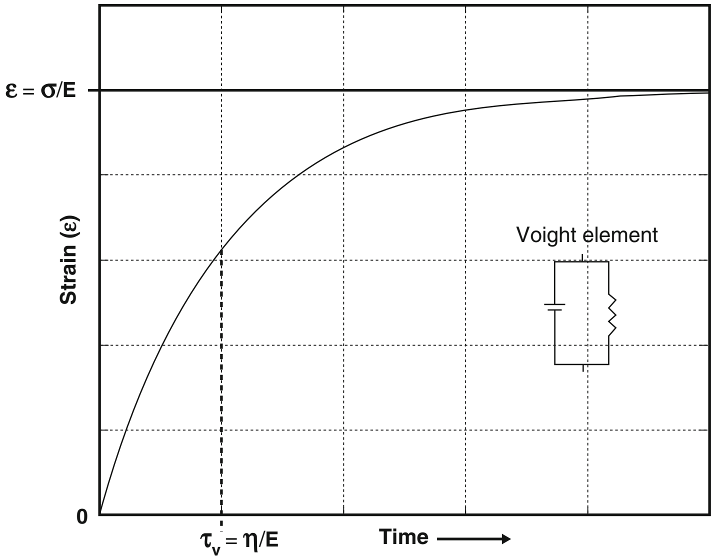

Figure 4.11. Illustration of the time behavior of a Voigt-solid, a model used to explain the rise of bubbles in sediments (Algar, 2009).

dependency from the visco-elasticity of the sediment. Thus, the speed of rise may be controlled by the rate at which sediment moves out of the way of the propagating crack, i.e., the bubble. A model of bubble rise can be based on a Voigt material, Equation 4.3; in such a material the elastic response is dampened by viscosity, such that the stress response is now time dependent. This can be represented schematically by a spring and damper (dashpot) connected in parallel (Figure 4.11). (Note that the viscous behavior of the sediment does not enter the bubble growth model because the overall time scale for growth appears to be long compared to the viscous response time. Thus, growth can be represented as an elastic equilibrium process, but the time scale of the viscous response seems to be essential to the much shorter rise process.)

Figure 4.12 illustrates time lapsed images of a simulation of a bubble rising in a cohesive sediment, where the false colors indicates the strength of the stress field from a solution of Equations 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.15, 4.16, 4.17, 4.18, 4.19, 4.20, and 4.21, including the lithostatic and hydrostatic components. The added concentration of stress at the bubble top tip, which drives the upward fracture, is clearly evident. Depending on the assumed sediment viscosity (Table 4.1), this bubble rises at a speed between 0.02 and 47 cm s^{-1} (Algar, 2009). These rapid rise speeds explain why bubble fluxes from sediments can be substantial.

Rising bubbles feedback into the chemistry of sediments by promoting the exchange of porewaters and overlying waters (e.g., Haeckel et al., 2007) and facilitating the release of volatile substances from porewaters (e.g., Yuan et al., 2007). Bubbles also can transport sediment grains, and their associated contaminants from within sediments to the sediment-water interface (Klein, 2006).

4.3.4 Animal Motion in Sediments

Infauna (i.e., the animals that live in sediments) profoundly affect the properties of sediments and the distribution of sediment components by feeding, burrowing, tube building, etc. The resulting mixing is known as bioturbation.

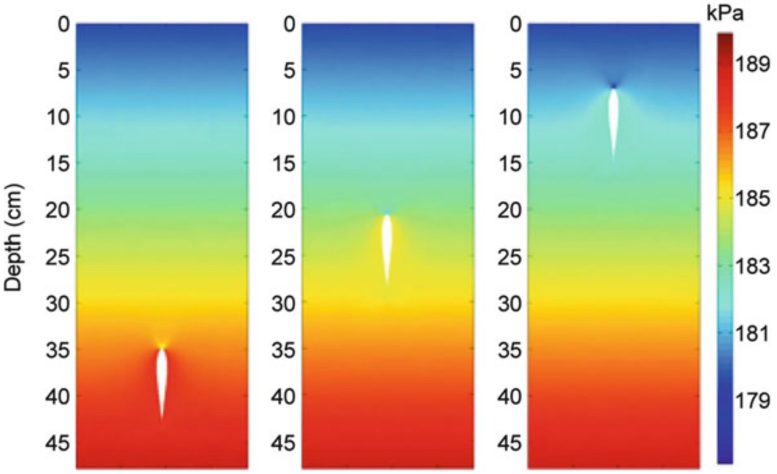

Figure 4.12. Time-lapsed illustrations of the rise of a bubble in sediments with characteristics similar to those at Cape Lookout Bight, North Carolina, USA. The color indicates the stress field, including the lithostatic load. Note the concentration of stress at the top tip of the bubble and the relaxation at the tail. The top stress propagates the bubble fracture upward (from Algar et al., 2011, reproduced with the kind permission of the American Geophysical Union).

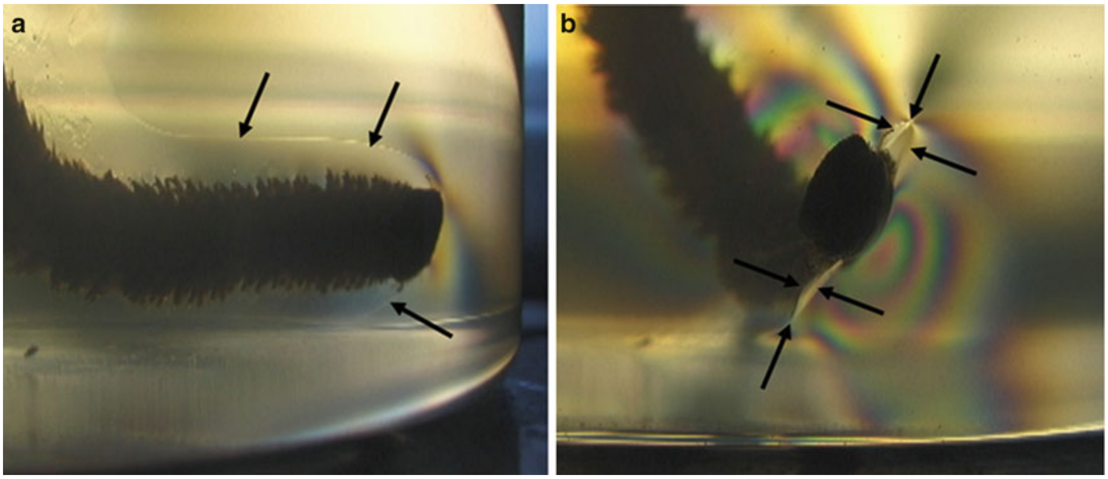

Figure 4.13. Photographs of a polycheate (*Nereis* sp.) burrowing in gelatin by propagating a fracture. The lateral and front edges of the fracture are indicated by the *black arrows* (from Dorgan et al., (2005), reproduced with the kind permission of the Nature Publishing Group/Macmillan Publishing Ltd).

As with bubbles, animal motion requires the displacement of the sediment. Dorgan et al. (2005) have shown that some organismal motions are accomplished by fracture and elastic displacement of the sediment. For example, the fracture created and propagated by a burrowing polychaete is visualized in Figure 4.13. The animal in this figure has been placed in a glass tank that contains gelatin, and the tank has been placed between a light source and a receiver (i.e., a camera). A polarizing filter has been placed between the light source and the tank and in front of the camera. The only way light reaches the camera is if the gelatin is stressed (i.e., acts as a solid) and alters the path of the light. The amount of light deviation is proportional to the degree of stress, and that is captured by the extent of the birefringence in Figure 4.13.

The edge of the crack being propagated by the polychaete is indicated by the black arrows in Figure 4.13. The cross section (Figure 4.13b) of the crack is identical to that of a bubble (Figure 4.8). The crack is, however, not coin shaped, but elongate; as such, it is formally known as an "edge" crack. Nevertheless, its shape is also consistent with LEFM.

The creation of tubes and feeding tracts in sediments leads to the transport of both solutes and solids within sediments. The creation of a crack-based worm burrow may not initially suggest significant animal-mediated transport of solids, but the animals create the burrows to expose food particles on the burrow walls; the latter are removed, ingested and defecated elsewhere in the sediment, creating bio-mediated mixing (e.g., Boudreau, 1997; Thibodeaux et al., 2001). This mode of mixing is directly related to how animals deal with the mechanical properties of sediments.

The fact that infaunal burrows and tubes also persist in sediments, at least for some periods of time, can enhance the exchange of porewaters, as first discovered by Aller (1980, 1982). This persistence is partly due to the mechanical properties of sediments. The persistence of tubes and burrows is also attributable to organic lining, shells embedded in the wall of the tubes, etc., and the continual presence of animals. Persistent tubes invaginate the sediment-water interface, and animal ventilation of the tubes means that tube water are exchanged, with some frequency, with overlying water. This means that porewater solutes need not diffuse vertically to the sediment surface to be released, but also may move laterally into tubes. Likewise, solutes in the overlying water, e.g., oxygen, can penetrated far deeper into such sediments because of irrigated tubes.

4.4 SUMMARY

The aim of this chapter has been to highlight the mechanics (stress-strain response) of cohesive soft sediments. The apparent "softness" of such sediments, characterized by the ease one can deform them with one's fingers, has generated the mistaken notion that such sediment are probably best considered to be a fluid. However, actual stress-strain studies show that cohesive sediment behavior is complex and often better described as a Hookean solid that is capable of fracture. Many phenomena in soft, cohesive sediments, e.g., compaction, bubble formation and rise, and animal burrowing, can only be explained via an elastic or visco-elastic model of sediment behavior, regardless of preconceptions or biases towards fluid descriptions.

ACKNOWLEDGMENTS

We would like to thank our partners-in-crime over the years, Bruce Gardiner (The University of Western Australia), Peter Jumars (The University of Maine), Kelly Dorgan (Scripps Institution of Oceanography, California), Yoko Furukawa (Naval Research Laboratory [NRL]), and Allan Reed (NRL) for sharing their inspiration and understanding. This work was supported by Natural Sciences and Engineering Research Council of Canada and U.S. Office of Naval Research. We also thank our reviewers for their considered comments. While we might not always have made the desired changes, we appreciate the opportunity to think about these issues.

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APPENDIX 4A

If a material is mapped (each point given a coordinate), then deformed, and the same points in the medium remapped, the resulting change in the position of an arbitrary point is called its displacement vector, u. The spatial derivatives of the displacement define the strain tensor, ε. Formally,

$$\varepsilon = \frac{1}{2}\left[\nabla u + (\nabla u)^T\right] \qquad \text{(Eq. 4.A1)}$$

where $\boldsymbol{u}$ is the displacement gradient matrix and the superscript T indicates the transpose. Thus, the tensile/compressive strain that occurs in the x direction is given by

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x} \qquad \text{(Eq. 4.A2)}$$

and the subscripts can be dropped for a purely one-dimensional system, e.g., steady-state sediment compaction.

CHAPTER 5

ADVANCES IN RISK ASSESSMENT IN SUPPORT OF SEDIMENT RISK MANAGEMENT

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5.1 INTRODUCTION

Over the past few decades, risk assessments have become an important component of remedial investigations (RI) and feasibility studies (FS) for contaminated sediment sites. In the United States, the National Contingency Plan (NCP) requires that risk assessments be conducted to address the threat posed by the release of contamination to the environment. Risk assessment is typically viewed as an important early step in the process of determining whether remediation of contaminated sediment is necessary. Risk assessments have, however, become increasingly process oriented, with more emphasis on how to do the risk assessment and less on how to ensure that the assessment is useful for decision-making. Although following a defined process that is supported by guidance is advantageous, a process-dominated approach that lacks consideration of other important factors for managing contaminated sediments has shortcomings. The risk assessment needs to include early and explicit consideration of potential risk management options.

The U.S. Environmental Protection Agency's (USEPA's) *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (USEPA, 2005a) provides a comparative risk assessment framework that considers numerous factors as part of the process of judging the relative merits of various remedial alternatives. The example framework in Table 5.1 presents detailed information on a variety of general characteristics of a water body including the range of human and ecological environmental conditions, hydrodynamics, and sediment and contaminant characteristics. The key lesson from this guidance is that management goals should be considered early, and a comparative framework should be used to guide the collection of information that will ultimately be used to judge the efficacy of the remedial options. Risk assessments must do more than answer the question "Is there a site-related risk?" Risk assessment must also inform decision makers about the site-specific dimensions of risk: magnitude, spatial and temporal scales, risk under future conditions, opportunities for risk-reduction, as well as collateral risks associated with remediation.

Holistic and integrated sediment contaminant risk assessment and management approaches have been recognized by others who have reviewed this topic (Apitz and Power, 2002). *Holistic* means that all critical aspects of a sediment contamination problem are considered upfront and not separately when the approach for assessing the problem is being formulated. Included in this holistic approach is an *integration* of stakeholder input on the desired management goals for the water body upfront as part of the assessment approach, so that the best way to manage the sediment is evaluated in light of these stakeholder desires for

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Table 5.1. Some Site Characteristics and Conditions Especially Conducive to Particular Remedial Approaches for Contaminated Sediment (USEPA, 2005a)

Characteristics	Monitored Natural Recovery (MNR)	*In Situ* Capping	Dredging/Excavation
General site characteristics	• Anticipated land uses or new structures are not incompatible with natural recovery • Natural recovery processes have a reasonable degree of certainty to continue at rates that contain, destroy, or reduce the bioavailability or toxicity of contaminants within an acceptable timeframe	• Suitable types and quantities of cap material are available • Anticipated infrastructure needs (e.g., piers, pilings, buried cables) are compatible with cap • Water depth is adequate to accommodate cap with anticipated uses (e.g., navigation, flood control) • Incidence of cap-disrupting human behavior, such as large boat anchoring, is low or controllable	• Suitable disposal sites are available • Suitable area is available for staging and handling of dredged material • Existing shoreline areas and infrastructure (e.g., piers, pilings, buried cables) can accommodate dredging or excavation needs • Navigational dredging is scheduled or planned
Human and ecological environment	• Expected human exposure is low and/or reasonably controlled by institutional controls • Site includes sensitive, unique environments that could be irreversibly damaged by capping or dredging	• Expected human exposure is substantial and not well-controlled by institutional controls • Long-term risk reduction outweighs habitat disruption, and/or habitat improvements are provided by the cap	• Expected human exposure is substantial and not well-controlled by institutional controls • Long-term risk reduction of sediment removal outweighs sediment disturbance and habitat disruption
Hydrodynamic conditions	• Deposition of sediment is occurring in the areas of contamination • Hydrodynamic conditions (e.g., floods, ice scour) are not likely to compromise natural recovery	• Hydrodynamic conditions (e.g., floods, ice scour) are not likely to compromise cap or can be accommodated in design • Rates of groundwater flow in cap area are low and not likely to create unacceptable contaminant releases	• Water diversion is practical, or current velocity is low or can be minimized to reduce resuspension and downstream transport during dredging
Sediment characteristics	• Sediment is resistant to resuspension (e.g., cohesive or well-armored sediment)	• Sediment has sufficient strength to support cap (e.g., has high density/ low water content)	• Contaminated sediment is underlain by clean sediment (so that over-dredging is feasible) • Sediment contains low incidence of debris (e.g., logs, boulders, scrap material) or is amenable to effective debris removal prior to dredging or excavation

(*continued*)

Table 5.1. (continued)

Characteristics	Monitored Natural Recovery (MNR)	*In Situ* Capping	Dredging/Excavation
Contaminant characteristics	• Contaminant concentrations in biota and in the biologically active zone of sediment are moving toward risk-based goals • Contaminants readily biodegrade or transform to lower toxicity forms • Contaminant concentrations are low and cover diffuse areas • Contaminants have low ability to bioaccumulate	• Contaminants have low rates of flux through cap • Contamination covers contiguous areas (e.g., to simplify capping)	• Higher contaminant concentrations cover discrete areas • Contaminants are highly correlated with sediment grain size (i.e., to facilitate separation and minimize disposal costs)

the water body. Knowing the management goals for the water body will help to ensure that the critical risk information needed is gathered and assessed during the evaluation. If these management goals are not considered early in the process, the assessment will likely not be able to answer the key management questions that will need to be considered when choosing a sediment remedy, and thus could add years to the project timeline.

5.1.1 Focus of This Chapter

This chapter discusses how risk assessment and other considerations that are critical to the ultimate remedial decision for contaminated sediments can be incorporated into a comparative analysis of remedial options. The intent is not to provide an exhaustive overview of risk assessment, but to focus on innovative risk assessment tools that have been used in the United States. While there are many available risk assessment tools, several are described that illustrate aspects of an integrated comparative approach for sediment management, which is the main theme for this chapter, as it is the key evolution in the risk assessment process that can help sediment contamination projects to be executed more cost-effectively, in a timely manner, and more successfully. To begin, a brief overview of the traditional risk assessment process is provided, since elements of this process will still be a cornerstone of future sediment risk assessments, and it provides insight into the historical state of the practice of sediment risk assessment. Examples are provided of three specific risk-related approaches – risk zones, Receiver Operating Characteristic (ROC) curve analysis, and Relative Environmental Benefits Evaluation (REBE) – that the authors have found useful in providing the integrated comparative risk information needed by risk managers to make informed sediment management decisions. Risk zones are spatially-explicit representations of risk. ROC is a quantitative tool that can be used to establish the boundaries of risk zones. REBE is an approach that has been used to capture various dimensions of risk, including the risk of habitat destruction during remediation. Integral to both the risk zone approach and REBE approaches is recognition of the current and future uses desired by the stakeholders and trustees of the water body, how these uses affect the potential for exposure to sediments and risks, and the likelihood that a given remedial option will be compatible with these desired uses.

5.2 OVERVIEW OF RISK ASSESSMENT FOR SEDIMENTS

Traditional risk assessment approaches are well documented in various guidance documents, and it is essential that compliance with regulatory guidance be evident in the assessment process (USEPA, 1989, 1997, 1998; Cal-EPA DTSC, 1994; MDEP, 1995; Ohio EPA, 2008; Wentsel et al., 1994). Because exposure to sediment and associated risks are highly dependent upon the characteristics of the specific water body, the use of that water body, and the nature of the natural resources that are present, characterization of risks associated with contaminated sediment tends to be more complex and less prescribed than risk assessments for other media such as soil and groundwater.

5.2.1 Human Health Risk Assessment

The process used to evaluate human health risks follows the four-step process developed by the National Academy of Science in the early 1980s and formulated into the Risk Assessment Guidance for Superfund (USEPA, 1989) in 1989. This process includes:

- Hazard identification,
- Exposures assessment,
- Toxicity assessment, and
- Risk characterization.

A screening step is conducted as part of hazard identification to eliminate environmental media (e.g., surface water) that are not of concern or to narrow the list of contaminants of potential concern (COPCs) that require further risk evaluation. The screening step compares maximum sediment concentrations of COPCs to conservatively derived risk-based criteria for each media (e.g., surface water and sediment). The exposure assessment develops site-specific exposure scenarios to describe the populations most likely to be exposed to sediment, and the routes by which they may be exposed. Exposure routes may include direct oral or dermal exposure to sediment, or indirect exposure via consumption of fish and shellfish that accumulate the COPC from sediment. Site-specific conditions that can influence exposure scenarios include depth of overlying water and climate. For example, seasonal freezing of lakes and ponds will likely reduce the amount of human contact with the sediments.

Most sediment exposure assessments assess risk to the recreational user. Uncertainty regarding incidental ingestion of sediment and dermal contact by the recreational user is often addressed by using upper bound estimates of exposure. For example, rates of dermal contact for sediment that have been derived from limited data on the adherence of wet-soil or mud to skin do not account for the fact that sediment is likely to be washed from the skin during most recreational activities. Therefore, estimates of chemical exposure from dermal exposure to sediment tend to be high-end estimates. Since dermal uptake is typically small in comparison to other routes of exposure, the methodology for quantifying dermal exposure risks has not been well developed.

More attention has been given to estimates of exposure to bioaccumulative compounds that accumulate in edible fish and shellfish. This exposure pathway is commonly evaluated for bioaccumulative COPCs that can be transferred from sediments into fish and shellfish. USEPA and state regulatory agencies have gathered information on typical annual fish consumptions rates. Site-specific information on fish consumption from a given water body (e.g., creel census) can be used if they are available. Concentrations in food items can be either measured in field-collected samples or estimated using bioaccumulation models. Each approach has drawbacks.

Tissue analyses are a direct measurement, but can be expensive. Also, measured concentrations in mobile species may not reflect uptake from the site under consideration. Bioaccumulation models are less direct, but can help address the uncertainty of whether uptake from the site under consideration is likely to result in risk.

The remaining two steps of a human health risk assessment for sediments (i.e., toxicity assessment and hazard assessment) follow the prescribed approaches presented in the guidance referenced previously (e.g., USEPA, 1989). Within the United States, toxicity assessments rely primarily on two sets of toxicity values derived by USEPA scientists to address the systemic (non-cancer type) health effects of chemicals, referred to as a reference dose (RfD), and the carcinogenic potency of the chemical, referred to as a cancer slope factor. These two types of toxicity factors (RfD and slope factor) are used to gauge the magnitude of toxicity of the COPCs. Within the risk characterization section of the risk assessment, the magnitude of the chemical exposure associated with sediment estimated within the exposure assessment is combined with the chemicals' toxicity values to estimate risks. Systemic effects are predicted to occur if the magnitude of exposure exceeds the RfD. The ratio of the magnitude of exposure over the RfD is referred to as a hazard quotient. If the hazard quotient is >1, then systemic health effects are predicted to occur, and remedial action should be considered to lower exposure and risk. For carcinogenic effects, a probability of contracting a specific form of cancer is estimated by multiplying the exposure value by the slope factor. As the level of exposure increases, the probability or risk of cancer increases. At the federal level (and within many states) the risk of cancer is compared against a cancer risk range from one-in-a-million to one-in-ten thousand. This risk range was incorporated within the NCP when it was created as required by Section 105 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980. Risks above this range normally require remediation actions, whereas cancer risks below this risk range are considered negligible. Cancer risks within the risk range may or may not be acceptable to the particular trustees entrusted with protecting the environment (e.g., USEPA or state agency). The hazard quotients and cancer risks are summed across COPCs and exposure pathways to provide an overall estimate of risk associated with sediment exposures and are used to gauge whether the concentrations of COPCs in sediment are of concern to people utilizing the water body and whether remedial action should be considered within the regulatory process.

5.2.2 Ecological Risk Assessment

Although ecological risk assessments for sediments have been conducted since at least the 1980s, the main guidance on ecological risk assessment, *Ecological Risk Assessment for Superfund: Process for Designing and Conducting Ecological Risk Assessments*, was published in 1997 (USEPA, 1997). This guidance defines an eight-step process to be used to perform ecological risk assessments. Numerous sediment quality benchmarks were developed for use in screening-level ecological risk assessments to identify COPCs and determine whether further ecological risk assessment was needed at a site. The benchmarks are typically based on impacts to benthic invertebrates (most common) or higher trophic level ecological receptors (e.g., aquatic birds). It is recommended that the end user understand the technical basis of the sediment benchmark and apply it appropriately based on its intended use.

The two main exposure pathways commonly evaluated in ecological risk assessment for sediments are direct contact with the sediments and bioaccumulation through the food chain for bioaccumulative chemicals. Although sediment screening values that address higher trophic level transfer of bioaccumulative contaminants to wildlife are available, bioaccumulative contaminants are typically carried forward into a site-specific ecological risk assessment (e.g., USEPA, 2005b).

For chemicals that do not bioaccumulate through the aquatic food chain, direct contact to sediment by benthic invertebrates is the key exposure pathway evaluated at many sediment contaminated sites. Some of the reasons for this focus on benthic invertebrates are as follows:

- Benthic organisms spend most of their life within a very small area; other aquatic species and wildlife tend to range over larger areas and thus experience less exposure than benthic invertebrates.
- Benthic organisms are in direct contact with potentially contaminated sediments and surface/pore waters; fish, small mammals, and bird species contact these media incidentally. For example, the main exposure to fish is associated with foraging on benthic invertebrates or resting on the bottom.
- Benthic invertebrates have less developed metabolic systems that do not metabolize many organic contaminants as readily as higher-level organisms (e.g., fish and waterfowl).

On a site-specific basis, consideration of whether benthic invertebrates are the best choice to be the indicator species that is used to assess risks to other ecological receptors at a site must be given each time a new site is investigated. This evaluation is performed during the conceptual site model development for the site, which describes the relevant ecological receptors at a site and how they are likely to be exposed to contaminants in sediment.

Since the 1980s, the sediment quality triad approach has commonly been used in the United States to evaluate risks to benthic invertebrates (Chapman, 2000). The triad approach uses three measures to evaluate ecological risk to benthic invertebrates: sediment chemistry characterization, laboratory-based sediment toxicity testing, and comparison of the abundance and diversity of the benthic invertebrate community with that of a similar, but uncontaminated, reference area. The triad evaluation is conducted at multiple sample locations that span a range of chemical concentrations to determine whether observed adverse effects are related to the concentrations of contaminants. In the United States, it has been observed that assessments most often rely on sediment chemistry and toxicity to address potential risk to benthic invertebrates. Analysis of benthic invertebrate community structure is more often reserved for sites where it is cost-effective to conduct such a study. In addition, high variability in the abundance and diversity of benthic invertebrates and their susceptibility to natural physical/chemical variables (e.g., salinity) often hampers the ability to detect significant differences among sites and limits the ability to interpret the data.

For bioaccumulative chemicals in sediment, exposure of higher trophic level wildlife receptors is typically estimated using a process that is similar to that described for human receptors. In the case of ecological risk assessment, site-specific habitat conditions and geographical location are used to define the most appropriate wildlife receptors to evaluate. Common species that are evaluated in sediment ecological risk assessments include fish-eating mammals (e.g., mink) and birds (e.g., great blue heron). Calculations of potential wildlife risks follow similar methods to those described for the human health risk assessment process, except that cancer risk is not typically evaluated for ecological risk assessments, which emphasize survival, growth, and reproduction endpoints. Risk assessments for contaminated sediments commonly use wildlife risk models to back-calculate ecologically protective concentrations in sediment that can be used to define areas in the water body potentially requiring remedial action.

5.3 DEFINING "RISK ZONES" TO COMMUNICATE RISK

Simple numerical estimates of site-wide risk often do not provide a meaningful representation of the spatial extent of risk at a site. A spatially-explicit representation of risk can be a more useful tool for communicating the results of the risk assessment to environmental engineers, stakeholders, and trustees. Illustration of the spatial scale of risk facilitates a clearer understanding of where particular receptors may be exposed and impacted. The risk zone concept, as it is called in this chapter, is not new and relies on standard assessment methods. Although spatial aspects of risk are typically considered during the FS, it is beneficial to clearly convey the spatial aspects of risk within the risk assessment. An example of the risk zone approach is presented below.

5.3.1 Conceptual Risk Zone Approach

In collaboration with USEPA (Region 5), the risk zone approach has been incorporated into a multi-site risk assessment framework for a large group of manufactured gas plant (MGP) sites. The Campmarina former MGP in Sheboygan, Wisconsin, has been the subject of an RI/FS under the USEPA Alterative Superfund Program. One of the operable units (OU) at the site is a short section of the Sheboygan River adjacent to the location of the former MGP where elevated concentrations of polycyclic aromatic hydrocarbons (PAHs) and the presence of nonaqueous phase liquid (NAPL) in sediments are of concern. Based on the results of the site investigation and risk assessment, four risk zones were defined for the river (Figure 5.1). The zones for this project include a zone of ambient conditions, a zone of insignificant chemical exposure and risk, a zone of low chemical exposure and risk, and a zone of chemical exposure and risk. These four zones are described in more detail later in Section 5.3.3.

Separate sets of risk zones are typically developed for each receptor group (e.g., human recreational users, foraging birds) because types of exposure will differ among groups. The human and ecological risk zones are eventually integrated to provide a comprehensive set of risk zones that are used to communicate the areas of potential concern that may require remedial action.

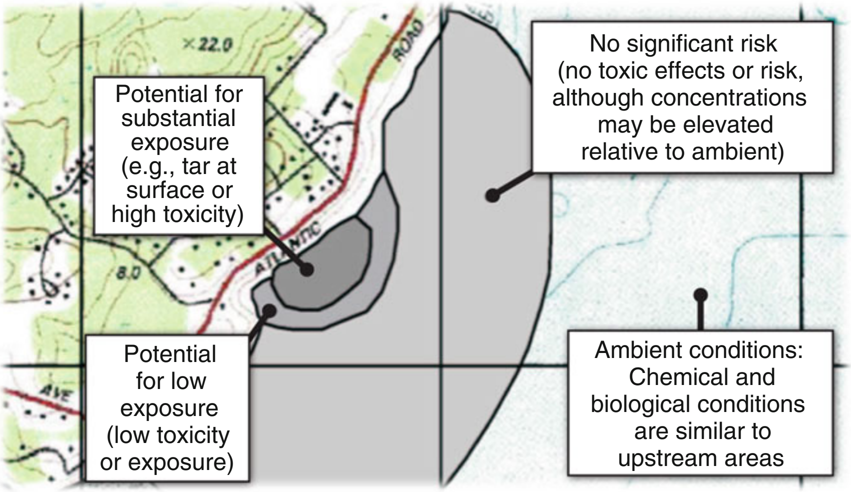


Figure 5.1. Conceptual view of risk zones used to characterize contaminated sediments.

5.3.2 Developing Risk Zones for Human Receptors

The concentrations-based limits that define the boundary between the zones of insignificant chemical exposure and risk, and zones of significant chemical exposure and risk, can be developed using traditional risk assessment methods. An important first step in this assessment is the characterization of the *area of potential sediment exposure*. At the Campmarina site, wading and direct contact with sediment were considered to be unlikely in areas with water depths >3.5 feet (ft) or 1.07 meters (m) in the flowing river. The area where wading would be possible was constrained to a narrow area along the shoreline and a small area near an island located in the main channel of the river. Traditional risk assessment methods are used to define concentration limits based on direct contact and incidental ingestion of sediment above which adverse impacts to health could occur. If further definition of the *significant chemical exposure and risk zone* is desired, this zone can be divided into sub-zones based on, for example, varying cancer risk levels (1×10^{-6}, 1×10^{-5} and 1×10^{-4}) or hazard index levels (HI: 1–10, HI: 10–100). In addition, areas of intensive use, such as waterfront residences and beaches, that overlap with the zone of sig*nificant chemical exposure and risk* can be illustrated and prioritized for remedial action. In the case of the Campmarina site, the potential risk to recreational receptors was below regulatory risk benchmarks and was not a driver for assessing the need for remediation.

If bioaccumulative chemicals are present at a site, indirect exposure to people (and ecological receptors) by consumption of contaminated fish or invertebrates may be a concern that will need to be addressed. In these cases, the development of the risk zones will require consideration of multiple spatial scales: contamination footprint, foraging areas of fish, and patterns of exposure of human and ecological receptors. This scenario is much more complex because the spatial scale of the *zone of significant chemical exposure and risk* is not readily apparent from a simple examination of the footprint of the sediment contamination. The conceptual approach to address bioaccumulative compounds is described in more detail in the subsection on ecological receptors.

5.3.3 Developing Risk Zones for Ecological Receptors

Certain ecological receptors, such as benthic invertebrates and fish, contact sediment directly, and the *area of potential sediment exposure* would not be spatially constrained by the depth of the overlying water. Direct exposure of other species, such as aquatic birds and mammals may, however, be limited by the water depth. Delineation of the risk zones associated with direct exposure of ecological receptors to sediment can be established in various ways, including sediment toxicity testing. At the Campmarina site, site-specific sediment toxicity data, concentrations of total PAHs, and a statistical technique called ROC curve analysis (described later in this chapter) were used to define the concentration limits of the various risk zones.

Four primary risk zones (A, B, C, and D) were identified at the Campmarina site (Table 5.2). Zone A represents ambient conditions of PAHs in river sediments, Zone B represents the zone of insignificant risk, and Zone C represents the zone of limited exposure where toxicity was inconsistently detected. Zone D was the zone of exposure where toxicity to benthic invertebrates was clearly documented based on the site-specific toxicity testing. An additional Zone E was used to delineate an area of NAPL in near-shore sediments, which by default was assumed to be potentially toxic to both human and ecological receptors.

Within the risk assessment, data were used to characterize the risk to benthic invertebrates under current site conditions (see Figure 5.2). Because only two locations were considered to be potentially toxic to invertebrates, the overall community of benthic invertebrates was not

Table 5.2. Campmarina River OU Ecological-Based Risk Zones and Associated Criteria (NRT, 2011)

Zone and Associated Criteria	PAH (sum of 13 PAHs) Concentration (milligrams per kilogram [mg/kg])
Zone A	
Ambient – Applies to human and ecological receptors, defined by site-specific sampling in areas located near but outside the influence of the site. Statistical methods are applied to define this zone based on the analytical data.	**Less than approximately 18 mg/kg**
Zone B	
No significant risk to benthic populations – The range is above ambient but below the concentrations at which toxicity was sometimes observed. Site-specific toxicity testing showed no incremental increases in the toxicity. The lack of toxicity in these samples is consistent with the equilibrium sediment partitioning approach.	**18–45 mg/kg**
Zone C	
Potential for low exposure to benthic populations – Higher concentrations of MGP residuals that are associated with potential toxicity. Toxicity begins to be observed in the laboratory tests but is not consistent and it is possible to have false positives (PAHs are elevated but without toxicity). Toxicity is uncertain.	**45–129 mg/kg** Samples with concentrations in this range must be geographically and physically consistent with anticipated footprint of effects.
Zone D	
Potential for exposure to benthic populations – As concentrations increase above this range, toxicity is consistently observed.	**Greater than 129 mg/kg** Samples with concentrations in this range must be geographically and physically consistent with anticipated footprint of effects.

considered to be at risk under current conditions. The FS also considered risk under future conditions after implementation of the proposed dredging plan to remove polychlorinated biphenyl (PCB)-contaminated sediments associated with the larger Superfund site on the Sheboygan River (i.e., not related to the Campmarina MGP site). The estimated change in total PAH concentrations in surface sediment under future conditions was small and did not significantly change the area of sediment that was potentially toxic to benthic invertebrates.

Within the FS, the Zones B, C, D, and E were represented spatially assuming (1) that sediments in the top 2.5 ft (0.76 m) of the sediment column might become exposed in the future due to scouring (Figure 5.3) or (2) that contaminated sediments at any depth could become exposed in the future. The unshaded area on Figure 5.3 represents ambient conditions (Zone A) and were not considered further in the FS as they were representative of upstream conditions unrelated to the former MGP site. The area with concentrations of PAHs >18 mg/kg are elevated in comparison to ambient concentrations, but do not present a risk to benthic invertebrates, unless otherwise indicated. Since most of the contamination at this site is present at depth, the size of the risk zones increase as deeper sediments are considered.

For each remedial alternative considered within the FS, specific remedial technologies (e.g., no action, MNR, dredging, backfilling, etc.) were considered for risk Zones B, C, D, and E. The preferred remedy (Alternative 2) for the Campmarina River OU consists of a

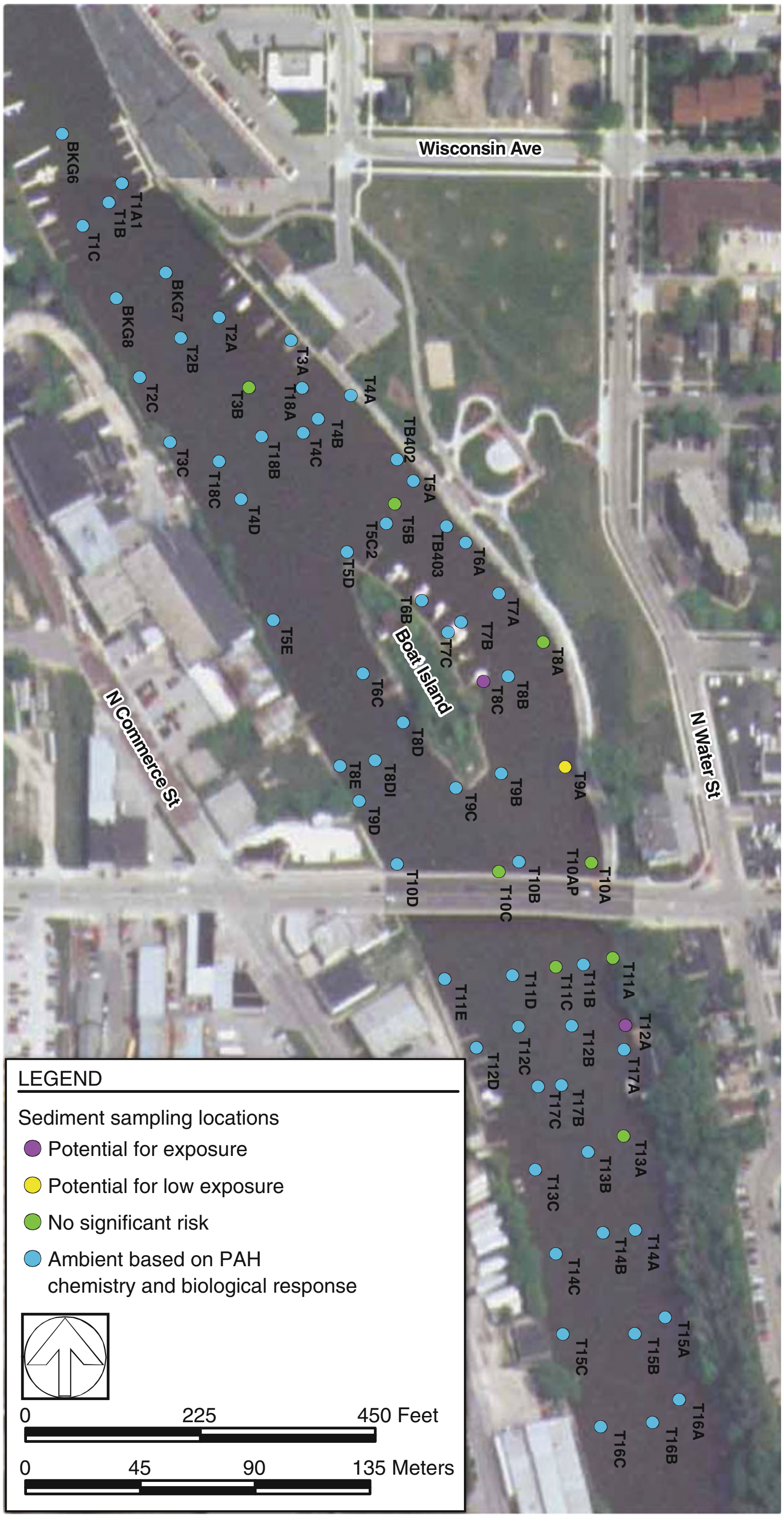


Figure 5.2. Surface sediment ecological risk zones within the Sheboygan River (Exponent, 2009).

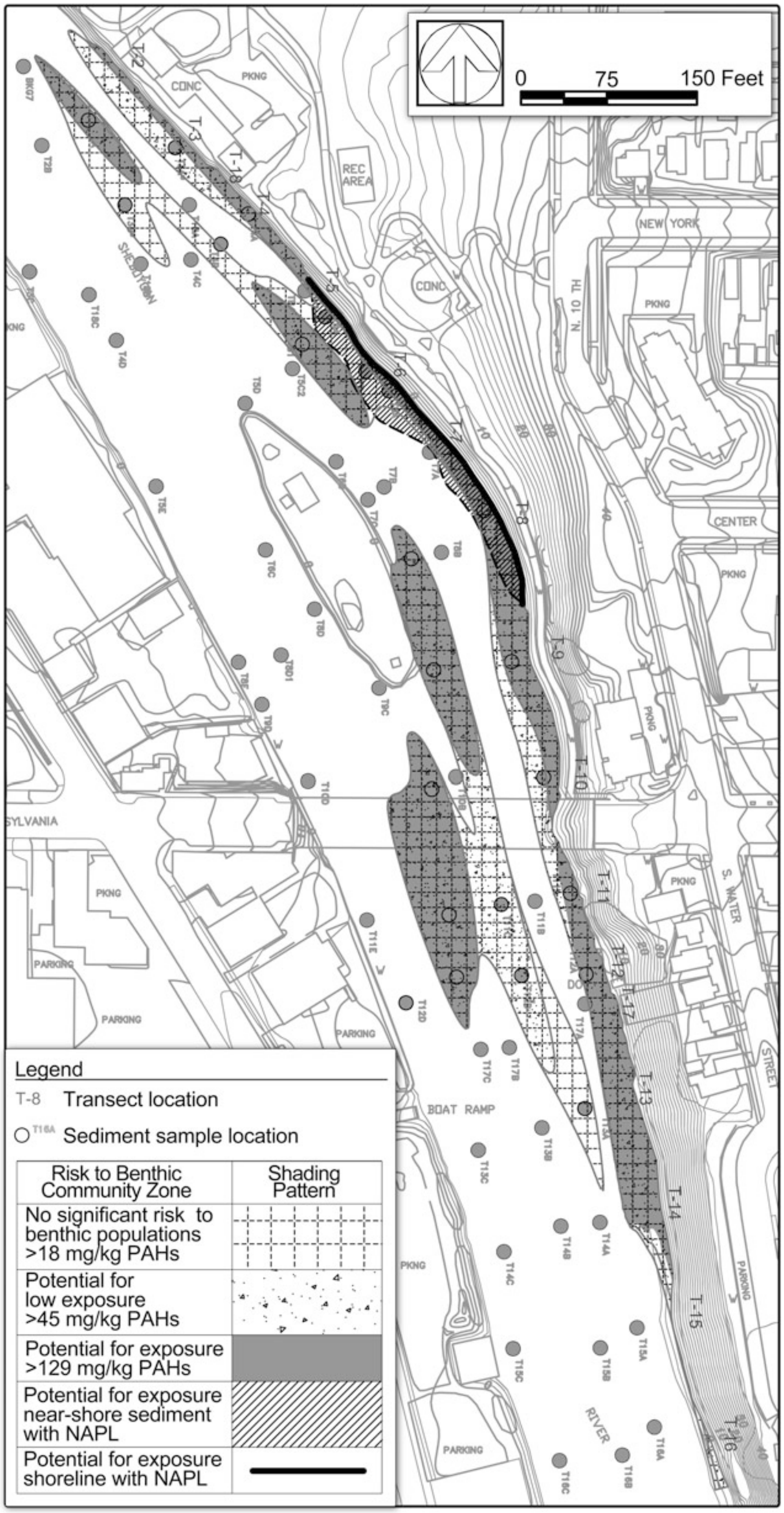


Figure 5.3. Ecological risk zone for sediment (0–2.5 ft) (NRT, 2011; Figure 11).

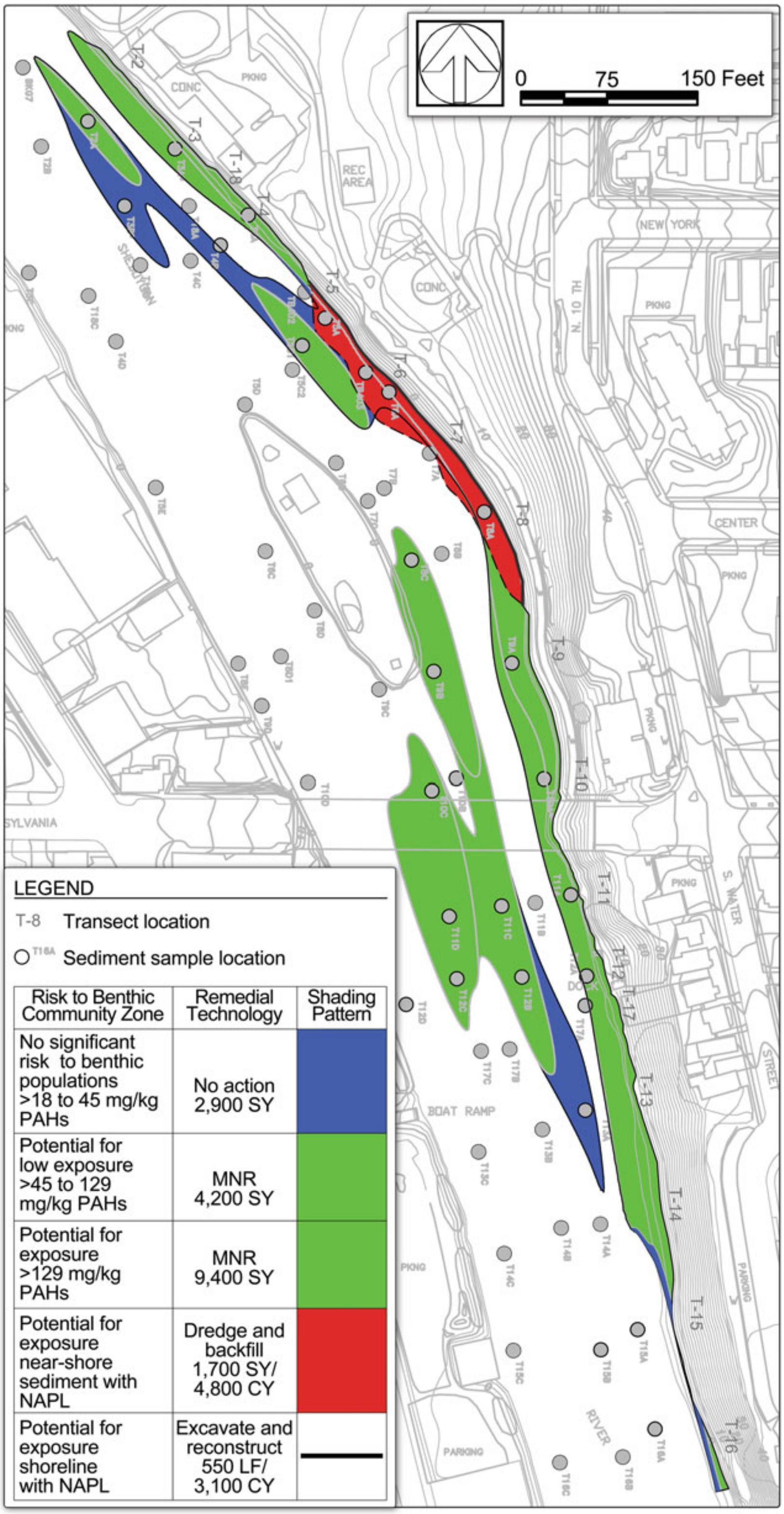
combination of no action, MNR, dredging, and excavation (Figure 5.4). This Case Study demonstrates how spatially explicit risk zones can be used to map areas where specific remedial technology could best be applied.

For bioaccumulative chemicals, the uptake of the contaminant into prey and corresponding exposure to higher trophic level wildlife consumers (or humans) must be considered. The first step is to estimate a threshold chemical concentration in a key prey item (e.g., fish, mussel) for the higher trophic receptor of concern (e.g., mink, bald eagle, or even human). The next step is to use a spatially-explicit bioaccumulation model, such as FishRand-Migration (von Stackelberg et al., 2002, 2005; Linkov et al., 2002), to estimate sediment chemical exposure and risk zones that would result in prey concentrations above these risk-based concentrations. The chemical risk zones are mapped in the same way as the direct exposure to the sediments was demonstrated for the Campmarina Case Study, but the methods used to arrive at the concentration limits is more complex. To the extent available, information on the movement of mobile prey (e.g., fish) and the suitability of the habitat for prey (e.g., fish habitat) and wildlife predators can be considered in the spatially-explicit bioaccumulation model. This approach can be used to evaluate the benefit of various remedial options by modifying the spatial scale of contamination to simulate different post-remediation exposure and risk scenarios. California is in the process of considering how to combine these spatial scales as part of an effort to develop sediment quality objectives for bioaccumulative chemicals such as PCBs and chlorinated pesticides.

5.3.4 Use of ROC Curves for Defining Chemical Risk Zones

ROC curve analysis is a statistical technique that can be used to select concentration-based thresholds that aid in delineating risk zones. ROC curves were developed in the field of statistical decision theory, and later used in signal detection for analyzing radar images during World War II (Collison, 1998). During World War II, ROC curves allowed radar operators to distinguish between an enemy target, a friendly ship and noise. ROC curves assess the value of potential predictors by providing a standard measure of the predictor's ability to correctly classify subjects. The biomedical field uses ROC curves to quantify the ability of diagnostic tests to discriminate between healthy and diseased individuals (Metz, 1978). ROC curves have recently been applied to environmental problems, including evaluating beach water quality indicators and sediment quality guidelines (Morrison et al., 2003; Shine et al., 2003). This section presents the results of the ROC curve analysis that was performed for the Campmarina site, described previously under the *Conceptual Risk Zone Approach*, as a case example of how this method can aid in selecting concentration limits for risk zones. The ROC curve method is used to identify an appropriate predictor (e.g., total PAH) that can be used to discriminate between conditions that are potentially toxic and those that are not, and between levels of toxicity.

The first step is to appropriately define thresholds that can be used to predict whether samples are likely to be toxic or non-toxic. In this case, the threshold for a low level of toxicity was defined by the site samples with toxicity responses (e.g., survival, growth, or reproduction) that were statistically significantly different from responses of samples collected from ambient areas. In the case of Campmarina sediments, 85% amphipod survival represented a level of response for site samples that was significantly different from that of ambient samples and was used to define the threshold for a low toxicity response. A 20% reduction in survival beyond that observed for ambient samples (i.e., [85−20%] or 65% survival) was used to define the threshold between low toxicity and medium (or higher) levels of toxicity. A 20% reduction in survival is also used by other agencies to define toxic responses of concern (USEPA and USACE, 1991). Ultimately, toxicity thresholds must be agreed upon by stakeholders.



Risk to Benthic Community Zone	Remedial Technology	Shading Pattern
No significant risk to benthic populations >18 to 45 mg/kg PAHs	No action 2,900 SY	🟦
Potential for low exposure >45 to 129 mg/kg PAHs	MNR 4,200 SY	🟩
Potential for exposure >129 mg/kg PAHs	MNR 9,400 SY	🟩
Potential for exposure near-shore sediment with NAPL	Dredge and backfill 1,700 SY/ 4,800 CY	🟥
Potential for exposure shoreline with NAPL	Excavate and reconstruct 550 LF/ 3,100 CY	━

Figure 5.4. Mapping of remedial technologies to ecological risk zone for Remedial Alternative 2A (NRT, 2011; Figure 13). Note that SY = square yard, CY = Cubic yard, and LF = Lineal feet.

Table 5.3. Confusion Matrix for Predictive Model Evaluation and Common Terms Derived From the Confusion Matrix

Actual	Predicted	
	Negative	Positive
Negative	a	b
Positive	c	d

True positive rate or TPR (sensitivity) = $d/(c + d)$
True negative rate or TNR (specificity) = $a/(a + b)$
Positive predictive rate or PPR (precision) = $d/(b + d)$
False positive rate or FPR = $b/(a + b)$
False negative rate or FNR = $c/(c + d)$

A predictor with good discriminatory ability has both a high sensitivity (the ability to correctly identify a condition of concern) and high specificity (the ability to correctly identify conditions not of concern). Sensitivity (true positive rate [TPR]) and specificity (1-false positive rate [FPR]) are two elements of the confusion matrix, which is a table that displays the matrix of predicted and actual classifications from a predictive model (Table 5.3) (Please refer to Kohavi and Provost, 1998, for a detailed description). Several additional metrics can be computed from the confusion matrix, including the false negative rate, the positive predictive rate (precision), and the true negative rate. These metrics may provide further insight into a potential predictor, but only the TPR and FPR are used in ROC curve construction.

The next step is to sort the toxicity test results by increasing indicator concentration and evaluate each sample as a potential threshold separating toxic from nontoxic samples, with all samples above the threshold classified as toxic and all samples below the threshold classified as being nontoxic. The TPR (percent of all toxic samples that have chemical concentrations greater than or equal to a particular predictor concentration and are correctly identified as toxic) and FPR (percent of all non-toxic samples that have chemical concentrations greater than or equal to the predictor concentration and are falsely identified as toxic) are calculated for each sample concentration. This information is used to construct the ROC curve and calculate the area under the curve (AUC). At the Campmarina site, sediment chemistry and toxicity data were used to evaluate whether total PAHs were a good indicator of toxicity to amphipods (*Hyalella azteca*) (refer to Table 5.4). The AUC is used to evaluate whether the indicator (e.g., concentration of total PAH in sediment) is actually a good predictor of toxicity. An ideal indicator would be perfectly sensitive (TPR of 1 – all toxic samples are correctly identified as toxic), perfectly specific (FPR of 0 – all non-toxic samples are correctly identified as non-toxic), and would have an AUC of 1. An AUC of 0.5 is indicative of a poor predictor (Figure 5.5).

At the Campmarina site, total PAHs were found to be a good indicator of toxicity to amphipods. The ROC curve demonstrated that total PAHs were a good predictor of low toxicity (<85% survival) with an AUC of 0.92 (Table 5.4, Figure 5.6). The ROC curve for the medium-to-high toxicity predictor (<65% survival) had an AUC of 0.98, which also demonstrates that total PAHs were an excellent predictor of medium-to-high toxicity.

The ROC curve analysis for the Campmarina site illustrates how this statistical method can be used to define the chemical concentration thresholds (i.e., in this case total PAH concentrations) to define the risk zones with the risk assessment. At other sites, ROC analyses might be conducted for multiple contaminants to examine the influence of co-occurring contaminants. As described above, the toxicity of each sediment test sample was defined as:

- Low toxicity: Significantly different from ambient sample response and ≤20% increase in toxicity compared to ambient.
- Medium-to-high toxicity: >20% increase in toxicity relative to ambient areas.

Table 5.4. Example ROC Curve Analysis, Campmarina River OU Sediment Data (Exponent, 2009)

Sample ID	Total 13-PAHs (mg/kg)	Mean Amphipod Survival (% of control)	Significantly More Toxic versus Ambient	FPR	TPR	AUC
				1.00	1.00	0.000
BKG07_6-18	0.98	98.7	0	1.00	1.00	0.091
T02C_42-54	1.9	96	0	0.91	1.00	0.091
T02C_6-18	4.5	93.5	0	0.82	1.00	0.091
T04B_54-66	9.0	98.7	0	0.73	1.00	0.091
T02C_18-30	9.0	96.1	0	0.64	1.00	0.091
T11D_6-18	12	97.4	0	0.55	1.00	0.091
T04B_18-30	28	94	0	0.45	1.00	0.091
T02A_18-30	33	86	0	0.36	1.00	0.091
T04A_18-30	45	71.4	1	0.27	1.00	0.000
T12B_6-18	51	83.1	1	0.27	0.92	0.000
T11C_6-18	81	77.9	1	0.27	0.83	0.000
T12C_30-42	89	90	0	0.27	0.75	0.068
T12B_30-42	104	94	0	0.18	0.75	0.068
T04A_78-90	129	55.8	1	0.09	0.75	0.000
T10C_6-18	247	42	1	0.09	0.67	0.000
T11A_18-30	365	87.0	0	0.09	0.58	0.053
T10C_18-30	402	40	1	0.00	0.58	0.000
T12C_42-54	607	15.6	1	0.00	0.50	0.000
T04B_78-90	986	22.1	1	0.00	0.42	0.000
T11D_18-30	1,153	12	1	0.00	0.33	0.000
T05A_42-54	1,944	2.6	1	0.00	0.25	0.000
TB403_42-54	6,171	4	1	0.00	0.17	0.000
TB403_30-42	6,895	0	1	0.00	0.08	0.000
					Total	0.92

Note: All samples with percent amphipod survival <85% of laboratory control were statistically different (alpha = 0.05) from that of ambient samples and were considered toxic. TPR and FPR should be interpreted as "if concentration is ≥X"
AUC = area under the curve
FPR = # predicted to be toxic that were actually nontoxic/total # that were actually nontoxic
TPR = # predicted to be toxic that were actually toxic/total # that were actually toxic

The TPR and FPR for the sediment toxicity test data were calculated for each sample in order to define overall thresholds of low toxicity (total 13-PAHs of 45 mg/kg) and medium to high toxicity (total 13-PAHs of 129 mg/kg). An example of the ROC curve analysis data for the determination of the threshold for low toxicity (45 mg/kg) is presented in Table 5.4.

Based on the TPR and FPR, the investigator identifies a specific sample concentration that maximizes the correct classifications of toxicity (high TPR) and minimizes incorrect classifications (low FPR). Since thresholds are not usually perfectly sensitive (TPR = 1) or perfectly specific (FPR = 0), selection typically involves trade-offs that maximize the TPR and

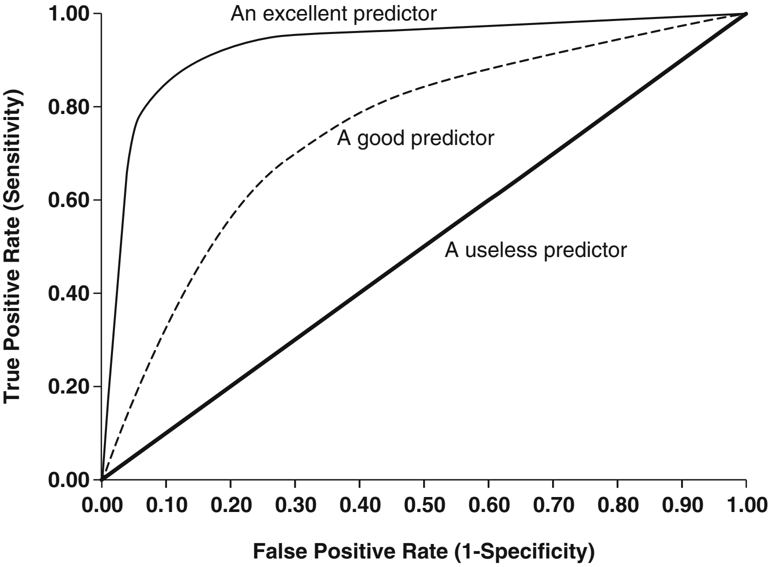


Figure 5.5. Example ROC curve.

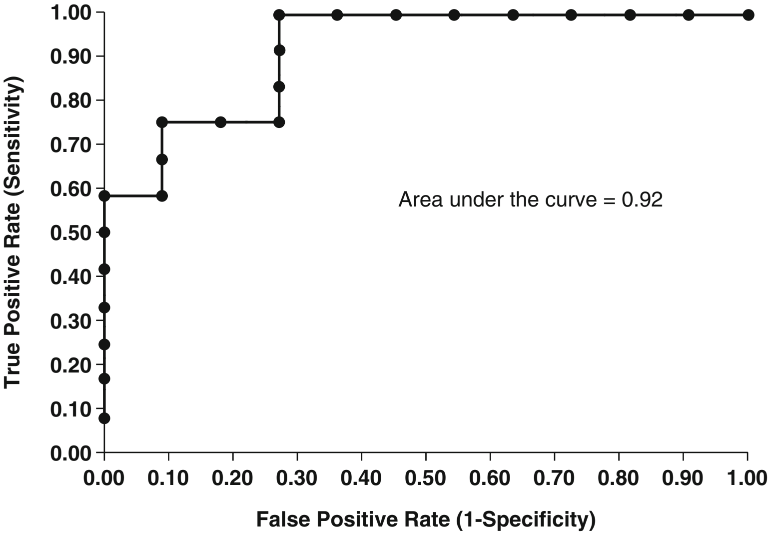


Figure 5.6. Example ROC curve for 85% survival data (Exponent, 2009).

minimizes the FPR. A 75% TPR can be considered a realistic goal for identifying a useful and appropriate indicator for environmental contaminants. Selection of the appropriate threshold concentration is usually negotiated between the interested parties using the ROC analysis to make informed decisions. In the case of the Campmarina site, the stakeholders requested that a TPR of 100% be used to select the threshold concentrations, which resulted in the selection of a conservatively low threshold of 45 mg/kg to define low toxicity. While the TPR was 100%, the trade-off in this case was that the FPR was relatively high (i.e., 27%) for the selected threshold.

5.4 UTILIZING NET ENVIRONMENTAL BENEFITS ANALYSIS AND RELATIVE ENVIRONMENTAL BENEFITS EVALUATION FOR JUDGING REMEDIAL ALTERNATIVES

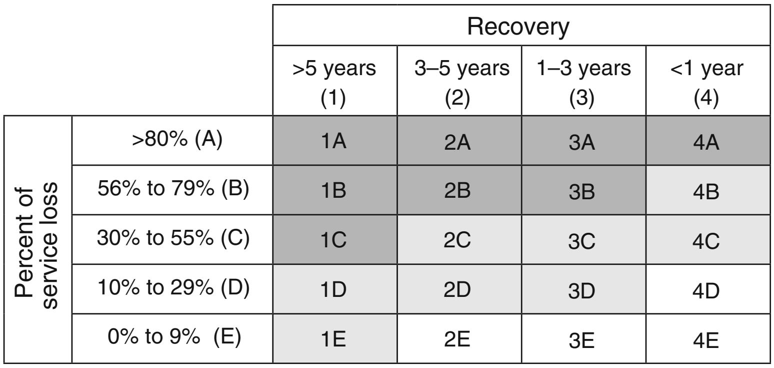
Another important dimension of the overall risk associated with a remedial alterative involves the explicit consideration of management goals in terms of the chemical and environmental risks of remediation. Explicit consideration of temporal scales is typically an important aspect of an FS, especially if an MNR or *in situ* treatment remedial alternative is being considered. These elements can be considered within a broader framework referred to as Net Environmental Benefits Analysis (NEBA). This section presents a Case Study of REBE, a related approach that places greater emphasis on the relative comparison of remedial alternatives. First, a discussion of NEBA is presented, as the basic principles apply to both approaches.

NEBA is used to compare existing chemical risks and risk reductions related to remediation with the short- and long-term impacts of the remediation. Because the goal of the remedial program is to achieve an overall environmental improvement, assessment of existing and potential future conditions after remediation provides insights into what can be gained by the implementation of various remedial alternatives. Potential gains are improvements in environmental conditions that must be weighed against negative effects associated with the implementation of the various remedial alternatives. Within the NEBA framework, the cost of inaction and remedial action are weighed in light of the chemical and environmental risks related to each remedial action. Risk managers can use NEBA to consider the range of environmental cost/benefits associated with each remedial alternative to make more informed decisions (Efroymson et al., 2004). NEBA can be used to achieve a more complete assessment of an action, a product, and/or a technology (Hunt et al., 1992). NEBA seeks to integrate the positive and negative aspects of an environmental action, such as sediment remediation, beyond consideration of chemical risks.

NEBA has not been formalized by USEPA in a manner similar to ecological risk assessments; however, including a comparative analysis of remediation alternatives is a natural extension of risk assessment and an important step toward ensuring that the overall environmental benefit is not prescribed solely by engineering technologies or cost (Efroymson et al., 2004). USEPA is moving toward explicit incorporation of ecosystem services into environmental decision-making, and a NEBA analysis would be consistent with that regulatory philosophy. Although issues of cost, human health risks, and technical feasibility are usually addressed outside of the NEBA framework (Efroymson et al., 2004), these elements can be integrated within more formal decision frameworks (Menzie et al., 2009).

Ecosystem services are the benefits people obtain from ecosystems and the nature and flow of these benefits are frequently discussed in terms of currencies and markets (Kroeger and Casey, 2007; Munns et al., 2009; Achterman and Mauger, 2010). The development of tools for mapping and quantifying ecological services and other uses is an active area of research. Demonstrations of these approaches are now being applied to guide sediment remediation (Robberson, 2006). Table 5.5 shows an example matrix key for coupling percent service loss, to time to recovery for a hypothetical contaminated river. The relative NEBA ranking that corresponds to the percent service loss, and time to recovery for a resource is then transferred to the final NEBA matrix, where the results of the analysis are displayed in a visual, easy-to-interpret figure (Table 5.6). The NEBA matrix can then be used to build consensus on the appropriate remediation approach.

Table 5.5. The Matrix Key is Used to Assign a Unitless Value to Each Element in the Matrix Based on the Percent Service Loss and Time to Recover



		Recovery			
		>5 years (1)	3–5 years (2)	1–3 years (3)	<1 year (4)
Percent of service loss	>80% (A)	1A	2A	3A	4A
	56% to 79% (B)	1B	2B	3B	4B
	30% to 55% (C)	1C	2C	3C	4C
	10% to 29% (D)	1D	2D	3D	4D
	0% to 9% (E)	1E	2E	3E	4E

Notes: Dark gray represents a “high” level of concern
Gray represents a “moderate” level of concern
White represents “limited” level of concern

NEBA is often based on subjective evaluations, although objective data are used if available. It is very important when conducting a NEBA to clearly state assumptions and describe the consequences of incorrect assumptions and the sufficiency of the data used in the analysis (Robberson, 2006). While NEBA can be a somewhat subjective analysis, transparency of the process is essential to encourage discussion of the projected consequences and benefits of remedial action. Through collaborative discussion, percent service estimates can be revised to reflect consensus among all parties, and the final product should have comprehensive support to guide remediation decisions. The end NEBA product is a thoughtful analysis of the most appropriate course of action to truly achieve a net environmental benefit.

REBE applies aspects of NEBA to examine the relative risks and benefits of remedial alternatives. The application involves integrating these considerations into the criteria used to judge remedial alternatives. The REBE approach was recently developed and applied to a dioxin-contaminated creek (Huibregtse et al., 2007). The REBE approach consisted of answering a number of questions that evaluated the significance of implementing each of ten proposed remedial actions. Each of the 17 questions was rated with one of the following scores:

- Net “– –” Significant Adverse Effect
- Net “–” Adverse Effect
- Net “0” Neutral or No Effect
- Net “+” Beneficial Effect
- Net “+ +” Significant Beneficial Effect.

Examples of some of the questions used to evaluate the remedial alternatives and a demonstration of how the ratings were developed are shown in Table 5.7. The total number of positive and negative scores for each of the ten alternatives are also shown in a simple but informative figure (Figure 5.7), which also cross-references these positive and negative scores to the estimated cost for implementing each remedial alternative. The questions used to evaluate alternatives were carefully selected based on the conceptual model that was developed and refined through the course of a detailed RI. The questions were carefully chosen to tie the REBE to key sediment risk management principles (USEPA, 2005a) and the NCP’s consideration of the nine criteria for selecting alternatives.

Table 5.6. NEBA Matrix for Difference Remediation Strategies

Example for Area X:	**Ecological Receptors**													
Habitats:	**Aquatic Bed Vegetation**					**Emergent Wetland Marsh**					**Open Water**			
Resources:	Benthic macroinvertebrate populations	Fish/shellfish populations	Avian populations	Mammalian populations	Submerged aquatic vegetation	Benthic macroinvertebrate populations	Fish/shellfish populations	Avian populations	Mammalian populations	Emergent and riparian aquatic vegetation	Benthic macroinvertebrate populations	Fish/shellfish populations	Avian populations	Mammalian populations
Risk Rating:														
Scenario 1: Natural recovery	1D	1B	1C	NR	NR	1E	1B	1C	NR	NR	1D	1B	1C	NR
Scenario 2: Dredge to remove contaminant	3B	3C	3C	3C	3C	3B	3C	3C	3C	3C	3B	3C	4C	4C
Scenario 3: Place impervious cap over contaminant	3B	3C	3C	3C	3C	3B	3C	3C	3C	3C	3B	3C	4C	4C
Scenario 4: Dredge to remove contaminant and replace emergent vegetation	3B	3C	3C	3C	3C	3B	4D	4D	4D	4D	3B	3D	4D	4D

Note: NR = No risk

Environmental decision-making involves many complex issues that must be addressed by multiple stakeholders, and determining the best management alternative often requires trade-offs. A systematic evaluation of the environmental benefits and impacts associated with existing conditions in comparison to environmental benefits and impacts associated with various remediation alternatives can facilitate the decision process. The NEBA and REBE approaches can both be used in part to meet this goal of facilitating the decision-making process.

Table 5.7. Example of REBE (Based on Work of Huibregtse et al., 2007)

NCP Remedy Selection Criteria	Threshold Criterion	Environmental Factors to Consider for Remedy Implementation[a]	Examples of Remedial Alternatives Considered[a]				
			No Action (1)	MNR (2)	Enhanced MNR (eMNR) (4)	Engineered Cap and eMNR (6)	Dredge and Thin-Layer Cap (9 and 10)
Overall protection of human health and the environment	Human exposure, risk, and habitat use	Will remedy control the critical contaminant exposure pathway?	–	–	+	+	–
		Will remedy implementation result in increased exposure to onsite workers?	0	0	0	0	––
		Will remedy implementation present physical hazards (i.e., increased truck traffic) to the surrounding community?	0	0	–	–	––
	Ecological exposure, risk, and habitat impacts	Will remedy control the critical contaminant exposure pathway?	–	–	++	++	0
		Will remedy preserve the wood debris, which serves as aquatic habitat?	++	++	++	+	––
		Will remedy adversely affect water quality?	0	0	0	+	––
Compliance with applicable or relevant and appropriate requirements (ARARs)	ARAR compliance	Will remedy implementation comply with ARARs?	–	–	+	+	––
Beneficial effects[b] (total number of pluses for complete set of questions)			+3	+3	+13	+11	+2
Adverse effects[b] (total number of minuses for complete set of questions)			–6	–5	–2	–4	–21

[a] The environmental factors and remedial alternatives listed in this example represent a subset of the complete list considered by Huibregtse et al. (2007). A cross-reference to the original alternative number shown in Figure 5.7 is provided in parentheses, as the alternative names were simplified for this example.

[b] The number of beneficial effects (pluses) and adverse effects (minuses) represent the actual composite scores developed by Huibregtse et al. (2007), for each alternative considering the complete list of environmental factors.

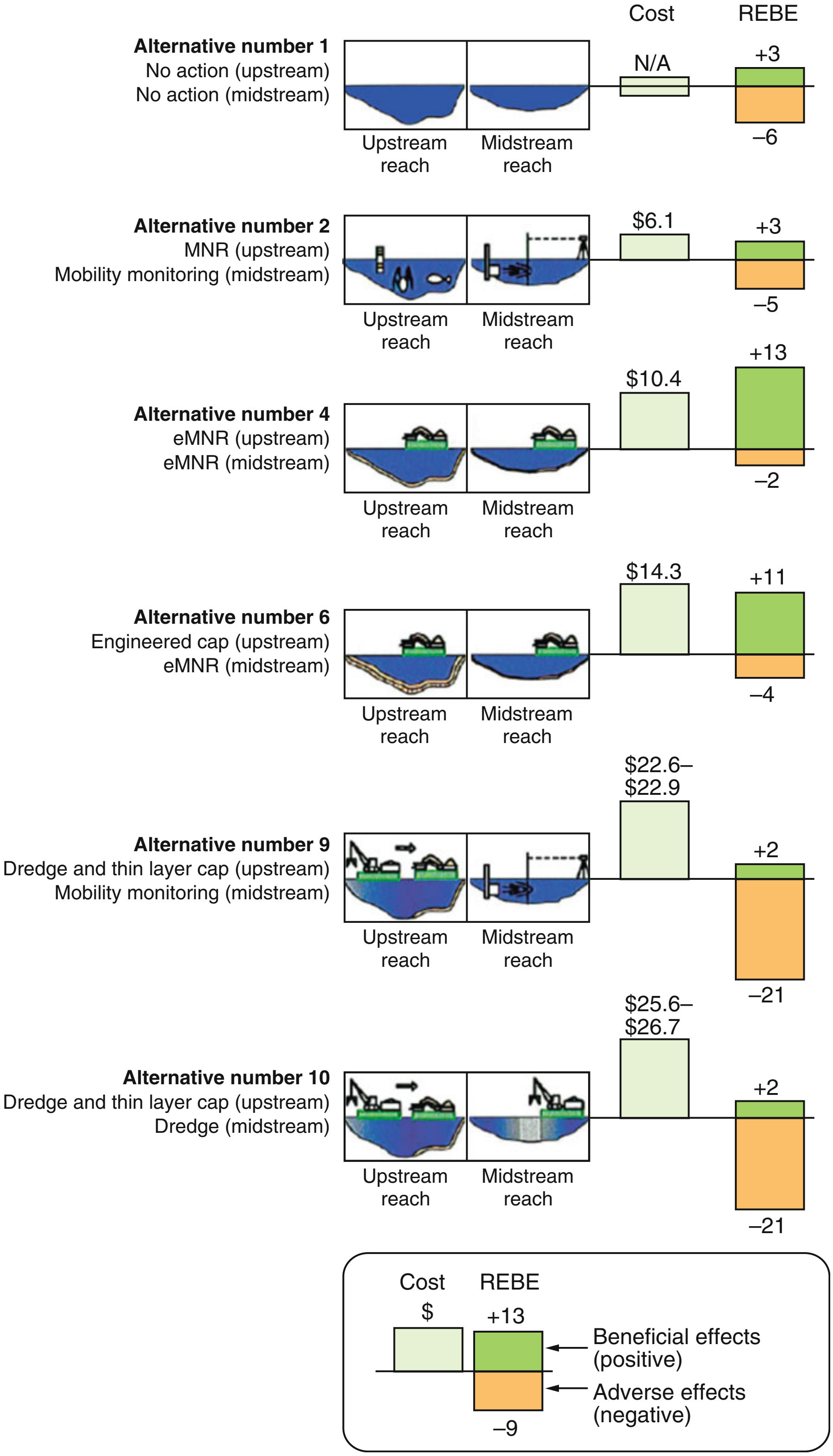


Figure 5.7. Comparison of cost and REBE (based on work of Huibregtse et al., 2007).

5.5 A PATH FORWARD

There is a strong and natural inclination to rely on historical precedents when evaluating and remediating sediments, and the premise of many chapters in this book is that those precedents do not necessarily lead us to good decisions or represent the most appropriate remedial strategies. Precedents also play a major role in determining how risks are evaluated; a few conceptual changes and approaches that benefitted the decision-making process were described. Experience over the last decade indicates that progress can best be made through concerted and collaborative efforts among regulatory bodies, the regulated community, scientists and engineers, and others that are involved in remedial decisions. The ideas discussed are currently being considered within these arenas along with many others. The value of an integrated approach to evaluate complex sediment contamination problems has been emphasized. Central to this approach is the use of spatially-explicit methods to communicate the results of risk assessments in a more meaningful way and to assess net environmental benefits associated with the range of remedial alternatives under consideration. The considerations articulated by USEPA (2005a) also provide a comparative framework for judging the appropriateness of alternatives for sediment management. In addition, the NEBA and REBE approaches described above provide a means of incorporating other environmentally relevant information into the overall decision context. Finally, presenting information in a spatially-explicit format and in terms of degrees of risk, levels of confidence, and other factors offers a set of blueprints that can enable managers to visualize the strengths and weaknesses of various remedial approaches. These integrated risk management approaches can help avoid blind spots and increase the opportunity for achieving overall environmental and health improvements.

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CHAPTER 6

ASSESSING BIOLOGICAL EFFECTS

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6.1 INTRODUCTION

Many hazardous substances associate readily with sediments in marine, estuarine and freshwater environments. The science of sediment quality evaluation associated with characterizing the ecological effects of these substances has progressed dramatically over the past 30 years. It is now apparent that to reach conclusions that are accurate (related to actual field conditions), assessments of sediment quality involve much more than simply assessing sediment toxicity using laboratory tests on field-collected sediments. Optimal assessments of quality, hazard or risk associated with sediments integrate multiple methods and approaches. For example, many authors now advocate that laboratory toxicity testing be performed concurrently with physicochemical characterizations, indigenous biotic community assessment and *in situ*-based approaches to characterize exposures from overlying waters, sediments and advective groundwater-pulse events (Burton, 1991; Burton et al., 2005a; Greenberg et al., 2002; Adams et al., 2005). Sediment quality assessment tools and approaches also include toxicity identification evaluations (TIEs) (USEPA, 2007; Ho and Burgess, 2009), assessment of abiotic factors as stressors (Burton and Johnston, 2010) and toxicological evaluation of tissue residue (Meador et al., 2008; Sappington et al., 2011). However, compartmentalization rather than integration of key approaches and issues is a potential pitfall for sediment quality evaluation. If only one or two assessment methods are used, or any are used incorrectly, the resulting conclusions may be erroneous or have a high degree of uncertainty.

Sediments are an integral and dynamic part of aquatic ecosystems. However, there has been a tendency in past assessments of contamination to treat sediments as a separate, temporally stable and/or static compartment, in isolation from overlying water or advective groundwaters (Greenberg et al., 2000). Sediment quality surveys have often consisted of a limited, one-time collection of sediment samples taken across a study area, which are then characterized from a physicochemical perspective. Despite the recognition by sediment experts that chemical concentrations alone are inadequate for sound decision making, this approach continues to dominate the regulatory process (Wenning et al., 2005a), and sediment quality surveys are too rarely coordinated with the investigation of overlying and groundwaters. The complex dynamics of stressor exposure and of chemical fate and bioavailability make the assessment of biological effects essential to the process. In extensive sediment quality surveys, chemical data are sometimes reviewed first, then selected stations are re-sampled for laboratory toxicity tests and possibly for benthic macroinvertebrate characterizations. However, this tiered process (chemistry, then biology) assumes that exposures across space and time are constant and homogeneous, which certainly is not the case. More recent, weight-of-evidence based

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approaches promote concurrent sampling with better characterizations of exposures that are well-linked to effects based on statistically sound experimental designs (Burton et al., 2002a, b; Adams et al., 2005).

Sediment quality evaluation has largely consisted of comparisons of the concentration of single chemicals to chemical benchmark values or performance in laboratory-based bioassays. Few published studies on this subject existed until the 1980s, which coincides with the initial development of sediment quality criteria (Burton, 1991, 2002; Engler et al., 2005). Since the late 1980s, there has been a steady increase in interest among regulatory authorities and the regulated community in sediment-toxicity testing and the associated assessments of hazard or risk, because management of sediment contamination has become more common. These often large, expensive and continuous assessments and management efforts, in many cases, coincide with dredging of navigation channels and harbors (Figure 6.1), or occur at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites, commonly known as "Superfund" sites, where there has been a long history of contamination from industrial or military operations (NRC, 2001).

All sediment quality assessments are conducted for a specific reason and most are done for some type of regulatory purpose. Numerous regulations exist throughout the world that authorizes programs that address contaminated sediments. Sediment quality assessments are conducted to initially screen sediment quality, for general monitoring, to support navigation dredging projects and for the evaluation of sediment quality to support sediment management decisions such as capping or removal (Ireland and Ho, 2005). It is generally accepted that the more important or costly the decision (such as the removal of sediment from an aquatic environment), the more information should be collected. As outlined in Power and Chapman (1992), there are five general categories of measurements of sediment quality. These include sediment chemistry, sediment toxicity, benthic biological community structure, tissue chemistry of resident infauna and pathology of resident or sediment-exposed organisms. Sediment

Figure 6.1. Navigation channel dredging using a clamshell (or bucket) mechanical dredge.

chemistry is compared to chemical benchmarks to predict adverse effects or the lack of effects on the biota. The objective of a sediment toxicity test is to determine whether contaminated sediments are harmful to benthic organisms in the field, although surrogate species are often required for the tests (USEPA, 2000; ASTM, 2005). The structure of benthic invertebrate communities represents an important indicator of sediment quality conditions by providing a direct way of evaluating chemical effects on resident biota within an assessment area (USEPA, 2002). Contaminated sediments represent important sources of substances that accumulate in aquatic food webs (Ingersoll et al., 1997; ASTM, 2010; Gobas and Arnot, 2010). Therefore, tissue chemistry of resident infauna or test organisms exposed to field-collected sediment in the laboratory can be used in exposure and risk analysis to evaluate whether these substances may adversely affect fish, aquatic-dependent wildlife and/or human health (PIANC, 2006; ASTM, 2010). Pathology is defined as the assessment of disease and modifications in cellular function. Sediment quality conditions can also be evaluated by examining fish health because fish that are exposed to contaminated sediments can exhibit impaired health, such as liver tumors (USEPA, 2002).

This chapter discusses the assessment of biological effects of contaminated sediments from a holistic, integrated approach. Key issues for conducting accurate assessments are reviewed. Each of these methods has associated strengths and limitations. This chapter is not a comprehensive literature review, but rather will highlight traditional and novel methods used to predict the likelihood that contaminated sediments will suffer significant ecological alteration. The decision point of what constitutes “significant” contamination (e.g., contamination resulting in “significant” ecological effects) varies from study to study; however, the importance of establishing an a priori benchmark for significant effects cannot be overstated. Without this understanding, managers and stakeholders will likely be frustrated and uncertain as to what the results of the assessment mean (NRC, 2001; USEPA, 2002; Wenning et al., 2005a). The following discussions will emphasize the various approaches that are most useful in making those determinations.

6.2 SEDIMENT QUALITY GUIDELINES

Sediment Quality Guidelines (SQGs) have been defined as numerical chemical concentrations intended to be either protective of biological resources, or predictive of adverse effects to those resources, or both (Wenning and Ingersoll, 2002). SQGs that relate the potential for adverse effects on sediment-dwelling organisms have been derived using both mechanistic (often referred to as “theoretical”) and empirical approaches. These effects-based values have been derived to be used, at least to some extent, as a surrogate for direct measures of adverse effects of contaminants (e.g., sediment toxicity tests on benthic organisms) (Wenning et al., 2005a). SQGs have been used to interpret historical trends, identify potential problem chemicals or reaches in a waterway, interpret or design ambient monitoring programs, classify hot spots, establish baseline conditions in non-urbanized systems, rank contaminated waterways and help choose sites for more detailed studies (Long and MacDonald, 1998; Wenning et al., 2005a).

The mechanistically derived SQGs have been developed and tested using laboratory spiked sediment and subsequently compared to toxicity tests by using field-collected sediments. These types of guidelines are based on the equilibrium partitioning (EqP) theory (Di Toro et al., 2005) EqP-based mechanistic SQGs are also called equilibrium partitioning sediment benchmarks (ESBs). According to this theory, a nonionic organic chemical in sediment partitions between sediment organic carbon, pore water and benthic organisms. At equilibrium, if the concentration in any one phase is known, then the concentration in the others can be predicted (Di Toro et al., 2005)

Burgess et al. (2013) provides an overview of EqP theory, ESB derivation, examples of applying ESB values, and factors to consider when using ESBs. Uncertainties and advantages in the use of the EqP model to predict the bioavailable and toxic concentrations of nonionic organic chemicals are discussed in Maruya et al. (2012).

Equilibrium partitioning for metals uses the simultaneously extracted metals acid-volatile sulfide (SEM-AVS) approach and is based on the observation that sulfides are an important controlling factor for the bioavailability of certain metals in sediments. In sediments where the molar concentration of AVSs exceeds that of the metals simultaneously extracted in the AVS determination, metals are considered to be unavailable and, therefore, not likely to cause toxicity (USEPA, 2005a). In later versions of the AVS model, binding of metals to sediment organic carbon was also included. Maruya et al. (2012) explains that a potential difficulty of the AVS-SEM approach is that it does not account for interactions among metals that make up the underlying SEM pool of potentially bioavailable metals.

U.S. Environmental Protection Agency (USEPA) documents describing procedures for the derivation of equilibrium partitioning sediment benchmarks (ESB) for the protection of benthic organisms were published for polycyclic aromatic hydrocarbons (PAHs) mixtures (USEPA, 2003a), the insecticides dieldrin (USEPA, 2003b) and endrin (USEPA, 2003c), metals mixtures (cadmium, copper, lead, nickel, silver and zinc) (USEPA, 2005a) and for 32 nonionic organic chemicals, including several low molecular weight aliphatic and aromatic compounds, pesticides and phthalates (USEPA, 2008). These guidance values typically address single chemicals or groups of related chemicals and do not consider the antagonistic, additive or synergistic effects of sediment contaminants in combination with those for which toxicity predictions are being made or the potential for bioaccumulation and trophic transfer to aquatic life, wildlife and humans (USEPA, 2008).

Empirically based SQGs have typically been derived from databases of sediment chemistry (based on concentrations of specific contaminants) and observed biological effects (such as sediment toxicity test endpoints and indicators from benthic community analysis). Various algorithms are used to define specific concentrations associated with particular levels of effect or no effect (Wenning et al., 2005a). Common empirically derived approaches include: screening-level concentrations (SLC) (e.g., von Stackelberg and Menzie, 2002), effects range low/effects range median (ERL/ERM) (Long et al., 1995), threshold effects level/probable effects level (TEL/PEL) (MacDonald et al., 1996), apparent effects threshold (AET) (e.g., Ginn and Pastorok, 1992), consensus-based evaluation (e.g., Swartz, 1999; MacDonald et al., 2000a, b) and logistic regression modeling (LRM) (e.g., Field et al., 2002). In contrast to the other approaches outlined above, the LRM approach does not develop threshold values. Instead, it develops models that enable users to select the probability of observing sediment toxicity that corresponds to their specific objectives or to estimate the probability of observing effects at a particular chemical concentration (Field et al., 2002). An example of a study comparing the predictive ability of major SQGs to predict the presence and absence of sediment toxicity was provided by Vidal and Bay (2005). Using coastal southern California contaminated sites, those authors reported large differences in predictive ability among the SQGs evaluated. Sediment quality guidelines that performed well in identifying nontoxic samples were not necessarily the best predictors of toxicity. In general, the ERM quotient, the mean sediment quality guideline quotient and consensus moderate-effect concentration approaches had a better overall predictive ability than the apparent effects threshold and equilibrium partitioning for organic contaminants (Vidal and Bay, 2005).

Considerable controversy exists regarding the use and viability of SQGs. In an attempt to improve the understanding and use of SQGs, a Pellston workshop entitled “Use of Sediment Quality Guidelines and Related Tools for Assessments of Contaminated Sediments” was conducted, and proceedings were subsequently published (Wenning and Ingersoll, 2002;

Wenning et al., 2005b). A few conclusions reached from this workshop include: (1) that although the scientific underpinnings of the different SQG approaches vary widely, none of the approaches appear to be intrinsically flawed; (2) chemically-based numeric SQGs can be effective for identifying concentration ranges where adverse biological effects are unlikely, uncertain and highly likely to occur and (3) in all cases, application of SQGs in a "toxic or nontoxic" context must be cognizant of the types and rates of errors associated with each type of SQG (Wenning and Ingersoll, 2002).

Approaches for applying sediment quality guidelines have been developed to facilitate decision making (e.g., Bridges et al., 2005; Environment Canada and Ontario Ministry of the Environment, 2008). An example of the use of sediment chemistry indices integrated with direct assessment of sediment toxicity and benthic community impairment is described in Bay and Weisberg (2008) as a way to evaluate the condition of bays and estuaries in California. Some consensus exists for using lower-level guidelines, in combination with physical and biological data, to predict that a material poses a small likelihood to cause adverse effects of the type considered by the guideline. In cases where upper sediment quality guidelines are exceeded, toxicity tests with contaminated sediments from the site of interest are usually applied as the principal factor in decision making (e.g., PIANC et al., 2006; Environment Canada and Ontario Ministry of the Environment, 2008). The selection and use of chemical sediment benchmarks and guidelines should be based on existing regulatory requirements, as well as matching the assessment question with the narrative intent of the guideline, e.g., guidelines predicting an absence of direct toxicity to benthic organisms provide no information about effects mediated through bioaccumulation to upper trophic levels (PIANC, 2006).

6.3 LABORATORY SEDIMENT TOXICITY TESTS

Assessment of sediment quality commonly includes the evaluation of direct measures of toxicity using laboratory testing procedures in which live organisms are exposed to field-collected whole sediment, sediment elutriates or sediment pore water. A variety of toxicity tests have been developed into tools with widely recognized utility for providing direct and quantifiable evidence of adverse biological impacts from the direct contact with the bioavailable fraction of sediment contaminants (Ireland and Ho, 2005; ASTM, 2008a). When applied to field samples, these tests measure cumulative effects of all bioavailable contaminants as well as their interaction as mixtures, typically without the requirement of complex or expensive laboratory equipment and supplies (e.g., USEPA, 2001; ASTM, 2008a). Biological testing is considered a necessary component of integrated sediment evaluation.

Since the mid-1990s, a number of standard methods have been extensively used to assess biological effects as a tool to monitor and manage contaminated sediments. Tests using contaminated sediments have been established for marine, estuarine and freshwater environments. Overviews and discussions of laboratory toxicity test methods are provided in Rodriguez and Reynoldson (1999), Burton et al. (2003), Anderson et al. (2004), Ireland and Ho (2005) and PIANC (2006). Ireland and Ho (2005) summarize some of the more widely used sediment toxicity tests, and include information on how test organisms can be obtained, test endpoints, the volume of sediment or pore water needed, test duration, references for standard methods and examples of how the tests have been used. Infaunal invertebrates that live in and ingest sediments are expected to have high exposure to sediment-associated contaminants due to their intimate contact with sediment particles and pore water, and are commonly used in sediment toxicity testing (PIANC, 2006). A comprehensive list of test organisms and the respective published methods for their use in sediment toxicity testing is provided in PIANC (2006) and ASTM (2008a).

Research aside, most toxicity testing is conducted for regulatory purposes, including support for decision-making regarding sediment remediation, dredged material disposal, sediment monitoring and natural resource damage assessment (Ireland and Ho, 2005). Technical guidance describing the use of sediment toxicity testing in the context of dredged material management is provided in PIANC (2006) and a summary of the use of this approach in various countries is provided in Ireland and Ho (2005).

Sediment toxicity tests are commonly used in environmental risk assessments (ERA) developed to assist in identifying sites where the risks to the environment are unacceptable due to sediment contamination (USEPA, 1997), including for use in association with Superfund activities. The use of toxicity testing in Superfund ERA is summarized in Ireland and Ho (2005). A critical first step is problem formulation, which identifies assessment endpoints. These endpoints are an explicit expression of the environmental value (e.g., species, ecological resource or service or habitat type) that is to be protected, but because these values are difficult to measure directly, sediment toxicity tests are commonly used as surrogates. These tests are conducted as part of the site investigation and analysis. ERA guidelines for Superfund sites state that the "selection of the test organism is critical in designing a study using toxicity testing. The species selected for toxicity testing should be representative of the assessment endpoint."

The success of sediment quality evaluation depends largely on the accuracy and representativeness of the sediment sample collected for chemistry and toxicity testing (Ireland and Ho, 2005). Recommended procedures for the collection, transport, handling, storage of sediment from field sites, as well for manipulation of sediments and pore water are provided in Environment Canada (1994), USEPA (2001) and ASTM (2008b) and a concise synthesis and discussion on the subject is provided by Burton et al. (2003) and Ireland and Ho (2005). Ample consideration should be given to the above tasks as they are known to influence the physiochemical properties and the results of chemical, toxicological and bioaccumulation analyses.

Toxicity tests vary in their relevance according to the biological receptors of concern, the biological response of concern and exposure pathways by which receptors take up sediment contaminants. Sediment toxicity testing utilizes a broad variety of species belonging to taxonomic groups from bacteria to amphibians and a variety of life-history stages.

ASTM (2008a) provides general guidance on the selection, application and interpretation of biological tests with sediments. The test matrix is typically whole sediment (also referred to as solid phase or bedded phase), pore water or elutriates. Whole sediment is defined as the combination of sediment and associated pore water that has had minimal manipulation following collection or formulation (ASTM, 2008a). Since most sediment-dwelling organisms are exposed directly to contaminants by the ingestion of sediments and by the uptake of sediment-associated contaminants from the pore water and overlying water, whole-sediment toxicity tests (Figure 6.2) are considered the most appropriate for most sediment quality evaluations (Ireland and Ho, 2005; PIANC, 2006), and whole sediments are the test matrix of choice for dredge-material evaluation (PIANC, 2006). Whole sediment is also typically the most appropriate test matrix because sediment-dwelling invertebrates may be stressed by the absence of sediment (ASTM, 2008a).

Sediment pore water is considered a key contaminant exposure route for many infaunal invertebrates. Pore water in the volumes needed to conduct pore water toxicity testing is challenging to acquire and the feasibility of such tests may, therefore, be limited. Another concern is the relative instability of pore water after it is removed from sediment (Adams et al., 2003); e.g., oxidation processes may cause a decrease in pH resulting in toxicity. Loss of hydrophobic compounds (e.g., due to sorption to glass containers) may also be a concern, because isolation from sediment particles excludes equilibrium-partitioning driven

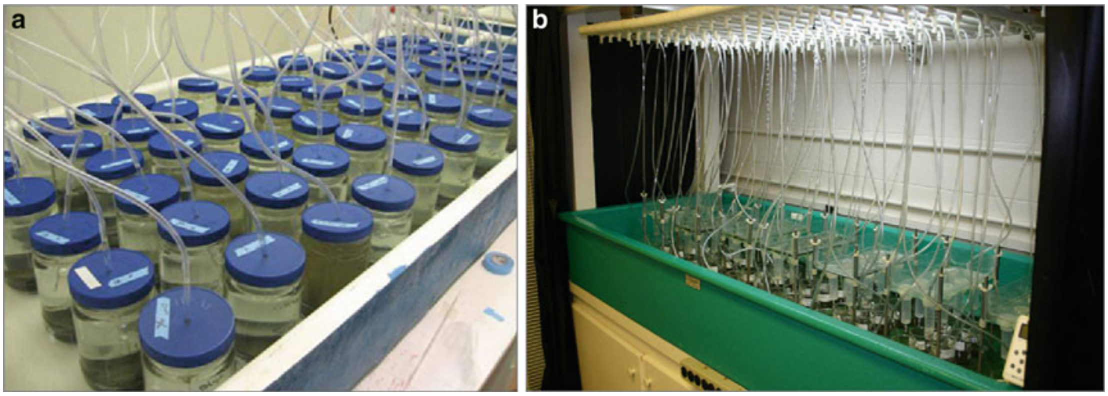

Figure 6.2. Laboratory whole-sediment toxicity testing set up for a 10-day amphipod test (a) and a 10-day midge test using water delivery apparatus (b).

replenishment as pore water concentration decreases. Removal of infauna from sediments also excludes direct sediment contact through deposit feeding, which may confound the assessment of toxicity of certain invertebrates. Invertebrates used in pore water toxicity tests have been reported to experience increased sensitivity to some toxicants relative to solid-phase tests (Carr et al., 1996, 2000), but some invertebrates were less sensitive in pore water tests (Winger et al., 2003). Several infaunal invertebrates are exposed to a mixture of overlying and pore water via irrigation of their burrows with overlying water. Therefore, pore water tests may overemphasize exposure to many water-soluble toxicants such as ammonia and metals while potentially underemphasizing toxicants with limited solubility (Batley et al., 2005). Detailed description and discussion of methods for using pore water as a toxicity test matrix are provided in Carr and Nipper (2003) and Anderson et al. (2004). Marine sediment pore water tests typically employ pelagic embryo-larvae of sea urchin and bivalves while freshwater pore water tests typically employ cladocerans as well as benthic invertebrates typically used in whole-sediment tests (Carr and Nipper, 2003; Anderson et al., 2004). Discussions of the usefulness and limitations of pore water testing are presented in Chapman et al. (2002) and Anderson et al. (2004). While there may be specific reasons to perform pore water testing, such as use in TIE and use of sensitive species and life-history stages, whole-sediment exposures are considered a more realistic testing alternative (Ireland and Ho, 2005). In addition, the use of pore water toxicity testing in sediment quality evaluations is discouraged because exposure matrices other than whole sediment are believed to poorly reflect the bioavailable fraction of sediment-associated contaminants or real world conditions in bedded sediments (Word et al., 2005). Despite limitations in the use of pore water in toxicity testing, approaches for directly measuring pore water concentrations using equilibrium passive samplers (Chapter 7) have successfully been used to predicted toxicity of sediment-associated contaminants (You et al., 2011).

Sediment elutriate toxicity testing is typically used only in specialized circumstances. An elutriate is a sample generated by washing contaminants from a sediment by mixing water with the sediment, allowing the sediment to settle and extracting the sample from the overlying water. Sediments will be suspended to different degrees within the water column during dredging and dredged material disposal operations, as well as during flood events and by boat and ship traffic in shallow areas (Haring et al., 2010). Concerns regarding the potential for effects from suspended sediments on organisms within the water column are typically addressed using elutriate toxicity tests described in USEPA and USACE (1998). Methods for the preparation of sediment elutriates are presented in ASTM (2008b). Although elutriate tests have shown a level of sensitivity comparable to whole-sediment tests, the ability of elutriate tests to predict toxicity was not statistically correlated with bulk sediment methods for field-collected freshwater sediments (Haring et al., 2010), leading the authors to recommend the use of both tests for sediment quality evaluations.

The most commonly used endpoint for tests applied to sediment quality evaluation is survival. Organismal-level, sublethal endpoints include individual growth (change in biomass over the exposure period), reproductive output (number of offspring produced) and behavioral responses. Subtle physiological and biochemical responses, including changes in gene expression, have also been used as toxicity test endpoints and are discussed in more detail below. Survival is widely accepted as an indicator of sediment quality, especially when a strong relationship between the test endpoint and the viability of populations under field conditions is demonstrated. In contrast, decision making based on endpoints expressed at lower levels of biological organization, such as molecular responses, often have a poorly-defined relationship to population viability and are more difficult to justify. Therefore, the biological and ecological relevance of the endpoints measured in a toxicity test must be well understood before using toxicity test data for making decisions on management options for contaminated sediments (PIANC, 2006).

The duration of exposure toxicity tests commonly used in sediment quality evaluations vary widely. Toxicity tests with short exposure duration with respect to the life cycle of the test organism are referred to as acute tests. Tests using longer exposures that include significant portions of an organism's life cycle, and in some cases multiple life-history stages, are called chronic tests. A chronic test should be at least 10% of the duration of the species' life span (Suter, 1993). Ten-day acute tests measuring survival and 4–6-week chronic tests measuring survival, growth and reproduction in whole-sediment exposures are most common (ASTM, 2005, 2008a; PIANC, 2006).

For marine evaluations, the two most commonly used species in whole-sediment tests are the sediment-burrowing amphipod *Leptocheirus plumulosus* and the infaunal tube-building polychaete *Neanthes arenaceodentata* (Figure 6.3). Standardized test methods that measure lethal and sublethal endpoints with whole sediments are available for both (for *L. plumulosus*, see ASTM, 2008c, and for *N. arenaceodentata* see ASTM, 2007a, and Farrar and Bridges, 2011). Other commonly used test species are the amphipods *Ampelisca abdita*, *Eohaustorius estuarius* and *Rhepoxynius abronius* collected in the wild (ASTM, 2008c). Amphipods of the genus *Corophium* have been used in sediment toxicity testing in Europe (Guerra et al., 2009), Canada (Hellou et al., 2008) and Australia (Birch et al., 2008). In addition to amphipods and polychaetes, benthic harpacticoid copepods have also been successfully used in whole-sediment tests that rapidly assess the chronic sublethal effects, such as on reproduction and development, of sediment contaminants (e.g., Ward et al., 2011).

For freshwater evaluations, two commonly used test species include the amphipod *Hyalella azteca* and the midge *Chironomus dilutus* (former name *C. tentans*) (Figure 6.4). Both are widely used in standardized methods for testing with whole sediments measuring lethal as well as sublethal endpoints (ASTM, 2005). Ingersoll et al. (2005) concluded that sublethal effects observed in laboratory toxicity tests (e.g., reductions in reproduction and length) provide a more sensitive and more protective measure of effects on invertebrates exposed to contaminated sediments in the field. Their study found that sublethal effects noted in the laboratory occurred at similar or lower concentrations observed to adversely affect colonization by several major taxa in the field. The tubificid oligochaete *Tubifex tubifex* and the mayfly *Hexagenia* spp. are also common test-species of choice for measuring sublethal endpoints using standard methods (ASTM, 2008a).

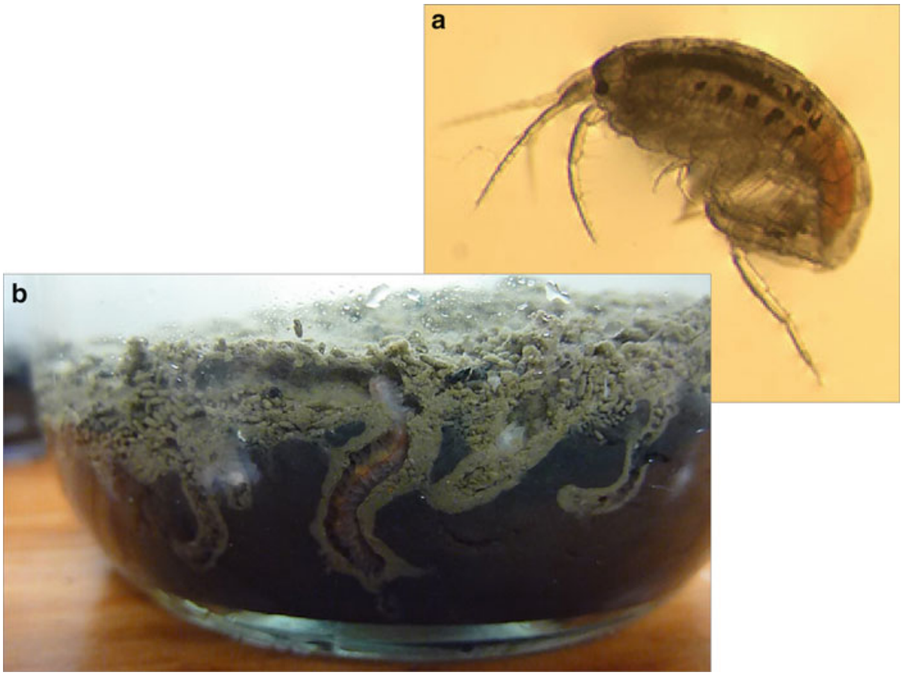

Figure 6.3. **The estuarine amphipod *Leptocheirus plumulosus* (a) and tube-building marine polychaete *Neanthes arenaceodentata* (b).**

Figure 6.4. **The freshwater amphipod *Hyalella azteca* (a) and the sediment-dwelling larval stage of the chironomid midge *Chironomus dilutus* (b).**

An innovative sediment testing approach was developed by Anderson et al. (1996) in which toxicity test protocols traditionally used for water column toxicity testing are used for assessing toxicity of solid phase samples at the sediment-water interface (SWI). This test, further described and discussed in Anderson et al. (2004) and Bay et al. (2007), is designed to be conducted on a relatively undisturbed core sample containing surficial sediment brought to the laboratory for tests using sea urchin or mussel embryos. In addition to invertebrates, sediment testing has been performed using luminescent bacteria or dinoflagellates, as in the Microtox^{TM} test with *Vibrio fischeri* (Doe et al., 2005) and the QwikLite^{TM} test with *Lingulodinium polyedrum* (Lapota et al. 2007), but are best suited as part of a battery of toxicity tests, particularly as a screening tool (van Beelen, 2003; Doe et al., 2005). On the other extreme, various methodologies and approaches involving the use of fish, including use in whole-sediment laboratory testing, have been successfully used in sediment quality evaluations, as reviewed in Hallare et al. (2011).

Behavior among sediment-dwelling invertebrates differs, and species will therefore experience different exposures to contaminants adsorbed to sediment particles or dissolved within pore water. Given this diversity, using a suite of toxicity tests that represent a diversity of benthic functional groups will provide enhanced confidence that the assessment will be protective of exposure conditions at the site (Adams et al., 2003; Ireland and Ho, 2005; PIANC, 2006). However, one needs to balance a large number of test types against both resource and time constraints. To assist in the determination of test type and organism type, one should consider the objectives of the test program, and the selectivity, sensitivity, appropriateness and acceptance levels of the test organism (Ireland and Ho, 2005).

Comparisons of marine and estuarine sediment toxicity test performance for the purpose of developing a suite of tests adequate for specific sediment evaluation objectives were made by Greenstein et al. (2008) and Kennedy et al. (2009). Those studies addressed relative test method performance, the relationship between sediment chemical concentrations and toxicity, and whether chronic and sublethal tests offered an enhanced level of sensitivity to contaminants for the suite of sediments evaluated. Using sediments from New York/New Jersey Harbor, Kennedy et al. (2009) showed clear performance differences for several marine sediment toxicity test methods. In particular, *L. plumulosus* sublethal growth and reproduction endpoints did not respond consistently to exposures because of high intra-treatment variability. Using sediment from coastal areas in California, Greenstein et al. (2008) compared the sensitivity of several acute and sublethal methods and concluded that reproduction of the benthic copepod *Amphiascus tenuiremis* was the most sensitive test overall. Only a couple of the test endpoints evaluated (i.e., *A. tenuiremis* reproduction and *N. arenaceodentata* growth) correlated significantly with sediment chemical concentrations, and poor correspondence occurred between the toxicity endpoints and the measured indicators of benthic community condition.

Factors other than sediment-associated contaminants can affect biotic responses during exposure to sediment. When interpreting the results of toxicity tests, it is relevant to ask if toxicity was caused by the presence of contaminants of concern or if so-called modifying or confounding factors contributed to the observed response. Examples of non-contaminant factors include the testing of benthic organisms outside their tolerance ranges for particle size, overlying water and pore water salinity and ammonia or sulfides. The physicochemical characteristics of the test sediment should be within the tolerance limits of the selected test organism (Word et al., 2005). If grain size effects are suspected, a control sediment encompassing characteristics of the test sediment should be included in the test design. Ammonia is a naturally occurring compound in sediments that results from degradation of organic material. Excessive loadings of nutrients and organic carbon cause the build-up of toxic concentrations of ammonia. Procedures to eliminate ammonia as an interference in sediment toxicity tests are available (Ferretti et al., 2000, and references therein). Hydrogen sulfide occurs naturally in anoxic marine sediment. Tube-building benthic invertebrates typically circulate oxygenated water through their burrows thus reducing exposure to pore water hydrogen sulfide (Sims and Moore, 1995). Sieving and homogenization of the sediment followed by test chamber aeration procedures typical of most laboratory toxicity tests is expected to eliminate sulfide as a potential confounding factor. Some toxicity tests require the addition of food so that organisms do not become stressed and maintain their growth and development within predictable ranges during long-term exposures to test material (Bridges and Farrar, 1997; Egeler et al., 2010). However, feeding with uncontaminated food may reduce the exposure of the test organisms to sediment-bound contaminants due to selective feeding (e.g., Akerblom and Goedkoop, 2003). Because of the potential for nutrition and supplemental food to influence toxicity, consideration of nutritional requirements of test species should be carefully addressed.

6.4 *IN SITU* SEDIMENT TOXICITY TESTS

An increasing demand exists for more realistic evaluations of exposure-response relationships for biota in contaminated ecosystems (Adams et al., 2002; Burton et al., 2005a; Crane et al., 2007). Natural populations and communities encounter multiple sources of stress that are difficult, if not impossible, to replicate in laboratory-based assays. Experimental approaches include *in situ* toxicity testing, bioaccumulation and biomonitoring, artificial streams and mesocosms, the transplantation of organisms or communities among sites, and the colonization of substrates or modifications of habitats to alter contaminant exposure. Laboratory studies, by virtue of their ability to control extraneous environmental factors, allow identification of cause and effect relationships, but they lack the level of complexity and variability of the natural environment. *In situ* studies may provide some of the realism, but are nevertheless subject to experimental artifacts (Crane et al., 2007). An implicit assumption of manipulative experiments, in the laboratory or field, is that any shortcoming associated with experimental artifacts will be more than offset by the gain in control of the pertinent variables. However, under conditions of moderate contamination, the variables that most strongly affect stressor fate and effect are often difficult to identify (e.g., hydraulics vs. substrate and food availability).

This section focuses on *in situ* toxicity testing, which involves field exposure of test organisms to a potential contaminant source using either caged indicator species or the introduction of a contaminant(s) to a resident community. Most of the recent applications utilize exposure of caged individuals (using inclusions containing a single species) to transplanted or dosed sediments, or the measurement of community responses to such sediments. Often the exposure time is relatively short (days to weeks) and is limited by feeding and response-detection requirements. These *in situ* studies of various stressors and contaminant sources have used a variety of organisms, chamber devices and study designs in marine and freshwater environments, and the optimal design depends on the study objectives (Burton et al., 2005a, 2012; Rosen et al., 2012) (Figure 6.5).

Laboratory-based assays and field-based *in situ* toxicity tests provide distinct and unique strengths for teasing out stressors and their effects on aquatic ecosystems. *In situ* toxicity testing offers many advantages over laboratory-based tests. First, artifacts associated with sampling and manipulation (e.g., sieving and mixing of sediments) of the test samples is reduced in the *in situ* assays. Such manipulations may disrupt vertical contaminant gradients, thereby altering the contaminant exposure regime that organisms face in the field (Sasson-Brickson and Burton, 1991). Collection of pore water by deploying “peeper” devices has shown that sediment chemistry *in situ* differs from that of sediments obtained by traditional collection methods using grab or core sampling (e.g., Adams et al., 1992; Sarda and Burton, 1995) and that treated for use in

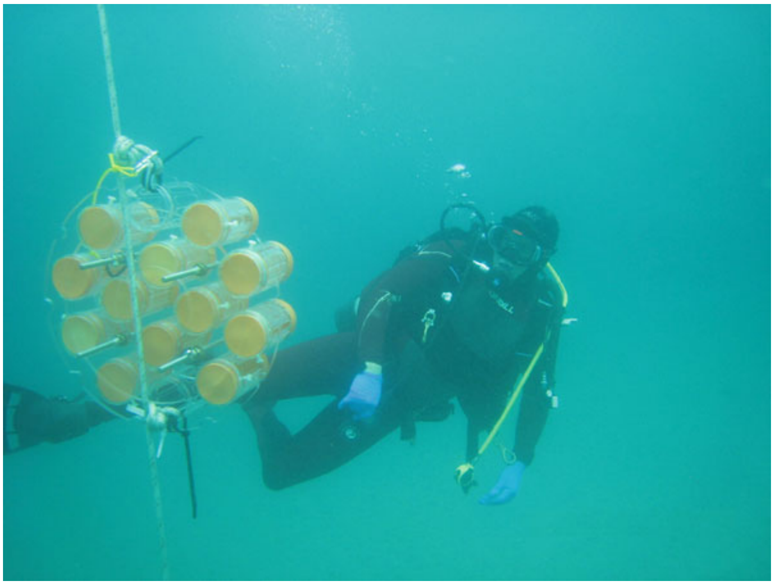

Figure 6.5. Diver-assisted field deployment of *in situ* toxicity testing apparatus.

laboratory-based organism exposures. This artifact appears to be primarily an issue with inorganic species that are either redox sensitive or of microbial origin.

Second, *in situ* toxicity tests are more realistic than laboratory tests at integrating stressors (both measured and unmeasured) and can be used to study a variety of effects including photo-induced toxicity of PAHs (interactions with sunlight, solids and contaminants), stormwater runoff (interactions of contaminants, suspended and dissolved solids, flow and food), sediment-associated contaminants and physicochemical stressors, point source effluents and contaminant gradients (Sasson-Brickson and Burton, 1991; Dickson et al., 1992; Postma et al., 1994; Jones et al., 1995; Roper and Hickey, 1995; Hickey et al., 1995; Absil et al., 1996; Ireland et al., 1996). Annelids, amphipods, bivalves and fish have been used *in situ* in toxicity and bioaccumulation studies (e.g., Monson et al., 1995; Warren et al., 1995; Rosen et al., 2012).

Third, the integration of time-varying stressors, such as those related to wet weather flow (i.e., water entering storm drains during rainstorms), pesticide runoff or tidal inundation, are best conducted with field-deployed tests allowing continual exposure, as opposed to static exposures of field-collected sediment in the laboratory. Evidence for this statement comes from studies that show that the first-flush of stormwater and pesticide run-off produce acute to sublethal responses to organisms exposed *in situ* (e.g., Maltby et al., 1995; Crane et al., 1995). Groundwater-surface water interactions are another example of a time-varying stressor to surficial sediments. Often tidally influenced, accurate assessment of potential groundwater impacts on sediment quality is unlikely using laboratory tests with sediment samples collected by grabs (Greenberg et al., 2002; Rosen et al., 2012).

Fourth, *in situ* tests may be used to identify the source and nature of the stressor by simply altering the exposure via chamber design and placement. Field methods using the TIE approach may allow the relative importance of exposure from overlying water, bulk sediment and pore water or light, suspended solids, flow velocity and predator effects to be assessed. Strategic placement of chambers at reference and potentially impacted sites can identify both natural and anthropogenic stressors. Placement along known or suspected contamination gradients can provide an exposure-response relationship when combined with physicochemical measurements.

For example, utilization of naturally occurring gradients (e.g., within and beyond a mixing zone) may facilitate an exposure-response characterization and regression analysis rather than a paired comparison (e.g., analysis of variance [ANOVA]) (Liber et al., 1992).

Fifth, *in situ* methodologies can be used to examine the responses to contaminants at the community level, and such field-based studies may be more cost-effective than mesocosm studies (i.e., the laboratory analog), which are detailed in the next section of this chapter. Typically, these experiments have been carried out by placing contaminant-amended sediments into the field (Berge, 1990; Watzin et al., 1994; Burton et al., 2005b) or carrying out contaminant dosing *in situ* (Pridmore et al., 1991; Morrisey et al., 1996).

The limitations of *in situ* toxicity tests should also be recognized. Laboratory tests control variability of non-treatment factors much better than their *in situ* analogs. Deployment of caged organisms introduces the possibility of acclimation and transportation stress. If these factors are not monitored, data interpretation may be flawed. *In situ* tests incorporate spatial and temporal variation, so the appropriate sampling design and analytical methods must be adapted to ensure there is adequate sensitivity and discriminatory power. The ease and practicality of *in situ* testing is site dependent. Deployment in intertidal or shallow water systems is easier than in deeper waters. Shallow subtidal deployment has advantages of inaccessibility to public and reduced disturbance of sediment, especially in the case of very soft mud where trampling of intertidal sites can be a major problem. However, subtidal studies may be impacted by fishing trawls (e.g., Morrisey et al., 1996). In some areas, destruction of enclosures by vandals is problematic.

A primary consideration in the design and analysis of *in situ* testing approaches is the availability of food or potential starvation associated with exposures. The bioaccumulation and toxicity of contaminants is strongly influenced by food or feeding (Postma et al., 1994; Absil et al., 1996). Laboratory feeding often cannot duplicate either the quality or quantity of food present in the field. Stimulatory or inhibitory effects in these situations will likely be most marked for filter- and/or deposit-feeding organisms (Roper and Hickey, 1995; Hickey et al., 1995).

Stressor exposures may be altered due to cage artifacts. Potential stressors include reduced flow, reduced light, altered suspended solids or food and interactions with predators, communities or the food web. Flow dynamics through screens varies and the design of enclosures may be optimized to reduce stresses for the organisms of interest. For example, it is essential in stormwater evaluations to reduce flow velocity to protect cages and organisms. This, however, increases the uncertainty concerning flow-related interactions in the receiving water (Vogel, 1994). Predator–prey effects, the concentration of suspended solids and settling within the cage may be increased or reduced depending on the enclosure mesh size. Selection of the appropriate controls and references is also important and is partially dictated by the source of sediments addressed by the study (e.g., disposal of dredged materials). In order to ascertain the existence of stressors, site controls may be needed as well as reference sites. Artificial (formulated) sediments are also useful tools for investigating effects of food and bioavailability controls in conjunction with *in situ* deployments. Because water quality conditions can also be a potential stressor, especially in enclosures, continuous monitoring of enclosure conditions (e.g., dissolved oxygen, salinity, temperature) are useful for the proper interpretation of *in situ* test data (Burton et al., 2012; Rosen et al., 2012).

Another approach to assessing sediment quality is the use of natural substrate-filled benthic colonization trays (Burton et al., 2005b; Christie and Berge, 1995). These trays are generally small plastic baskets filled with various types of sediments. The trays are then placed at a site and retrieved after about 5 weeks. These colonization trays have been used for a number of years to study benthic communities. Clements (1991) describes one of the drawbacks, especially in fresh water, of this method as being "selective for filter-feeding organisms." The advantages, however, include easier quantification due to less variability between samples and the ability to sample at the same location every time. Colonization trays also have the utility to be used in transplant studies to assess contaminant and stressor effects.

Evaluation of tissue residues of indigenous organisms serves as one of the oldest and most common assessment methods. For sediment quality assessments, fish and benthic macroinvertebrates, particularly bivalves, both have been commonly collected, and tissue levels compared to sediment concentrations. This approach has the strength of documenting exposures to site receptors, particularly for important species. A limitation of the approach, however, is the inability to separate exposure from overlying water (low and high flow) compared to that from sediments. In addition, for fish there is the confounding issue of migration and offsite exposure. Although these limitations can be dealt with by caging organisms onsite and to either overlying waters or sediments (Burton et al., 2005b), it is important to understand that natural fish mobility may alter actual exposure to contaminated sediments. *In situ* bioaccumulation techniques often include the use of caged bivalves, which tend to be sessile, as outlined in ASTM (2007b). Bivalves may be placed in mesh bags and deployed on the sediment. At test completion, the tissue of the bivalves is analyzed for the contaminant of concern.

6.5 MESOCOSM STUDIES

Mesocosms are model ecosystems ranging from small laboratory vessels to large outdoor artificial habitats such as experimental streams or ponds. Mesocosms may be seeded with specified communities (Taub, 1997) or initiated with indigenous organisms, e.g., with sediment and its natural complement of biota obtained from the field. The natural environment is simulated in mesocosms, to a greater or lesser degree, to mimic conditions typical for the habitat of interest. Factors such as toxicant concentration and frequency of application are easily controlled and many types of experimental manipulations are possible. Besides establishing risk from, or sediment quality criteria for, a toxicant, mesocosm experiments are also used to experimentally verify the causative agent of change in the field by mimicking the level and type of suspected contaminants. The investigator may note if changes in the community composition in contaminant-amended mesocosms results in a community that is similar to that at contaminated field sites. A good example is found in the study by Lee and Correa (2007) in which the effects of copper mine tailings on infauna were examined to establish copper pore water concentration as the causative agent of effects at field sites. Mesocosms are also useful in determining the mechanisms by which environmental contamination influence community structure and function. Mesocosms have been used to study stream quality *in situ*. The designs used varied depending on the type of application and cost constraints. Heckmann and Friberg (2005) placed a substrate-filled mesocosm with 16 different channels in a stream riffle. Pulse exposures of different concentrations of the pyrethroid insecticide lambda-cyhalothrin were sent through the channels and benthic effects were measured.

Although meaningful information is derived from mesocosms, they have limitations. For example, mesocosms cannot include all naturally occurring species, and at least some important predators, competitors or ecological engineers are usually excluded (Fleeger et al., 2006). Furthermore, environmental conditions cannot be perfectly mimicked in mesocosms (Carpenter, 1996) and some species are unable to maintain natural population densities in mesocosms even in the absence of toxicants (Carman et al., 1997). Such alterations in communities may confound the interpretation of toxicant effects because ecological interactions or context-dependent responses, rather than direct toxic effects, may be responsible for change under contaminated conditions. For example, some infauna decline in abundance in the absence of bioturbation (Sundelin and Elmgren, 1991). If bioturbators are not added to mesocosms or are highly sensitive to a toxicant, infauna may decline in abundance in exposure mesocosms due to a reduction in bioturbation rather than the effects of the toxicant. Adequate experimental design and controls are therefore essential so that toxicant exposed and non-exposed mesocosms can be compared to identify effects. Natural variability in benthic populations is high and mesocosm replication is essential. Another way to relate changes in density to toxicant exposure is to concurrently conduct bioassays of species from the mesocosm with the chemical of interest. Such tests would allow one to relate change in abundance to toxicant exposure or to suggest that changes in abundance are unrelated to the toxicant of interest.

6.6 TOXICITY IDENTIFICATION EVALUATION

Whole sediment toxicity TIE methods have been used to identify the causes of toxic effects in sediment quality evaluations, including ecological risk assessment and selection of remediation tools (Burgess et al., 2011). Sediment TIE is used to determine the causes of observed toxicity, generally to whole-organisms, in environmental samples. The TIE evaluation process uses a combination of whole organism toxicity endpoints and chemical manipulations that alter toxicant bioavailability or removes the toxicant from the aqueous sample or aqueous phase of the sample (Burgess et al., 2011). TIE approaches were originally developed for effluent and receiving-water samples (Norberg-King et al., 2005), leading to the development of adapted methods for use on sediment pore water (USEPA, 2007; Ho and Burgess, 2009). However, limitations associated with using pore water toxicity tests, such as those discussed above, led to the development of whole sediment TIE methods (Burgess et al., 2011). Similar to aqueous-phase TIE methods, whole sediment TIE methods accomplish toxicity reduction by either reducing contaminant bioavailability (e.g., coconut charcoal addition for sequestering hydrophobic organic compounds) or altering the form of the toxicant to a less toxic form (e.g., zeolite addition to eliminate pore water ammonia). Descriptions and discussions of the sediment TIE methods are provided in USEPA (2007), Anderson et al. (2007) and Ho and Burgess (2009). Burgess et al. (2011) discuss the status of selected innovations in whole sediment TIEs not included in earlier publications. Basic TIE structure involves three phases (Figure 6.6).

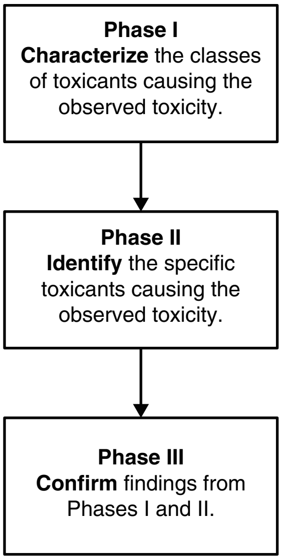

Figure 6.6. Basic structure and objectives of each phase of a toxicity identification evaluation (TIE).

Phase I employs sediment treatments effective at reducing or eliminating exposure to broad groups of target contaminants (e.g., nonionic organic chemicals, cationic metals, anionic metals, ammonia) in order to determine a general cause of toxicity. Phase II evaluation targets the identification of the specific compounds causing toxicity (e.g., PCB congeners). As the final step of the evaluation, Phase III targets confirmation of the toxic agents identified in the previous two phases. Generally, independent methods are used to perform the confirmation Burgess et al. (2011). Examples of the successful use of sediment TIE for identifying chemicals of concern at contaminated sites in North America are provided in Anderson et al. (2010) for San Diego Harbor, Brown et al. (2010) for California wetlands, Mehler et al. (2010) for the Illinois River, and Weston et al. (2013) for California Central Valley.

6.7 HISTOPATHOLOGICAL, CELLULAR AND MOLECULAR ASSESSMENTS

The term "biomarker" is usually used to mean a change in a biological response, including molecular, cellular, physiological, histopathological, as well as behavioral, that are related to exposure to, or the toxic effects of, environmental chemicals (Peakall, 1994). In contrast to survival, growth and reproduction endpoints, biomarkers address subtle changes in the biochemical, physiological, genotoxicological, immunological and endocrinological status of individual organisms, as well as behavioral perturbations (Blaise and Gagne, 2009). Biomarkers essentially indicate change from the normal status. Van der Oost et al. (2005) provide a comprehensive overview of the use of biomarkers for assessment of exposure and toxic impact to various organisms, including the description of several standard procedures.

The study by Jimenez-Tenorio et al. (2008) of damage caused by an oil spill to benthic fish *Solea senegalensis* serves as an example of the assessment of multiple biomarkers using chronic laboratory sediment exposures. Fish were exposed to sediments during 42 days and then analyzed for histopathological diseases as a biomarker of effect that allows the identification of specific target organs and cells that have been impacted in vivo. The use of histopathological parameters in fish as a biomarker for contaminant of effects has been reviewed by Hinton et al. (1992) and more recently by Meyers and Fournier (2002). Fish were also assayed for enzymatic activity ethoxyresorufin-O-deethylase (EROD) and the glutathione S-transferases (GSTs) activities in the liver as biomarkers of exposure. EROD represents a good marker in mixed function oxidase, the first mode of detoxification of many organic contaminants. Increases in EROD activity have been observed in fish and invertebrate species after exposure to contaminants (Van der Oost et al., 2005). GST is a group of detoxifying enzymes, which catalyze the conjugation of reduced glutathione with a variety of compounds, facilitating their excretion. Their induction response, usually slow, can be enhanced by nonionic organic compounds. In the study by Jimenez-Tenorio et al. (2008), a significant positive correlation between the biomarkers of exposure (EROD and GST), biomarkers of effect (histopathology) and PAHs concentration in sediments was observed.

Biomarkers have been used for monitoring the reproductive health of fish at sites with high sediment contamination. As an example, Bugel et al. (2010) used a battery of biomarkers to evaluate the reproductive health and contaminant exposure of populations of Atlantic killifish. Newark Bay killifish exhibited both molecular and morphological changes indicative of impaired reproductive health and endocrine disruption compared to a reference population.

Much of the research on biomarkers focuses on their potential use as early warning indicators that respond before measurable effects on individuals and populations occur. Research also targeted the identification of potential underlying causes of observed population- and community-level effects. Traditional biochemical or physiological biomarkers have been considered to have limited utility as ecologically relevant indicators of effects resulting from exposure toxicants (Forbes et al., 2006). The confounding effects of nonchemical influences on the biomarker response (e.g., temperature, nutritional state and reproductive condition) may limit their ability to monitor chemical effects, and must therefore be well understood (Forbes et al., 2006). In a case study in which sibling species of the deposit-feeding polychaete *Capitella capitata* were exposed to fluoranthene, Forbes et al. (2006) showed that while the analysis of biochemical changes, such as deoxyribonucleic acid (DNA) damage, can provide important insights regarding how organisms deal with toxic chemicals, using such changes to predict either exposure to or effects of chemicals at higher levels of biological organization may be highly misleading. It was concluded that the ability of biochemical biomarkers to predict higher biological level effects requires substantial mechanistic understanding of how processes at each level of organization are functionally integrated in terms of whole-organism performance, posing limitations to the use of molecular approaches.

Other studies conducted with sediment-dwelling polychaetes highlight the challenges in establishing clear cause and effects relationships between biochemical and physiological biomarkers and sediment contamination. When the sediment-dwelling *Nereis diversicolor* from sites with different levels of contamination were compared, inter-site differences were shown for size/weight relationships, energy reserves as glycogen and lipids, sexual maturation patterns, total number of oocytes per female, total and relative fecundity and burrowing behavior (Mouneyrac et al., 2010). While observing a relationship between pollutants in sediment and the observed impairments, the authors acknowledged that food availability may act as a confounding factor, interfering with effects caused by contaminants in those systems. Nesto et al. (2010) evaluated the ability of infaunal polychaetes to cope with environmental stresses, by assessing oxidative status as measured by malondialdehyde (MDA) content. Results were inconclusive, as MDA levels were likely enhanced by other exogenous and endogenous stressors besides environmental contaminants.

Advances in molecular biology are extending the use of biomarkers to the level of the genes, which, when coupled with bioinformatics, are progressing towards the development of powerful new tools to ecotoxicologists. Environmental genomics (using gene expression profiles after exposure to toxicants, also called toxicogenomics) and more recently proteomics and metabolomics, have been applied to ecologically relevant organisms to better study the hazardous effects of chemicals on individuals and ultimately, to ecosystems (Garcia-Reyero and Perkins, 2011). The use of invertebrates and fish model organisms to evaluate the impacts of aquatic pollution is in progress (e.g., Raisuddin et al., 2007; Keiter et al., 2010).

Although the availability of genomic information about non-model organisms is limited but growing, the application of such toxicogenomic techniques to a variety of organisms have the potential to become a useful tool for evaluating the effects of chemicals on levels of organization higher than the organism (Watanabe and Iguchi, 2006; Bundy et al., 2009; Santos et al., 2010). Toxicogenomics might lead to a better understanding of the causation of direct contaminant effects at field sites where mixtures of chemicals are present (Bejarano et al., 2004; Gardestrom et al., 2008). Mixture effects may be determined by using gene expression profiling to identify genomic transcriptional responses. Menzel et al. (2009) found that overrepresented functional gene categories and upregulated metabolic pathways in the nematode *Caenorhabditis elegans* varied in sediments with unique contaminant mixtures.

Keiter et al. (2010) stressed the urgent need to combine sediment assays with gene expression analysis to investigate mechanism-specific sediment toxicity. Standard approaches exist for a fish egg assay for the measurement of teratogenic and embryotoxic effects in whole sediment exposures as well as for the detection of DNA-fragmentation in single cells of zebra fish (Hallare et al., 2011). Keiter et al. (2010) describe a concerted ongoing effort to develop a suitable test system for the assessment of bioavailable toxicants in sediments, which allows, at the same time, the investigation of the molecular and cellular mechanisms of toxicity, elucidating the causality of biological effects. Such goals would be fulfilled with their plan to develop a DNA chip containing selected genes as a tool for environmental screenings.

6.8 MEASURING AND INTERPRETING BIOACCUMULATION

Bioaccumulation is defined as the net accumulation of contaminants from the sediment matrix into the tissues of exposed organisms. Bioaccumulation tests measure the movement of contaminants into the tissues of the test organism and therefore provide quantitative information concerning potential for exposure and trophic transfer at the contaminated site. The primary objective of evaluating bioaccumulation resulting from exposure to contaminated sediments is to obtain a measurement of exposure rather than effect, as bioaccumulation itself is not an adverse effect. However, the bioaccumulation of sediment-associated contaminants by sediment dwelling organisms may result in ecological impacts to the benthic organisms themselves and to pelagic predators feeding on them. In addition, health hazards to humans may ensue from the consumption of shellfish or pelagic fish that may have directly or indirectly bioaccumulated sediment-associated contaminants. Therefore, assessment of bioaccumulation is commonly included in sediment quality evaluations.

An equilibrium partitioning model, Theoretical Bioaccumulation Potential (TBP), has been used for almost three decades as a screening tool to estimate levels of benthic bioaccumulation of nonionic organic chemicals resulting from exposure to contaminated sediments. This approach is commonly used in the evaluation of dredged material proposed for open-water disposal (USEPA and USACE, 1991, 1998; Moore et al., 2005).

Organic carbon in the sediment and lipid in the organism are assumed to be the primary compartments that account for partitioning of nonionic organic chemicals. Thus, the concentration of a chemical in the sediment is normalized on the basis of its organic carbon content, and the application of a partition coefficient enables calculation of the expected equilibrium concentration in an exposed organism of stated lipid content (McFarland and Clarke, 1999). The model equation is:

$$\mathrm{TBP} = \mathrm{BSAF}\ (\mathrm{C_s}/\mathrm{f_{OC}})\ \mathrm{f_L} \qquad \text{(Eq. 6.1)}$$

where the partition coefficient is the biota-sediment accumulation factor (BSAF), C_s is the concentration of neutral organic chemical in sediment, f_{OC} is the decimal fraction total organic carbon content of the sediment and f_L is the decimal fraction lipid content of the target organism. Empirically derived BSAFs are calculated as:

$$\mathrm{BSAF} = (\mathrm{C_t}/\mathrm{f_L})\ /\ (\mathrm{C_s}/\mathrm{f_{OC}}) \qquad \text{(Eq. 6.2)}$$

where C_t/f_L is the lipid-normalized contaminant concentration in the tissues of the exposed organism and C_s/f_{OC} is the organic carbon-normalized contaminant concentration in the sediment to which the organism has been exposed.

According to ASTM (2010), the use of BSAFs as a cost-effective, first-order estimate of tissue residues of nonionic organic chemicals has great potential because of their minimal data requirements. The predicted tissue residues can then be used to determine whether bioaccumulation tests or field surveys are needed. TBP is the simplest and most easily understood model for estimating bioaccumulation; it is also subject to large degree of uncertainty. The limitations and sources of uncertainty associated with the use of the TBP model are discussed in

Moore et al. (2005) and references therein. The quality of TBP estimations is highly dependent on selecting adequate BSAF values, for which variability may reach several orders of magnitude for a given species and compound or class of compound (Tracey and Hansen, 1996; Moore et al., 2005). BSAF values are typically derived from single sediment-tissue data pairs derived from laboratory for field bioaccumulation testing or from co-located sediment and tissue collected from a field-site. A BSAF/lipid database maintained by the U.S. Army Corps of Engineers (USACE, 2012a) provides access to such values compiled from the open literature. When multiple biota-sediment data are available from a given area, BSAF values may also be calculated as the slope of a linear regression of tissue concentration and sediment concentration (e.g., Naber et al., 2007; Melwani et al., 2009).

The equilibrium partitioning theory proposes that hydrophobic organic compounds (HOCs) reach a predictable equilibrium distribution between sediment organic carbon, pore water, and biota lipid (Di Toro et al., 1991). A variety of equilibrium passive samplers absorb pore water HOCs via partitioning of freely dissolved compounds only, as described in detail in Chapter 7 and references within.

The lipid–water partition coefficient, $K_{lip-w,}$ multiplied by the pore water concentration deduced using passive samplers is assumed to predict the lipid-normalized accumulation in infaunal benthic invertebrates ($C_{t,predict}$):

$$C_{t,\ predict} = K_{lip-w} \times C_{pw} \qquad \text{(Eq. 6.3)}$$

Equilibrium passive sampler measurements are expected to provide a more accurate estimate of the dissolved (therefore bioavailable) concentration of an HCO compared to those derived using theoretical predictions based on sediment geochemistry (Chapter 7 and references therein).

Standard test methods for conducting sediment bioaccumulation tests are still under development. Guidance based on techniques used in successful studies and expert opinion, rather than exhaustive experimental comparisons of different techniques, is provided in ASTM (2010). Relatively few marine and estuarine species are routinely used in sediment bioaccumulation tests. The use of species with a high potential to bioaccumulate contaminants is desirable, as wide differences have been observed among different species (ASTM, 2010). Organisms with a minimal biotransformation capability are desirable for those contaminants that are metabolized readily, such as PAHs. Recommended test species include the oligochaete *Lumbriculus variegatus* in freshwater evaluations and the polychaete *Nereis virens* and the clam *Macoma nasuta* (Figure 6.7) in marine and estuarine evaluations.

Bioaccumulation tests are performed in the laboratory with the assumption that body residues in the test species will be similar to those of the benthos inhabiting the test sediment at the field site. A recent critical review on this subject compared and evaluated paired laboratory and field measurement of BSAFs, and concluded that the limited available data on laboratory BSAFs can provide reasonable estimates of field BSAF values as long as the limitations of the extrapolation approach are considered (Burkhard et al., 2011).

Although measurable bioaccumulation of contaminants itself is not an adverse effect, organismal-level adverse effects (e.g., mortality, decreased growth or reproduction) may occur when contaminants accumulate within the organism to levels high enough to disrupt major biochemical and physiological processes. The “critical body residue” or “tissue residue-effects approach” (TRA) for assessing toxicity based on bioaccumulated chemicals utilizes tissue residues as the dose metric when defining dose–response relationships. This approach has gained increased recognition over the last decade as a valuable tool for evaluating mixtures, developing protective guidelines and conducting risk assessments (Meador, 2006; Meador et al., 2011). Tissue residue toxicity metrics are likely to be less variable among

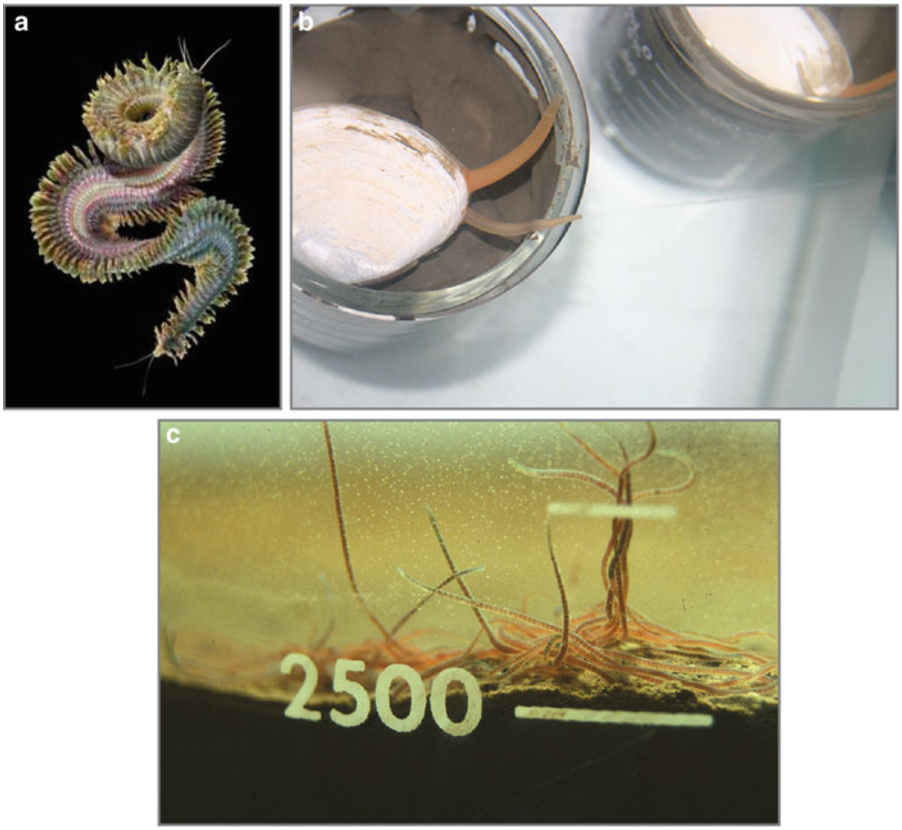

Figure 6.7. The marine polychaete *Nereis virens* (a), the marine and estuarine clam *Macoma nasuta* (b) and the freshwater oligochaete *Lumbriculus variegatus* (c).

species and environmental conditions compared to those responses expressed as a function of an ambient exposure concentration, such as the water or sediment concentration associated with the onset of the toxic effect (Meador et al., 2011) (Figure 6.8). Expressing toxicity of a chemical or chemical mixture in terms of whole-body tissue concentrations often substantially reduces variability because toxicokinetics and bioavailability characteristics for the compounds involved are incorporated in the tissue residue determinations (Meador et al., 2011). Due to complexities associated with bioavailability of contaminants in sediment leading to high spatial and temporal variability in exposure, the use of the TRA approach in sediment evaluations becomes especially appealing. Under this approach, tissue residues in sediment-exposed organisms are compared to published critical body residues for single chemicals or chemical mixtures, such as complex hydrocarbon mixtures (McGrath et al., 2005). Examples of the application of field studies that compare accumulated body burdens to levels at which effects are observed are provided in Salazar et al. (2005) and den Besten et al. (2003). The Environmental Residue-Effects Database, or ERED (USACE, 2012b) is a frequently updated compilation of data taken from the literature in which biological effects and tissue contaminant concentrations were simultaneously measured in the same organism.

For many compounds, critical body residues for a given toxicant exhibit relatively low variability among species. For those with higher variability, the use of tissue residues based on a species sensitivity distribution would be the most appropriate method for determining the critical body burden for protecting the most sensitive species (Steevens et al., 2005).

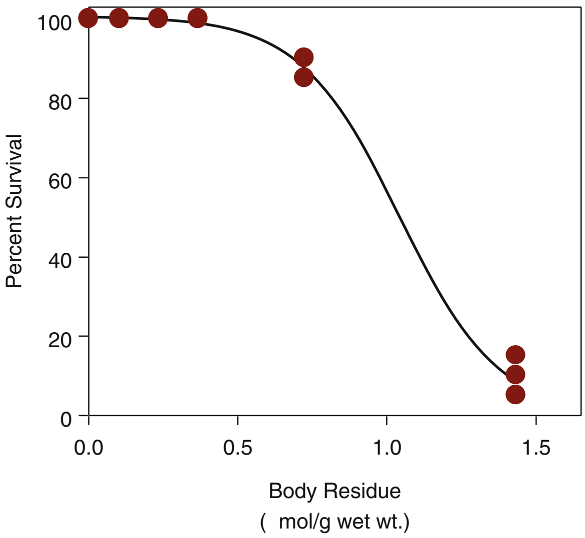

Figure 6.8. Relationship between percent survival of the freshwater amphipod *Hyalella azteca* and their dichlorodiphenyldichloroethylene (DDE) body residues (from Lotufo et al., 2000).

The application of the TRA approach for the evaluation of effects elicited by non-polar organic compounds and organometallic compounds has been critically reviewed and its strengths and limitations discussed (Barron et al., 2002; Landrum and Meador, 2002; McElroy et al., 2011; McCarty et al., 2011). For metals, the application of whole-body residues as threshold criteria associated with effects does not lead to a defensible prediction of risk to the organism largely due to the existence of metal- and species-specific physiological mechanisms that facilitate acclimation to metal exposure (Adams et al., 2011). Sappington et al. (2011) present a critical review of the application of the TRA in approach in ecological risk assessment and environmental criteria development. Those authors proposed that rather than supplanting exposure concentration-based toxicity assessments, the TRA can be highly effective for evaluating and reducing uncertainty when used in a complementary manner, as one among multiple lines of evidence in field studies.

6.9 BENTHIC INFAUNAL COMMUNITY CONDITION AS INDICATOR OF SEDIMENT QUALITY

Within the science of ecology, a community is defined as a group of potentially interacting species in a particular place and time. Community ecotoxicology is therefore the study of chemical effects on communities – their composition, relative abundance, richness, species interactions and resistance to and recovery from exposure. Benthic communities are studied because they provide a sensitive measure of change due to stressor effects, and shifts in community structure may reveal changes in ecological function. However, many aspects of the fundamental nature of communities increase uncertainty when trying to relate community change to a specific mechanism of causation, including exposure to contaminants, and the meaning of community change is often uncertain. For example, communities are rarely in equilibrium, and change over time occurs for many reasons unrelated to exposure to contaminants. In certain cases, it is difficult to quantify the relative importance of environmental contaminants and natural stressors in causing community change.

Stability is the absence of change, and change over time varies greatly among communities in response to stressors, including toxicants. Community stability is related to both resistance (the ability to maintain structure and function in face of disturbance) and resilience (the ability to recover from disturbance). It is widely believed that diverse communities are more stable; however, this theory has proven difficult to verify. Many communities do not return to pre-contaminant conditions after remediation or after chemical contamination subsides because other stressors act individually or interact with contaminants (Petersen et al., 2009) and continue to bring about change. In addition, community structure does not measure ecosystem function. Many species within a community have redundant functionality and change in species composition may not equate to a change in function. Measures of toxicant effects based on ecosystem function, rather than taxonomic affinity, will therefore likely grow in importance in the future.

Many communities are structured by strong interactions associated with predator or prey behaviors and competition, or by the presence of ecological engineers, such as bioturbators, foundation or keystone species. Tolerance to contaminants among the members of communities varies greatly, and the toxicant-induced loss (or change in behavior) of sensitive species that are strong interactors may cause unexpected effects on tolerant species. These indirect (or ecological) effects may be greater than the direct effects of a contaminant (Fleeger et al., 2003). The ability to account for such indirect effects is a strength of benthic community analysis (Fleeger et al., 2003; Shurin et al., 2006).

There are numerous ways to detect change in benthic communities including (1) univariate methods using endpoints such as total abundance or total biomass, and indices in which the numbers and relative abundances of species are reduced to a single metric (e.g., a diversity metric), (2) graphical or distributional methods that are used to graphically portray relative abundance or biomass of species (e.g., dominance curves) (Figure 6.9) and (3) multivariate methods that compare communities in terms of species biomass or more typically abundance (e.g., ordination models). These techniques offer the advantage of great sensitivity to detect community differences among reference and contaminated sites but they cannot independently assign causation. Typically, these techniques are applied to contaminated and reference sites that may be taken along a spatial gradient of toxicant intensity, from naturally or experimentally contaminated sediments in the field or from experimental mesocosms. Reference sites are necessary to detect toxicant effects; natural variability among sites is high and sites should be chosen with care to be as similar to each other as possible. Replication of reference sites is vital to better understand the influence of natural spatial-temporal variations on community composition and diversity.

Univariate and graphic models (1 and 2 above) are not species specific, and two or more communities with completely different taxonomic compositions may have the same diversity or dominance structure. Species diversity measures have been commonly used to access environmental contamination even though many factors unrelated to pollution are known to influence the number and relative abundance of species. Diversity measurement is also problematic because there are many indices and techniques available to estimate it. Diversity is typically expected to be reduced in contaminated environments either because some species are extirpated by the direct effects of toxicants or because direct or indirect effects may alter the relative abundance of species, favoring a high abundance (and therefore low evenness) of tolerant species. Dominance curves illustrate the abundance for each species by its rank in the community and measure the loss of species or the change in relative abundance at stressed sites (Figure 6.9) (Lambshead et al., 1983). Biomass curves quantify changes in the distribution of animal body size of a community for all species by rank (Figure 6.9); frequently animals are smaller in body size at stressed sites either because the average body size decreases within

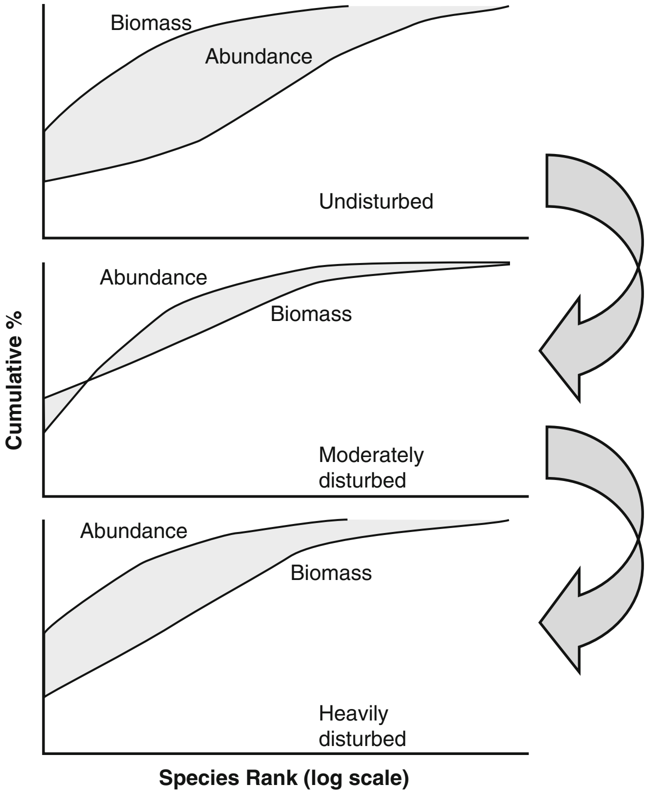

Figure 6.9. Species rank biomass and rank abundance curves plotted for all species in undisturbed, moderately disturbed and heavily disturbed communities. Disturbed communities are typically composed of a few very abundant but low biomass species compared to undisturbed communities.

species or because large-bodied species are replaced by smaller-bodied species (Warwick and Clarke, 1994). However, species diversity and distribution methods should not be used as a measure of stress or contaminant exposure alone because they do not take into account species identity as do multivariate methods.

Multivariate methods compare species composition and relative abundance patterns among contaminated and reference locations under the working assumption that exposure will cause a community change due to the direct and/or indirect effects of contaminants. One approach is classification in which a dendrogram (a tree-like diagram of relationships similar to a cladogram) of sampling locations is created based on shared species composition. The other is ordination, which is a graphical representation of relationships between reference and contaminated sites plotted on a coordinate system. In both methods, an index of similarity is first computed by comparing species composition for each pair of sampling sites. A large number of similarity indices have been developed; however, the Bray-Curtis index is most commonly used in benthic studies. Bray-Curtis has proven robust across the many studies in which it has been performed. An important characteristic is that joint absences of species in two communities have no effect on the value, putting greater weight on shared species composition. Furthermore, the value is readily interpretable (a value of 100 is achieved when communities are identical and 0 when no species are in common) as a similarity or (as its inverse) a distance measure. In effect, classification and ordination facilitate comparisons of similarities (represented as distance measures) among sampling locations under study to detect differences.

Many multivariate methods have been developed. Multidimensional Scaling (MDS) has become very popular (Clarke, 1999). Besides being very sensitive, an advantage of this non-parametric method over traditional parametric techniques (e.g., Principle Components Analysis) is that it produces sensible multidimensional relationships even when many species have zero values among locations sampled (a common observation of biological data). MDS is often coupled with analysis of similarity (ANOSIM), an analog of analysis of variance that determines if similarities differ among sampling sites using a permutation-based, hypothesis-testing approach (i.e., a probability value denotes differences among locations), and one-way and two-way crossed experimental designs may be accommodated. A popular computer program is PRIMER (Clarke and Gorley, 2006), which computes and graphically visualizes the results of many of the methods described in this section.

Population-level differences within collections from reference and contaminated sites may be analyzed by traditional ANOVA methods from estimates of density or biomass (Underwood, 1981). Additional techniques have been developed that use permutation procedures similar to ANOSIM to test for differences among populations. Permutational multivariate analysis of variance (PERMANOVA) tests the simultaneous response of one or more variables to one or more factors in an ANOVA experimental design on the basis of any distance measure. The program calculates distances (e.g., based on abundance) between each pair of sampling units to obtain a distance matrix. It then calculates test statistics according to the relevant experimental design based on re-sampling procedures. PERMANOVA may also be used as a multivariate tool to examine contaminant effects on communities using species-relative abundance and composition and is equivalent to ANOSIM under some conditions. A version of PERMANOVA is available in association with PRIMER software.

An important experimental design that is frequently used to provide strong evidence that community and population change is due to exposure to environmental contaminants is called Before-After, Control-Impact, or BACI (Stewart-Oaten and Bence, 2001). This sampling design uses reference and impacted sites that are sampled both before and after a planned disturbance (Weiss and Reice, 2005) or release of a chemical (Deegan et al., 2007). BACI can also be used to determine the success of sediment remediation. The technique employs a species-specific ANOVA model that tests for changes in species density or biomass in the before and after periods. A significant time period by treatment interaction term suggests the trajectory of change is different in reference and treatment areas. BACI may be used to compare unreplicated control and impacted sites, however the best designs include multiple control and impacted sites to better quantify natural variation. The choice of reference sites is critical but is challenging because natural variability is high. In sediments, particle size, sediment oxygen dynamics, organic matter content or other measures of contaminant bioavailability and invertebrate community structure should be used as indicators in the choice of replicate reference and experimental sites. Typically, BACI is a univariate approach applied to single-species density or biomass data, however PERMANOVA and second-stage MDS make it possible to examine community responses in a BACI format. Second-stage community analysis (Clarke et al., 2006) can be thought of as a plot of the pairwise similarities between MDS plots (e.g., of assemblage-time trajectories), which is used to illustrate interactions by ANOSIM permutation tests. The BACI approach is one of the best ways to establish a toxicant effect but it may be difficult to implement because "before" sampling is required and because environmental variation among reference and contaminated sites may be high. This is especially true in sediments that are highly variable in terms of natural conditions and stressors.

Linking population and community change to environmental contamination can be accomplished by several other means. Barbour et al. (1999) describe the dichotomy of benthic analysis as either multimetric or multivariate. The multimetric approach uses a combination of metric indices to compare the impaired site or experimental treatment to reference sites or reference treatment. A detailed list of metrics, as well as use and explanation of metric types, is presented in Barbour et al. (1999). The Ohio Environmental Protection Agency (OEPA) (1987) uses the following ten benthic metrics for calculating the Index of Community Integrity (ICI): total number of taxa, number of mayfly taxa, number of caddisfly taxa, number of dipteran taxa, percent mayflies, percent caddisflies, percent Tanytarsini tribe midges, percent other Diptera and non-insects, percent tolerant organisms and qualitative taxa. Each individual metric is given a score of 0, 2, 4 or 6 corresponding to poor, fair, good and exceptional. These scores are selected from tables created by OEPA, which were based on analysis of 232 reference sites with different levels of impairment. Once the scores are tabulated, comparisons between sites or treatments can be made. Multimetric indices such as this one not only provide insight into whether impairment exists, but can also provide evidence as to the type of impairment (e.g., organic vs. metal). Somewhat similar metrics have been developed in other habitats such as estuaries (e.g., Balthis et al., 2006). Another approach is to use sediment quality guidelines based on toxicity test results to determine which substance likely exceeds the tolerance limits for some members of a community (Long et al., 2006). Such effects-range data are generated from meta-analyses of sensitive benthic species from large databases of toxicity tests with various chemicals.

Techniques also exist to determine which environmental factors, including toxicants, may be driving community change by correlating environmental factors and community change. Canonical Correspondence Analysis (CCA) is unusual among ordination methods in that the ordination of the community data matrix is constrained by a multiple regression on its relationships to environmental variables. Because CCA uses data on the environment to structure the community analysis, CCA has been called a method for direct gradient analysis and correlations with toxicants may be inferred. An alternative approach is found in PRIMER's BIO-ENV, in which a group of samples is successively divided according to the environmental variable(s) that maximize the separation between the groups in multidimensional space. A statistical test is used to examine the significance level before each split, with division stopped when nonsignificant. This program, therefore, determines which environmental variables (including contaminants) best relate to community change.

6.10 GENETICS OF ACCLIMATION AND ADAPTATION

Organisms survive in toxic environments only if they tolerate the chemicals present in their environment. Toxicants hinder the success of sensitive individuals and species, and through selection, replace them with more tolerant ones. The resulting increase in community tolerance may be quantified through the use of short-term acute toxicity tests of a subset of community members. Such an analysis of community response is referred to as the Pollution-Induced Community Tolerance (PICT) test (Millward and Klerks, 2002). PICT may therefore be used to establish causal linkages between contaminants and effects. An increase in community tolerance compared to the baseline tolerance at reference sites suggests that the community has been adversely affected by toxicants. PICT has been used in aquatic and terrestrial environments with communities of periphyton, phytoplankton, bacteria, nematodes and insects (Rutgers, 1998; Millward and Grant, 2000), however, it does not straightforwardly address questions of sediment quality.

Many studies using various methods find that tolerance at contaminated sites increases by acclimation or adaptive genetic change (Klerks and Weis, 1987; Hummel and Patarnello, 1994; Fleeger and Carman, 2011). Adapted individuals usually experience a fitness cost associated with increased tolerance to pollutants and may be at a disadvantage in unpolluted sites. However, environmental contamination can have both positive and negative effects on genetic diversity, though through different mechanisms (Depledge, 1996). On the one hand, contamination may decrease population size (increasing the opportunity for genetic drift) or increase selection for homozygous genotypes, both of which decrease genetic variation. Indeed, some studies have clearly found reductions in genetic variation because of contamination (Street and Montagna, 1996). On the other hand, contamination may increase mutation rates at marker loci or increase selection for heterozygotes (DiBattista, 2008). The net effect of contamination on genetic variation should therefore reflect a balance between these various forces.

A cause and effect relationship between genetic variation and contamination effects in the absence of toxicity tests is suggested by the strength, consistency, timing and concordance of changes in genetic measures and contaminant exposure (see Theodorakis, 2003). Biogeographic surveys of genetic variation to understand geographic microevolutionary patterns (i.e., phylogeography) within a species may reduce spurious correlations and erroneous conclusions, but phylogeography has been underutilized to improve the understanding of relationships between contamination and genetic variation (Staton et al., 2001). Common garden experiments may also be used to determine if changes in response to contaminants are due to acclimation or genetic change (Eranen, 2008), but such experiments do not directly link contamination to a gene (or gene frequency) of interest.

Studies of contaminant-associated shifts in genetic diversity have paid less attention to another potential complication. Reductions in genetic diversity observed in some population samples from contaminated sites may represent a loss of species diversity through local contaminant-caused extinction of one or more members of a cryptic species complex rather than a within-species loss of less tolerant genotypes or haplotypes. Cryptic species are morphologically similar but genetically distinct sibling species. Such complexes occur within numerous cosmopolitan and previously well-studied invertebrates based on classical morphologically-based systematics (Knowlton, 1993; Rocha-Olivares et al., 2001). In fact, many taxa that thrive in contaminated habitats belong to complexes of cryptic species (Duan et al., 1997; Sturmbauer et al., 1999). For cryptic species to contribute to losses in genetic diversity at contaminated sites, (1) the taxa must form a cryptic species complex or be easily misidentified, (2) cryptic species must co-occur at uncontaminated sites and (3) cryptic species must exhibit different responses to contaminants such that differential mortality occurs at contaminated sites. If these three conditions are met, then apparent losses in intraspecific genetic diversity at contaminated sites may actually be the result of losses in species diversity because of a reduction in the number of cryptic species. Rocha-Olivares et al. (2004) found that a cryptic species complex of benthic copepods has variable tolerance to metals and hydrocarbons suggesting that contaminant-induced effects on cryptic species may occur.

6.11 PHYSICAL STRESS DUE TO SEDIMENTS

Both “clean” suspended and deposited sediments have been identified as a major pollutant of aquatic ecosystems, as recently reviewed in Burton and Johnston (2010). Physical impacts of increased sediment input on stream communities such as reduced light penetration, organism smothering and habitat reduction have been clearly documented (e.g., Newcombe and MacDonald, 1991). A vital physical characteristic of aquatic habitats, particularly lotic systems, is the degree of substrate embeddedness that occurs as a result of fine sediments filling the voids of interstitial spaces in the streambed. Elevated fine sediment loadings have different effects on hyporheic exchange and associated ecological processes depending on local hydrologic and geomorphic conditions (e.g., Rehg et al., 2005). Although alteration of streambed habitat is recognized as one of the most important stressors of benthic organisms, the reliability of the findings from existing embeddedness methodologies have been questioned and vary substantially in their quantification and assumptions (Style and Fischenich, 2002).

6.12 INTEGRATING LINES OF EVIDENCE FOR ASSESSING BIOLOGICAL EFFECTS

Weight of evidence (WoE) is an often used phrase in recent years in the field of environmental assessment implying that multiple types of data can be integrated to develop conclusions on dominant stressors, biological impairment or risk (Burton et al., 2002a). The term is used loosely. A review of the literature showed that it could be quite simplistic; two approaches were used and there was a best professional judgment used to decide weight. Conversely, advanced multivariate statistics have been used to define relationships with multiple lines of evidence (LoE) (Burton et al., 2002a). The process incorporates judgments about the quality, extent and congruence of the information in each LoE. Similar terminology has included "burden of evidence," "strength of evidence," or multiple "lines of evidence." Others have actually "weighted" specific data, giving some data more importance than others (e.g., a biotic response vs. a chemical concentration). This approach, however, requires subjective judgments on a weighting factor (e.g., 4x versus 1x). These widely varying applications of the WoE concept have been problematic and confusing as they vary widely in methods and degree of uncertainty (Burton et al., 2002a).

The WoE process can help determine the extent of pollution, its ecological significance, the optimal remedial options and the urgency of corrective actions. It is often used within the context of ecological risk assessments. The process incorporates judgments about the quality, extent and congruence of data. Though not always the case, it is ideal if evaluations are both observational (e.g., ecologically-based) and investigative (e.g., toxicological determinations of cause and effect in relation to chemical and/or physical stressors). This term "WoE" suggests that a level of certainty exists with the assessment's conclusion when, in fact, there may continue to be significant uncertainty in the conclusions. This misconception can impede the decision-making process that links the assessment with remediation alternatives, thereby resulting in incorrect management decisions that may be over- or under-protective of human health and resident biota.

There is no standardized method or limited regulatory guidance on how to conduct WoE studies. The Sediment Quality Triad (Long and Chapman, 1985; Chapman, 1990, 1996), the consensus-based approach of Menzie et al. (1996), considerations recommended for relative chemical rankings (Swanson and Socha, 1997) and the WoE Framework (Burton et al., 2002b) appear to be the only approaches published in the open literature that provide any degree of guidance on conducting environmental WoE assessments. However, the state of California's sediment quality objectives presented detailed discussions of using the WoE approach to establish sediment quality (California State Water Resources Control Board, 1998).

The WoE process combines facts with expert judgment. Although it is challenging, the process should include several systematic steps, which are transparent and communicated well with interested parties (i.e., stakeholders). The quality of the process can be compared to the quality of a model and its predictive capability. A model that well characterizes a system and its critical interactions, with high quality data as its foundation, and a qualified user will provide more realistic predictions. Such is the WoE process. A well-defined conceptual model with clearly defined technical question(s) and highly qualified scientists as the users will allow for a more meaningful WoE decision-making process (Peters et al., 1998). Unfortunately, all scientists have their own unique biases and expertise limitations. For this reason, the WoE process becomes increasingly credible, as statistical certainty is brought into the process, as opposed to subjective judgments of weight.

Improvements have been made to the WoE process, such as by defining a "consensus-based" approach or through the use of a variety of quantitative methods for improved integration of multiple LoE (Burton et al., 2002a; Wiegers et al., 1998). Yet, it is apparent that no single WoE study design is appropriate for all assessments of ecosystem impairment given the wide range of stakeholder concerns and resource availability and the differences in ecosystems, study design, expertise and execution. Nevertheless, a standard WoE framework that contains essential "certainty elements" is useful (Burton et al., 2002b). "Certainty" is used to describe the elements because their inclusion reduces uncertainty during each step of the process.

Typically, studies of contaminated aquatic sites have included the following LoE: (1) chemical concentrations (e.g., ambient concentrations, criteria/standards), (2) resident biota (e.g., species, populations, community indices), (3) laboratory-based toxicity responses of test organisms, (4) tissue chemical residue concentrations and (5) model predictions of fate and/or effects (e.g., contaminant transport, bioaccumulation, chemical toxicity probability distributions). The first three LoE are the most commonly used and comprise the original sediment quality triad approach (Long and Chapman, 1985), which has been widely used. On occasion, assessment approaches have included: habitat suitability, *in situ*-based toxicity, bioaccumulation and histopathology, behavioral responses, subcellular biomarker responses and ecosystem functioning. Rarely in these multiple LoE assessments have the data generated from each LoE been linked and analyzed statistically, thereby providing a strong WoE-based conclusion (Burton et al., 2002a, b).

The WoE framework is a multi-tiered assessment approach integrating many of the general methods described above (database, field and laboratory analyses) to determine the cause or causes of observed biological impairment within a study area (Burton et al., 2002b). The process may be described as a general three-tier process, beginning with a general approach defining the issues and establishing preliminary potential causal associations using available database evaluations (tier one), and refining the assessment with further sampling and analysis (tier two) guided and supplemented by the findings in the initial phase.

The WoE framework developed by Burton et al. (2002b) was for the assessments of sediment contamination and their effect(s) on ecosystem impairment. However, the framework is applicable to other ecosystem types and assessment process, such as the Metals Environmental Risk Assessment Guidance (MERAG) (International Council on Mining and Metals, 2007). Paramount factors in the application and usefulness of this WoE framework into the decision-making process are transparency and stakeholder involvement, strong scientific validity, ecological relevance with clear linkage of exposure and effects and known statistical variance in key assessment components. These issues are particularly important during the initial problem formulation and final risk characterization stages of the assessment. The methods employed in the final integration of the various LoEs will vary widely, based on the study design, types of data and availability of quality data. The quantification scenarios for analyzing the LoE will depend on the impairment, characteristics of the system and resource availability for the assessment. Ideally, LoE will be integrated in a contemporaneous study, to better link exposures with effects, but this is not possible in regional or continental, retrospective studies. More typically, the integration of LoE is to use a WoE matrix table, which is made up of the individual LoE that have already been statistically evaluated. Even when the various LoE evaluations are inconsistent with each other, reasonable WoE conclusions are still possible (Grapentine et al., 2002). Nevertheless, weighting or integrating multiple LoE into a conclusion does not remove uncertainty. It can, however, provide a sound, transparent process for reducing uncertainty by integrating the best available scientific information available at the time.

6.13 ASSESSMENT OF THE BIOLOGICAL EFFECTS ASSOCIATED WITH *IN SITU* SEDIMENT REMEDIATION MEASURES

Remedies for situations in which unacceptable environmental risk has been established at sediment sites include *ex situ* approaches (i.e., dredging, or the removal of contaminated sediment from a site) and *in situ* approaches including monitored natural recovery and passive or reactive capping (USEPA, 2005b). Dredging and excavation of contaminated sediments from a site may be desirable for multiple reasons. However, such practices can be more complex and costly than *in situ* management and also result in at least temporary adverse impacts on the aquatic community and habitat within the remediation area (USEPA, 2005b). This section focuses primarily on the requirement for appropriate understanding of the potential ecotoxicological impacts associated with current and emerging *in situ* remediation technologies prior to their full scale adoption.

Passive capping is a relatively economical remedy that consists of a covering or cap of clean, inert material (e.g., sand) on top of contaminated sediment to provide a physical barrier that reduces contaminant migration to subsequently deposited sediment and the overlying water column. Passive caps, however, do not completely prevent toxic contaminants from being released due to processes such as leaching and mechanical disturbance, and can lead to substantial alteration of the benthic community due to their required thickness (Knox et al., 2008). Reactive capping, in contrast, involves the use of capping materials that react with surficial sediment contaminants to reduce their toxicity or bioavailability (Millward et al., 2005; Reible et al., 2006; Knox et al., 2008). Reactive caps, therefore, are typically designed to provide both a physical barrier and permanent sequestration of sediment-associated contaminants. Alternatively, the reactive amendment material can be loosely mixed with the in-place sediments, minimizing physical separation of the underlying sediment and relying on the chemical reactions with the contaminants alone.

A variety of easily obtained materials show promise for enhancing sequestration of organic and inorganic (e.g., metal) contaminants in sediments. Activated carbon, for example, has been shown to be useful for reducing bioavailability of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (Millward et al., 2005; Cho et al., 2007; McLeod et al., 2007; Janssen et al., 2010), while metal sequestration has been shown to be viable in freshwater and saltwater environments with other natural materials such as apatite (rock phosphate) (Ma et al., 1993; Knox et al., 2008; Kan et al., 2011), which can irreversibly bind metals via the formation of insoluble metal phosphates (Fedoroff et al., 1999; Singh et al., 2001; Bailliez et al., 2004). Organoclays (e.g., bentonite) have been shown to remove both non-polar organic contaminants and metals from water (Alther, 2002; Knox et al., 2008). Other materials are continuously being identified and investigated for their potential applicability for in-place sediment management. Table 6.1 summarizes some recently evaluated amendments for in-place sediment remediation.

It is expected that benthic organisms (those already occurring at the remediated site or new recruits) will have direct contact with sediment amendments, which points to the need to understand not only their potential benefits, but their potential for causing adverse effects to benthic communities. Adverse effects on the biota could result from toxicity associated with the chemical activity of amendments, leaching of harmful chemicals from the amendments into the water (Knox et al., 2006), physical effects related to amendment characteristics such as texture or particle size, direct or indirect effects as a result of changes in basic water quality parameters (e.g., pH, dissolved oxygen concentration, ammonia concentration) or nutritive value of the substrate (Millward et al., 2005; Janssen et al., 2011).

Table 6.1. Examples of Recently Evaluated Reactive Amendments

Contaminants of Concern	Material	References
Divalent metals	Apatite	Ma et al., 1993; Knox et al., 2006; Knox et al., 2008; Paller and Knox, 2010; Rosen et al., 2011
	Chitin	Kan et al., 2011; Rosen et al., 2011
	Biopolymers	Knox et al., 2008; Paller and Knox, 2010
Nonpolar organics	Granular activated carbon	Millward et al., 2005; Cho et al., 2007; McLeod et al., 2007; Janssen et al., 2010; Janssen et al., 2011; Oen et al., 2012
	Powdered activated carbon	Jonker et al., 2009
	Coconut charcoal	Burgess et al., 2009
	Coal fly ash	Burgess et al., 2009
Nonpolar organics and divalent metals	Organoclays	Alther, 2002; Knox et al., 2008

Laboratory exposures with mixtures of apatite (North Carolina) and reference sediments have shown no effects on survival or growth to a range of freshwater, brackish and marine benthic invertebrates at sediment concentrations ranging from 5% to 50% by weight (Paller and Knox, 2010; Rosen et al., 2011). Organoclay (PM-199, CETCO Remediation Technologies) exposed in similar laboratory experiments at sediment concentrations ranging from 5% to 25% (by weight) also indicated inconsequential toxicity. Sediment organoclay concentrations above 25% sometimes resulted in reduced survival to the freshwater amphipod *Hyalella azteca*, but the cause of this response was not clear. Statistically reduced survival of the estuarine amphipods *Leptocheirus plumulosus* (Paller and Knox, 2010) and *Eohaustorius estuarius* (Rosen et al., 2011), however, was not observed in standard laboratory exposures at sediment organoclay concentrations of 25% and 5%, respectively. *In situ* exposures with *H. azteca*, the oligochaete *Lumbriculus variegatus* and the freshwater clam *Corbicula fluminea* revealed no reduction in survival from either apatite or organoclay, relative to control plots (Paller and Knox, 2010).

Unlike apatite and organoclays, some proposed amendments have been found to significantly alter sediment consistency, resulting in deleterious effects. *In situ* exposures with biopolymers designed for metal sequestration and applied at a 2.5% concentration (by weight) resulted in statistically significant reductions in *L. variegatus* recoveries and *C. fluminea* survival (Paller and Knox, 2010). The authors suggested that the high viscosity of the biopolymers resulted in physical entrapment or suffocation, with only those organisms not burrowing into the cap surviving. Similarly, high mortality of mysid shrimp *Americamysis bahia* exposed to sediments containing some sources of coal fly ash (proposed for PAH sequestration) may have been due to the natural tendency for fly ash to induce sediment hardening, which may have limited interaction with the sediment, and resulting in stress to the test organisms (Burgess et al., 2009). Many of the fly ash samples, however, served as a source of black carbon that sequestered PAHs and reduced toxicity with increasing concentration in contaminated sediment. It should also be noted that physical alteration of the sediment due to materials such as biopolymers and fly ash might result in organism avoidance of amended sites, which could in turn minimize bioturbation and prolong cap life.

Activated carbon has received considerable attention recently due to its potential to effectively sorb nonpolar organic contaminants including PCBs and PAHs. Substantially reduced uptake has been observed in bioaccumulation studies with both amphipods (*L. plumulosus*) and polychaetes (*Neanthes arenaceodentata*) (Millward et al., 2005; Janssen et al., 2010, 2011). Millward et al. (2005), however, reported a 50% reduction in polychaete growth in 28-day exposures to PCB contaminated sediment amended with granular activated carbon (GAC) at a concentration of 3.4% dry weight, relative to unamended contaminated sediment. The authors suggested that the ingested GAC likely reduced essential nutrient uptake due to its sorbent properties. In contrast, Janssen et al. (2010) did not observe an adverse growth response to the same species at the same GAC concentration from sediments at the same site. Janssen et al. (2010), however, did report a threefold reduction in *N. arenaceodentata* lipid content when exposed to 3.4% GAC relative to unamended treatments, and encouraged further studies to elucidate the cause of that reduction.

Unintended water quality changes associated with experimental reactive amendments has also been reported in laboratory studies, resulting in either deleterious or enhancement effects. Some of the fly ash exposures conducted by Burgess et al. (2009) also resulted in increased pH in the overlying water by as much as 1 pH unit. Although the changes in pH alone were not expected to contribute to toxicity, pH-dependent toxicants such as ammonia were of concern, with overlying water unionized ammonia concentrations frequently exceeding thresholds for both mysids and amphipods.

Ammonia-induced toxicity was also observed in experiments that evaluated chitin as an amendment for potential sorption and stimulation of sulfate reducing bacteria for metal sequestration (Rosen et al., 2011). In that study, sediment chitin concentrations of 2.5% (dry weight) resulted in ammonia concentrations that exceeded thresholds for *E. estuarius* and juvenile sheepshead minnows, *Cyprinodon variegatus*. Ammonia is a normal breakdown product of chitin, a polysaccharide that can serve as a food source for aerobic and some anaerobic bacteria. Large bacterial blooms observed in the exposure chambers likely served as a food source for *N. arenaceodentata*, and no effects on survival and enhanced growth in the presence of chitin-amended sediments were observed.

Many of the above summarized responses to experimental reactive amendments may or may not be present under actual field conditions. As discussed earlier in this chapter, *in situ* conditions at the study site may result in differences in contaminant bioavailability and organism response relative to *ex situ* studies. Janssen et al. (2011) reported lower tissue PCB concentrations in polychaetes exposed to GAC-amended sediment (relative to unamended sediment) in the field when compared to results from exposures conducted *ex situ*. The difference was attributed to deposition of unamended PCB contaminated sediment into the *in situ* exposure chambers containing amended sediment, providing a mixed diet in the field and reducing the beneficial effect of the GAC treatment. Differences in food availability and lower ingestion rates in the field hypothesized using a biodynamic model were also noted. New approaches (e.g., integrated *in situ* toxicity and bioaccumulation strategies) are required to improve the assessment of amendment performance without compromising the integrity (e.g., repeated coring, grab sampling) of the treatment. Passive samplers have proven to be a valuable tool for use in field assessment of cap performance (Lampert et al., 2011). The integration of passive samplers and *in situ* bioassays providing multiple lines of evidence has been recommended for the assessment of in-place sediment remedy effectiveness (Rosen et al., 2012).

6.14 CLOSING REMARKS AND PATH FORWARD

Multiple assessment tools exist to characterize sediment quality. When multiple LoE are used in carefully constructed study designs, wedding exposure and effects characterizations, along with measures of spatial and temporal dynamics, then uncertainty in the decision-making process can be reduced. In most cases, the key LoE for sediment quality assessments include: measures of toxicity and bioaccumulation, physicochemical site characterization (including habitat) and benthic macroinvertebrate community characterization. The more these LoE link field exposures and effects, the less uncertainty associated with the extrapolations and sample manipulations. These characterizations and linkages must consider coexisting stressor effects, such as from habitat, flow, suspended solids, sedimentation/embeddedness, nutrients and invasive species (Burton and Johnston, 2010). These "non-contaminant" stressors often dominate the ecosystem responses and therefore, factor heavily into any decisions on remediation and its subsequent effectiveness and restoring beneficial uses and ecosystem services. Perhaps the most important and challenging research needs to be addressed are related to our ability to better link exposure with effects in the context of multiple stressors and spatial/temporal dynamics of the stressors and receptors. Nevertheless, robust tools exist to reduce those uncertainties and when combined with stakeholder input will allow for effective management decisions.

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CHAPTER 7

ASSESSING BIOAVAILABILITY OF HYDROPHOBIC ORGANIC COMPOUNDS AND METALS IN SEDIMENTS USING FREELY AVAILABLE POREWATER CONCENTRATIONS

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7.1 INTRODUCTION

Sediments are the ultimate sinks for most hydrophobic organic compounds (HOCs) and metals in aqueous systems. These contaminants can then pose a long-term risk to organisms that dwell or interact with the sediments or to higher organisms through the food chain. The starting point for the assessment of sediment toxicity or effects is bulk contaminant concentrations normalized by sediment mass (Chapman et al., 1999). The values are relatively easy to obtain and are useful as an initial screening tool to assess contamination. These values do not take into account important properties of the sediment, such as the concentration of sulfides, iron oxides, and organic contents, which greatly affect metals availability in sediments, or organic sequestering phases, which can reduce organic chemical availability. Hence, the toxic level of contaminants derived from bulk sediment loading has been proven to vary significantly among different sediments (Di Toro et al., 1990; Chapman et al., 1999).

Many studies have demonstrated that the effect of the soil or sediment-associated contaminants on the organism is not controlled by the total concentration of the contaminant, but instead by the fraction that is biologically available (Meador et al., 1995). A review of a number of studies (Di Toro et al., 1991) found that bulk sediment concentrations do not reflect actual exposure of biota and, therefore, provide an unreliable predictor of effects. Simply stated, the organism response, e.g., toxicity or the extent of bioaccumulation, often appears to be less than what would be expected based upon the entire mass of contaminants in the sediment. Better understanding of bioavailability processes and indicators of the contaminants that are available and/or mobile can lead to better and more protective risk estimates (NRC, 2003).

Bioavailable contaminants can be defined as those that directly relate to observed organism effects and may only be a small fraction of the total contaminant concentration. The reduced bioavailability is usually associated with physical or chemical sequestration mechanisms that are not normally or easily overcome by environmental processes including digestion in deposit-feeding organisms. Partitioning into organic phases is the principal mechanism dictating bioavailability for hydrophobic organic compounds (HOCs) while chemical speciation is the primary overriding factor for bioavailability of metals (Maruya et al., 2011). The goal of this chapter is to explore techniques that provide a better indication of the actual risks posed by sediments than simply measuring total concentration. Because the definition of bioavailability used here is based on observed effects in organisms, biological assays represent perhaps the

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best indicator of bioavailability. The challenges to conduct and interpret such assays are the subject of other chapters. The focus of this chapter is on chemical measures of availability; in particular measurements of the freely available concentration of the contaminants in porewater and compare its ability to predict effects in organisms, particularly bioaccumulation or toxicity in deposit-feeding benthic organisms. By focusing on deposit-feeding benthic organisms the emphasis is on exposure and effects that are directly linked to contaminant availability. For example, species that live and feed in the water column are exposed only after mass transfer from the sediment surface or via the food chain, the rate of which may be controlled by physical processes that are not strongly linked to intrinsic availability in the sediments.

Biota-sediment accumulation factors (BSAF), as outlined in Chapter 6, have been used to provide an indication of bioavailability under specific environmental conditions. Environmental factors such as the rate of mass transfer between sediments and water, organism factors such as metabolic processes and the route and rate of uptake, and sediment- and contaminant-specific factors such as sequestration of contaminants, however, lead to BSAFs that are site- and species-specific and subject to substantial uncertainty (Lake et al., 1990; Trimble et al., 2008). As an alternative, abiotic methods using a variety of extraction tests had also been used to measure the readily extractable fraction to mimic bioavailability of HOCs and metals. Dean and Scott (2004) summarized the extraction approaches for assessing sediment bioavailability of HOCs, which includes sequential extraction with different organic solvents, supercritical CO_2 extraction, subcritical water extraction, solid phase sorbents (e.g., TenaxTA, XAD-2) extraction, solid phase micro-extraction (SPME), extraction with membranes dialysis, extraction with gases (gas purging), extraction with temperature (thermal desorption), and in vitro extraction (gastrointestinal). Extraction methods have also been proposed for metals. Dilute acid extractable metals could be a good indication of the bioavailable fraction of metals in sediments because some benthic organisms are ingesting particles and leaching metals by mildly acidic gut fluids (Chen and Mayer, 1999; Lee et al., 2000). Extraction tests for metals include passive extraction with water and neutral salt and aggressive extractions with acids, e.g., 0.1 molar (M) hydrogen chloride (HCl) and disodium ethylenediaminetetraacetate (EDTA) (NRC, 2003).

Different indirect methods as described in the previous paragraph may give different estimates of bioavailability. A more realistic approach would be a direct measurement of exposure concentrations or the bioavailable fraction of a contaminant (Van Der Heijden and Jonker, 2009, cited from Reid et al., 2000). Ideally, a direct measure would allow *in situ* measurement of bioavailability without resorting to extraction or other processing of sediment. There is growing evidence showing that sediment porewater concentration of HOCs, particularly the freely dissolved porewater concentration, represents the highly bioavailable fraction and thus is a good indicator of bioavailability (McElroy et al.,1989; Kraaij et al., 2003; Jager et al., 2000; You et al., 2007). Moreover, free metal ion activity appears to be a better estimator of metal bioavailability and toxicity in soil and sediment (Lofts et al., 2004).

Thus, freely dissolved sediment porewater concentrations are increasingly used as an indication of a highly bioavailable fraction of both metals and organics. The basis for such a conclusion appears to be the relatively static nature of many contaminated sediment deposits, which results in a quasi-equilibrium between organisms, porewaters as a highly bioavailable phase, and solid phases that contain both available fractions and sequestering phases or unavailable species. Contaminants in a sequestering phase may only be available under dynamic conditions that cause release of the contaminants, e.g., oxidation of low availability sulfide phases upon resuspension of sediments (Hong et al., 2011a). Under static conditions, however, the *in situ* measurement of porewater concentrations of contaminants may provide a good indication of available contaminants to benthic organisms even if the route of exposure is via other means, e.g., sediment ingestion. The porewater burden of contaminants may not be the source of organism exposure but may indicate the available contaminants and magnitude of that exposure. This concept is explored further in the next section. Subsequently, assays of freely available contaminants in porewaters will be described and their ability to predict organism effects will be summarized. These assays are of two basic types: prediction of porewater concentration on the basis of models of equilibrium partitioning and direct measurement of porewater concentration; both will be summarized.

7.2 SEDIMENT POREWATER CONCENTRATIONS AS INDICATOR OF BIOAVAILABILITY

7.2.1 Hydrophobic Organic Compounds

A study assessing the effect of polycyclic aromatic hydrocarbons (PAHs) on mortality of amphipods (*Hyalella azteca*) provides a good illustration of the relationship between porewater concentrations and toxicity of HOCs (Hawthorne et al., 2007). Bulk sediment concentrations yielded a wide range of toxic response results, making prediction of bioaccumulation unreliable (Figure 7.1a). Extraction approaches improved the ability to estimate sediment toxicity but the best predictor of sediment toxicity was measured porewater concentrations (Figure 7.1b). Porewater measurements show a more well-defined and narrower range of toxicity. Similarly, Lu et al. (2003, 2006) observed a strong correlation ($r^2 = 0.90$) of bioaccumulation of PAHs by oligochaete worms with truly dissolved porewater concentrations from both laboratory spiked sediments and field sediments from the Anacostia River, Washington, D.C. Truly dissolved concentrations are thermodynamically available for partitioning to other phases, e.g., organism lipids and sediment organic carbon, while total porewater concentrations may also include colloidally and fine particulate bound contaminants.

With the ability to more easily measure truly dissolved porewater concentrations via the methods that are discussed herein, additional support for porewater concentration as a predictor of bioavailability has come available. Hereafter, porewater concentration refers specifically to truly dissolved porewater concentration and will be denoted by the symbol, C_{pw}. Kraaij et al. (2003), You et al. (2006) and van der War et al. (2004) have found porewater concentrations to be a good indicator of bioaccumulation in soil and sediment organisms. The ratio of bioaccumulation in tissues (C_t, lipid normalized) of HOCs to porewater concentration, C_{pw}, C_t/C_{pw}, has been found to be approximately given by the octanol-water partition coefficient (K_{ow}), suggesting that bioaccumulation, even via active uptake through ingestion, achieves an equilibrium equivalent to that suggested by passive uptake from the porewater. Experiments supporting this conclusion include the following:

- In Anacostia River (Washington, DC) sediments, the bioaccumulation of PAHs and polychlorinated biphenyls (PCBs) in a deposit feeding freshwater oligochaete, *Ilyodrilus templetoni*, was well predicted by the product of porewater concentration (C_{pw}) and compound octanol-water partition coefficient K_{ow}, (as reported in Lu et al. (2011)). The measured ratio of the lipid- normalized tissue concentration to $K_{ow}C_{pw}$, was 1.08 ($r^2 = 0.76$). The data is shown in Figure 7.2.
- In a sediment from New Bedford Harbor (New Bedford, Massachusetts) diluted with a fresh-water sediment from Brown Lake (Vicksburg, Mississippi), the bioaccumulation of PAHs and PCBs in the freshwater oligochaete, *Ilyodrilus templetoni*, was also well predicted by the product of porewater concentration and K_{ow} (Lu et al., 2011). The use of the sequentially diluted sediment allowed evaluation of a much larger range of

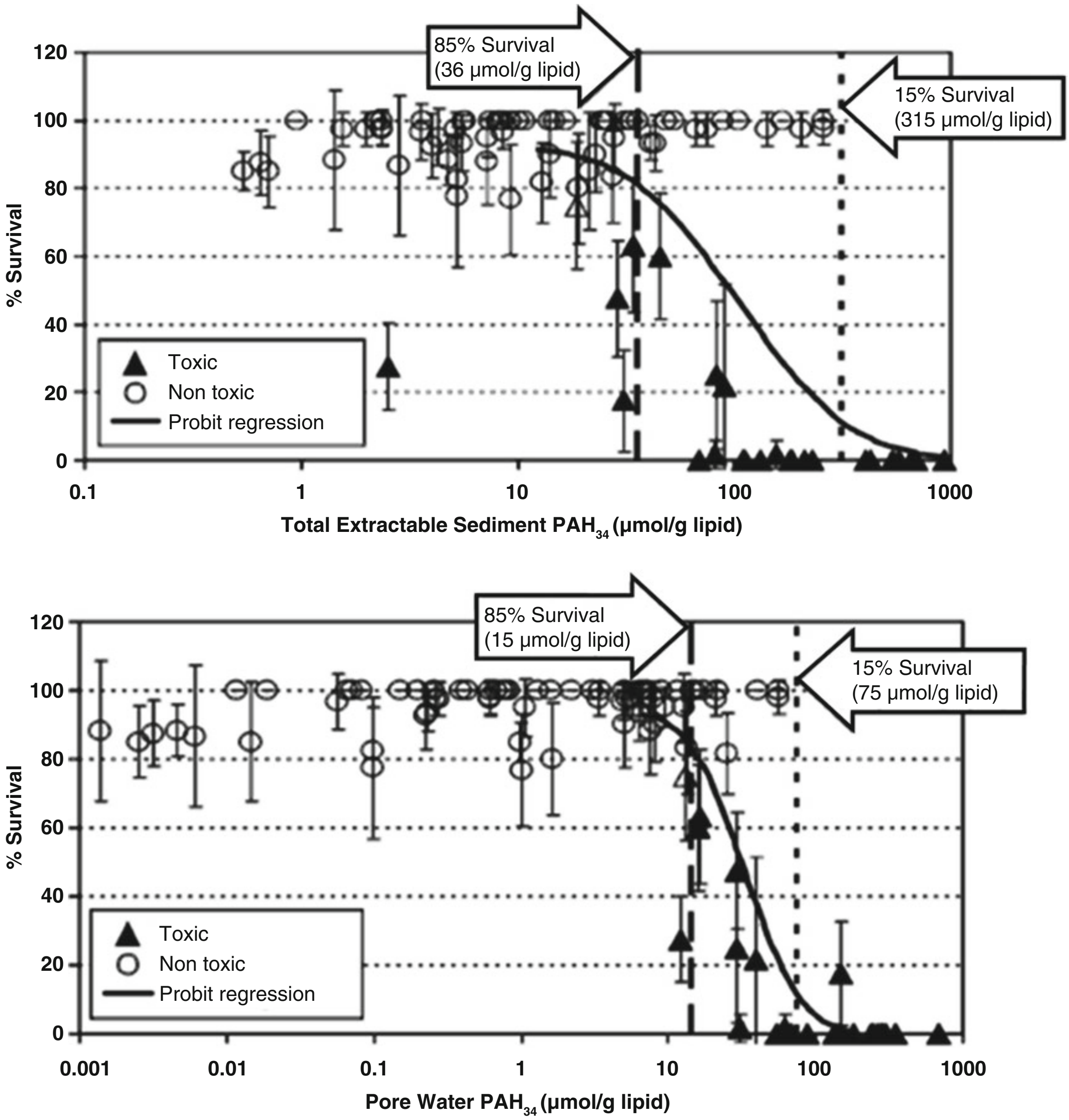

Figure 7.1. Amphipod survival correlates with bulk sediment concentration and sediment pore-water concentrations (reprinted with permission from Hawthorne et al., 2007. Copyright 2007 American Chemical Society).

sediment and porewater concentration than could be evaluated using the fresh sediment. In addition, the dilution with freshwater sediment allowed use of the freshwater oligochaete in the bioaccumulation testing. The measured ratio of the lipid-normalized tissue concentration to $K_{ow}C_{pw}$ was 1.24 ($r^2 = 0.76$).

- In sediment from Hunter's Point, California, the bioaccumulation of PCBs in the marine polychaete, *Neanthes arenaceodentata*, was also well predicted by the porewater concentration with a lipid-normalized tissue accumulation divided by $K_{ow}C_{ow}$ equal to 1.17–2.21 ($r^2 = 0.7$–0.76) as reported in Gschwend et al. (2011). The range of slopes primarily reflects uncertainty in porewater concentration measurements in that work.

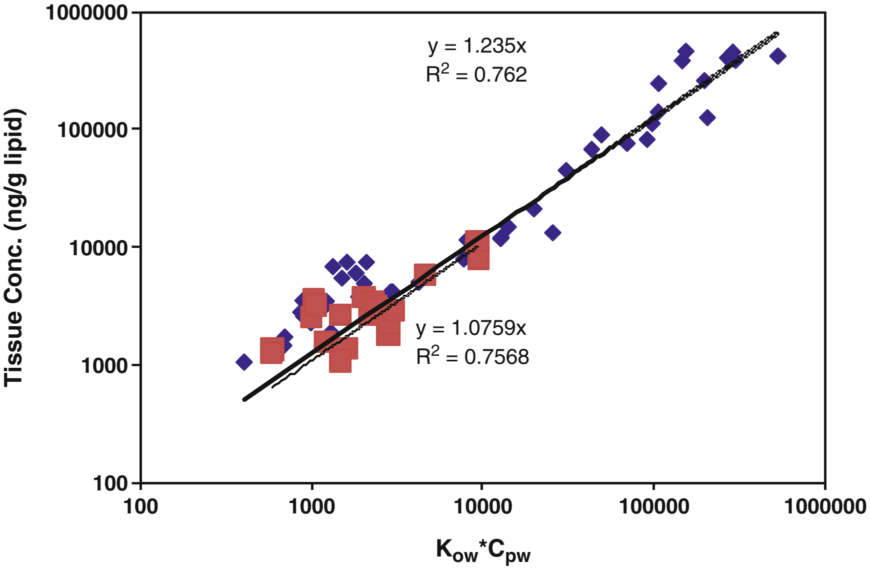

Figure 7.2. Comparison of measured tissue concentrations (lipid normalized) with predictions from porewater concentrations: Anacostia river sediment (*solid square*), sequentially diluted sediments (*solid diamond*). *Solid lines* represent best fit of data ($C_{t,\ measured} = 1.08\ C_{t,\ predicted}$, $r^2 = 0.757$ (Anacostia), $C_{t,\ measured} = 1.24\ C_{t,\ predicted}$, $r^2 = 0.762$ [sequential]). The *dashed line* represents the 1:1 relationship (Lu et al., 2011).

These studies all included deposit feeding organisms that process many times their own weight in sediment every day and thus are likely to attain a state of quasi-equilibrium with the sediment and porewater. Organisms that have less intensive interactions with the sediments are likely to exhibit less bioaccumulation on a lipid normalized basis. Although PAH metabolism is often an issue in oligochaete bioaccumulation studies, the organism *Ilyodrilus templetoni* used in the Anacostia River and sequential dilution experiments was shown to have limited metabolism for PAHs (<15%) (Lu, 2003).

Freely dissolved porewater concentration is also the basis behind the equilibrium partitioning sediment quality benchmarks used as a guideline for protecting benthic organisms in PAH-contaminated sediments (USEPA, 2004). In this approach, porewater concentrations of concern are used to estimate equivalent bulk solid concentrations through equilibrium partitioning (Di Toro et al., 2000; Di Toro and McGrath, 2000). The downfall of the approach, however, is that predictions of equilibrium partitioning do not normally account for the increased sorption due to strongly absorbing organic phases, e.g., black carbon phases (Ghosh et al., 2000), while direct measurement of porewater concentration does reflect the partitioning to strongly sorbing phases.

The conceptual model of uptake from porewater or from digestive juices in the gut of a deposit feeder is shown in Figure 7.3. Uptake of HOCs into deposit feeding organisms involves a two-stage partitioning processes: partitioning into the fluid phases of either porewater or gut juices and partitioning between the fluid phases and the organism lipids. Digestive fluids and porewater both represent intermediate phases for contaminants after desorption from sediment particles. At equilibrium, the four phases – sediment particles, organism lipid, sediment porewater, and organism digestive fluid – are at equilibrium with each other, and equilibrium between any two of these phases can be used to define overall equilibrium as long as the organism cannot effectively process the organic matter responsible for sequestration of

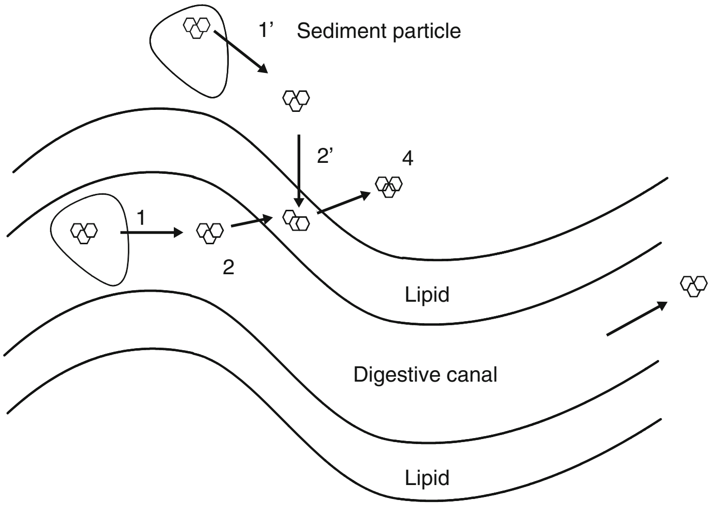

Figure 7.3. Two-stage processes for uptake of sediment-bound organic contaminants into the lipid of the organisms. K_{sw}, sediment-water partition coefficient, and K_{lw}, lipid-water partition coefficient.

the HOC in the sediment and cannot rapidly metabolize the contaminants. In particular, bioaccumulation of partitioning HOCs can be indicated by partitioning between the sediment porewater and organism lipids even though the primary route of uptake is from sediment ingestion. Effectively, bioaccumulation can be predicted by porewater concentrations and lipid-water partition coefficients, or a BCF, even if uptake is via active processing rather than simply passive partitioning. As indicated by the examples above, BCF is well-correlated with K_{ow}. That is:

$$C_{t,\,predict} = BCF^{*}C_{pw} = K_{ow}{}^{*}C_{pw} \qquad \text{(Eq. 7.1)}$$

Please note that the observed relationship between porewater concentration and organism bioaccumulation would not necessarily be expected under dynamic conditions such as fast groundwater upwelling rates or rapid contaminant degradation when sediment, porewater and organism may not be in a state of quasi-equilibrium.

7.2.2 Metals

Porewater concentrations of metals have also been linked to toxicity of benthic organisms. Figure 7.4a shows organism mortality with respect to total cadmium (Cd) concentrations in sediment (Di Toro et al., 1990). Three sediments with different sulfide contents were spiked with a range of dissolved Cd concentrations and mortality of test organisms were evaluated in the sediments. Multiple dose–response curves were obtained from total Cd concentrations in sediments indicating total Cd correlated only weakly with the observed toxicity. During the experiments, free Cd activities in sediment porewater, $Cd^{2+}{}_{(aq)}$, were measured by ion-selective electrode. From the measurement, the multiple dose–response curves were collapsed into one curve based on free metal ions activity in sediment porewater, which is shown in Figure 7.4b. More interestingly, the overlapped single dose–response curve followed the dose–response curve acquired from water exposure only toxicity tests. This finding suggested that porewater

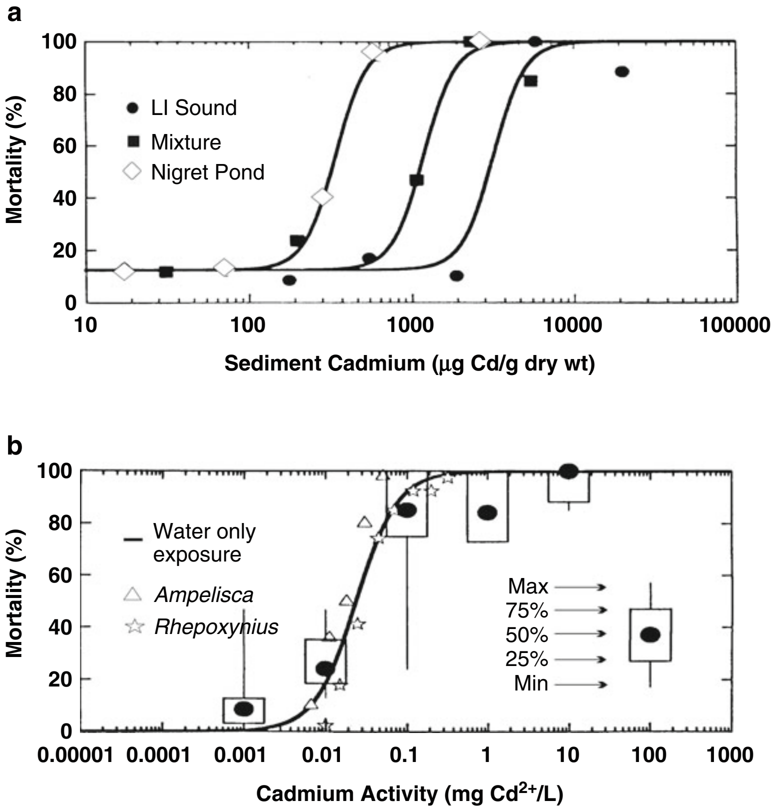

Figure 7.4. Organism mortality (%) versus sediment Cd concentration on a dry-weight basis (a) for three different sediments. Organism mortality (%) versus porewater Cd activity for the same three sediments and for water only exposures (b) (USEPA, 2005).

free metal ion concentration could be a better indicator than bulk solid concentration in predicting the bioavailability and toxicity of metals in sediments. The hypothesis leads to an equilibrium partitioning model (EqP), which estimates the presence of free metal ions and suggests a guideline for metals toxicity in sediments (USEPA, 2005).

7.3 ASSESSING BIOAVAILABILITY WITH EQUILIBRIUM PARTITIONING THEORY

7.3.1 Equilibrium Partitioning for HOCs

It has been demonstrated in Section 7.2 that porewater concentration is a good indicator of bioavailability. This has been recognized by the development of equilibrium partitioning sediment guidelines based on defining bulk sediment concentrations that relate to toxic water concentrations (USEPA, 2004) although, as indicated previously, the use of predicted rather than measured porewater concentrations limits the applicability of the approach. For HOCs, sediment organic carbon is the assumed primary sorption site and sorption is normalized by the fraction organic carbon (f_{oc}) and an organic carbon normalized sediment-water partition coefficient (K_{oc}) ($C_{pw-pred} = C_s/f_{oc}/K_{oc}$). K_{oc} is typically estimated from correlations with K_{ow}. For example, $\log K_{oc} = \log K_{ow} - 0.21$ (Karickhoff et al., 1979) has been widely used to estimate K_{oc} for PAHs. These generic models do not consider the characteristics of the carbon phase and its effect on the partition coefficients and often overestimate the porewater concentrations in actual sediments. The predictions for PAHs by equilibrium partitioning could be 100-times higher than the measurement values (Lu et al., 2011; TerLaak et al., 2006). Although biphasic models were proposed to account for the strong sorption by sequestering carbon phases (Kan et al., 1998; Accardi-Dey and Gschwend, 2002), the uncertainty in determining the partition coefficients to these phases could introduce great errors in estimating the freely dissolved porewater concentrations (Ghosh et al., 2000; Jonker and Keolmans, 2002). Direct measurement of the porewater concentration in the sediments can overcome these limitations and provide a more direct link between water toxicity concentrations and sediment quality.

7.3.2 Equilibrium Partitioning for Metals-AVS/SEM Model

In anoxic sediments, complex biogeochemical reactions often produce reactive sulfide minerals (Rickard and Morse, 2005) that are believed to control the availability of metals. Iron monosulfide is one of the key partitioning phases controlling metal speciation since the phase could precipitate dissolved free metals to insoluble metal sulfide rapidly as follows (Di Toro et al., 1990):

$$M^{2+}{}_{(aq)} + FeS_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + MS_{(s)} \qquad \text{(Eq. 7.2)}$$

where $M^{2+}{}_{(aq)}$ represents dissolved free metal ions such as Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}; $FeS_{(s)}$ represents iron monosulfide; $Fe^{2+}{}_{(aq)}$ is dissolved ferrous iron; and $MS_{(s)}$is precipitated metal sulfide. As a result, sediments containing more reactive sulfides (e.g., iron monosulfide) than metals would have low porewater free metal ion activity ($M^{2+}{}_{(aq)}$) and metals in sediments would be less bioavailable and toxic because the metals would be bound in insoluble metal sulfides.

Due to the complexities and difficulties in extracting reactive sulfide minerals, operationally defined acid volatile sulfide (AVS) has been used to indicate total sulfide binding. AVS represents sulfides that are evolved from acidified sediment by adding 1 M HCl and includes dissolved sulfides (H_2S, HS^-, S^{2-}), amorphous iron monosulfide ($FeS_{(s)}$), mackinawite ($FeS_{(s)}$), and greigite ($Fe^3S^4{}_{(s)}$). The 1 M HCl also dissolves almost all metals and evolves sulfides from $CdS_{(s)}$ and $ZnS_{(s)}$, but partially from $CuS_{(s)}$ and $NiS_{(s)}$ (Allen et al., 1993; Cooper and Morse, 1998). At the same time, the total metals, such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, that are dissolved in 1M HCl are defined as simultaneously extracted metals (SEM) (Allen et al., 1993). Incomplete recovery of Cu^{2+} and Ni^{2+}could underestimate the potential availability of the metal sulfides, but the metals that are not dissolved from 1 M HCl are not likely to be available (USEPA, 2005).

There have been extensive studies that correlate the toxicity and the quantitative differences between AVS and SEM in a variety of anoxic sediments (Di Toro et al., 1990, 1992; Ankley et al., 1996; Berry et al., 1996, 2004; Hansen et al., 1996; Liber et al., 1996) and these efforts lead to the AVS/SEM model (USEPA, 2005). The model assumes if SEM $\leq$ AVS, then all the extracted metals are likely to present as $MS_{(s)}$ and no toxicity would be predicted. However, if SEM $>$ AVS, then toxicity may or may not occur and other binding phases in solid become important. Figure 7.5a, b supports this hypothesis. The paradigm could be viewed, however, as a tool to indicate when there are significant quantities of dissolved metals in the porewater. When AVS $>$ SEM, the presumption is that the metals are not dissolved but present only as the essentially insoluble sulfides and little toxicity is observed as a result.

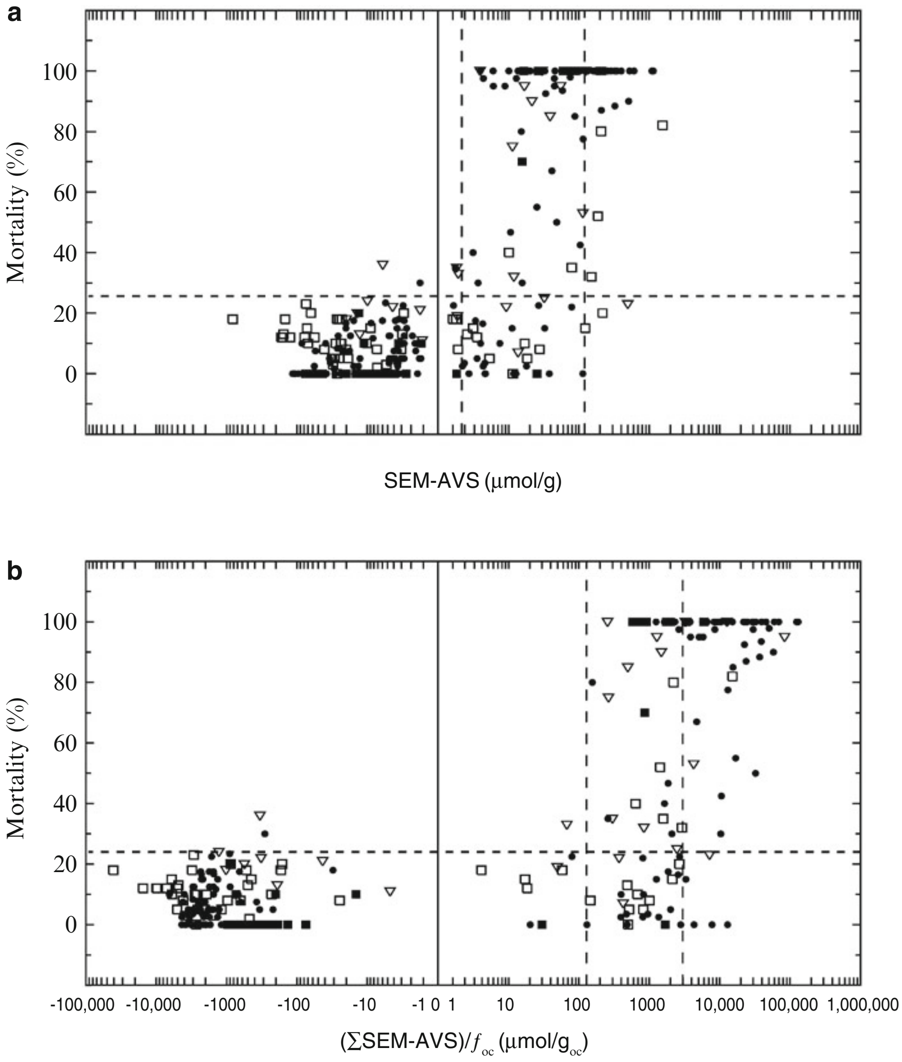

Figure 7.5. Percent mortality versus (a) SEM/AVS and (b) (SEM-AVS)/foc showing effect of organic carbon normalization on SEM/AVS (USEPA, 2005). The data were from laboratory experiments using spiked freshwater and saltwater sediment and from field experiments in freshwater and saltwater. *Vertical dashed lines* are the 90% uncertainty bound limits.

7.4 BIOTIC LIGAND MODEL (BLM) TO ESTIMATE BIOAVAILABILITY OF METALS

The equilibrium-based AVS and SEM model has been successful in predicting metals toxicity in anoxic sediments. The model may not be applicable to sediments where low AVS is expected, i.e., aerobic surficial sediments, and where other mineral and organic phases may control metals availability. In aerobic sediments, the idea that dissolved metals will be precipitated as insoluble metal sulfides is not applicable due to the absence of iron sulfides, which are rapidly oxidized by oxygen with a half-life of a few hours (Burton et al., 2006; Hong et al., 2011a). Thus, suspended and surficial sediment may exhibit greater dissolved metal toxicity and bioavailability. This can also be problematic in the entire biologically active zone of sediments because of localized oxidized microenvironments around burrows of indwelling organisms (e.g., Reible and Mohanty, 2002). Moreover, fluctuations in pH, salinity, and O_2, which are commonly observed in estuarine environments, complicate characterization of the surficial sediments and metals' adverse effect on aquatic life (Chapman and Wang, 2001; Hong et al., 2011b). To predict metal toxicity at the surficial sediments, a more quantitative model is necessary and the Sediment Biotic Ligand Model (S-BLM) has been developed for that purpose (Di Toro et al., 2005).

The bioavailability of metals in water only exposures was initially understood using the Free Metal Ion Activity Model (FIAM) (Morel, 1993), which assumes free metal ion activity is directly related with the toxicity of metals to aquatic organisms rather than total dissolved metals, which include ligands complexed metals. In the BLM (Di Toro et al., 2001), a generalization of the FIAM, toxicity is assumed to occur when the concentration of metal bound to the biotic ligand exceeds the critical body burden for that metal and organism. The metal cation (M^{2+}) complexes to inorganic anions (e.g., OH^-, Cl^-) and dissolved organic carbon (DOC) as well as competes with other cations (e.g., H^+, Ca^{2+}, Mg^{2+}) for biotic ligand binding sites. These reactions account for toxicity variations due to changes in salinity, pH and DOC. Hence, the BLM accounts for the varying bioavailability of metals as a function of varying water chemistry.

BLM has been successful in estimating cupric ion's toxicity to fish in bulk water (Santore et al., 2001) and the Terrestrial BLM (T-BLM) has been developed for assessing metals toxicity in complex soil systems and has estimated toxicities of copper (Cu) and nickel (Ni) on organisms (Thakali et al., 2006a, b). In BLM and T-BLM, DOC and particulate organic carbon (POC) are modeled as fulvic and humic acids, respectively, and metal ion binding to humic substances are modeled by employing Windermere Humic-Aqueous Model (WHAM) V or VI (Tipping and Hurlely, 1992; Tipping, 1998). Recently, sediment BLM (S-BLM) has been developed (Di Toro et al., 2005) to predict metals toxicity in low AVS sediments. The model assumed POC as a dominant metal scavenging phase in sediments, which is similar with T-BLM. Although S-BLM is the most updated model for estimating free metal ion activity in aerobic surficial sediments, the model is considered to be preliminary (Di Toro et al., 2005). Metals oxides, which are neglected in current BLM, are one of the dominant sorption phases for metal sorption as well (Tessier et al., 1985; Wang and Chen, 1997), and these phases should be included to the BLM for better description of metal partitioning to sediment particle.

7.5 PASSIVE SAMPLING FOR MEASURING POREWATER CONCENTRATIONS AND ASSESSING BIOAVAILABILITY

7.5.1 Passive Sampling for HOCs

The sections above have indicated the potential for porewater concentration of HOCs to predict bioaccumulation and hence provide a chemical measure of bioavailability. In the absence of an ability to accurately and consistently predict porewater concentration, however, the most direct way to determine porewater concentration is through direct measurement. The most commonly used conventional method for porewater measurement is centrifugation or filtration, which includes sediment centrifugation or filtration, solvent extraction, solvent exchange, concentration or blowdown, and analysis. However, due to high hydrophobicity of most HOCs and thus very low porewater concentration, especially for HOCs with log

$K_{ow} > 6.0$, an impractical large volume of sample is usually needed to achieve detectable concentrations. Additionally, this approach suffers from incomplete water phase separation (Carr and Chapman, 1995), sorption, or evaporation loss during sample preparation and interference from contaminants associated with colloids and DOCs (Baker et al., 1996). In the presence of colloidal matter, freely dissolved porewater concentration can be estimated by:

$$C_{\mathrm{pw}} = \frac{C_{\mathrm{wm}}}{(1 + C_{\mathrm{DOC}} K_{\mathrm{DOC}})} \tag{Eq. 7.3}$$

where C_{wm} and C_{pw} are the measured total and freely or truly dissolved water concentration (milligrams per liter [mg/L]), respectively. C_{DOC} and K_{DOC} are DOC content in water and DOC-water partition coefficient of HOCs. Since K_{DOC} is of the order of K_{ow} (e.g., log K_{DOC} = log $K_{\mathrm{ow}} - 0.58$ by Burkhard, 2000), the difference between the total concentration in the porewater and the truly dissolved concentration can be large for log $K_{\mathrm{ow}} > 6$. Several chemical techniques have been developed to overcome these limitations and detect freely dissolved water concentrations. These approaches include equilibrium dialysis (McCarty and Jimenez, 1985), gas purging (Resendes et al., 1992), alum flocculation to remove colloids (Ghosh et al., 2000), and passive sampling with polymer sorbents. With passive samplers, porewater concentrations can be inferred from the uptake in an easily separable and well-defined synthetic phase, e.g., polymeric sorbents or lipid as used in semi-permeable membrane devices (SPMD) (Huckins et al., 1990). In contrast to SPMD, solid phase microextraction (SPME) using a minimal volume of polymeric sorbents is non-depletive and equilibrium-based sampling of the porewater concentrations is feasible (Maruya et al., 2011).

SPME for hydrophobic organic contaminants involves the insertion of a small volume of polymer sorbent into the sediments, withdrawal after a period of time (preferably after achieving equilibrium), and measuring the contaminants sorbed to the polymer. The achievement of equilibrium allows the estimation of porewater concentration with the ratio of the concentration in the sorbent, $C_{sorbent}$, and a polymer sorbent-water partition coefficient, $K_{sorbent\text{-}water}$, as shown in Equation 7.4.

$$C_{pw} = \frac{C_{sorbent}}{K_{sorbent-water}} \tag{Eq. 7.4}$$

Non-equilibrium exposures must be corrected for the kinetics of uptake. In SPME, the amount sorbed to the polymer does not significantly modify equilibrium in the soil-water system due to the small mass absorbed. Polyoxymethylene (POM) (Jonker and Koelmans, 2001), polyethylene (PE) (Fernandez et al., 2009a; Cornelissen et al., 2008), and polydimethylsiloxane (PDMS) (Lampert et al., 2013; Maruya et al., 2009; Mayer et al., 2000) are three polymer sorts that have been widely used to measure porewater concentrations of HOCs. POM and PE are normally used in thin (25–100 micrometers [μm]) bulk layers while PDMS is coated in a thin layer (10–30 μm) on glass fibers. The term "solid phase microextraction" (SPME) has been most often applied to the use of PDMS, but use of POM and PE are essentially equivalent extraction processes. PDMS is available as a thin coating (10–30 μm) on a variety of glass capillaries of various sizes (110–1,000 μm). The capillary can be of arbitrary length and can be coiled in long, continuous lengths. The cylindrical shape is convenient for insertion into sediments and the availability of thin layers with modest sorption capacity (compared to the slightly more sorbing POM and PE) speeds equilibration kinetics. The length can be segmented to achieve the desired vertical resolution or to provide sufficient sorbent volume to meet detection limit requirements. Costs of fabricating the PDMS-coated glass fibers range from approximately $1 per meter (m) (for commercial available optical fibers) to $10–25/m (for specially fabricated coated fibers). Only 1–5 centimeters (cm) of this fiber is necessary for detection of HOCs at sub-nanogram per liter (ng/L) concentrations and, therefore, the cost of the PDMS is negligible compared to the chemical analysis. In addition, the analysis method demonstrated herein generally requires no special extraction or sample processing procedures and the analysis cost is equal to or less than conventional water sample analysis costs.

These three sorbents have similar but not identical sorption capacities for HOCs (Gschwend et al., 2011). Gschwend et al. (2011) compared porewater concentrations of selected PCB congeners by three polymer samplers with the results obtained using air bridges. All sorbents were capable of measuring porewater concentration and were essentially equivalent at equilibrium. Sorbent-water partition coefficients reported by Gschwend et al. (2011) were:

$$\begin{aligned} LogK_{PDMS-water} &= 1.06 LogK_{ow} - 1.16 \qquad r^2 = 0.94 \\ LogK_{PE-water} &= 1.00 LogK_{ow} - 0.287 \qquad r^2 = 0.96 \\ LogK_{POM-water} &= 0.791 LogK_{ow} + 1.018 \qquad r^2 = 0.95 \end{aligned} \tag{Eq. 7.5}$$

Passive sampling with polymer sorbents has extremely low detection limits due to the high sorbent-water partition coefficients of HOCs. Another promising feature of passive sampling is that only freely dissolved water concentrations are measured because only a very small amount of HOC is extracted with passive sampling, and the extraction does not influence the existing equilibrium between the bound and free form of a chemical (Van der War et al., 2004). The big challenge for passive sampling especially for *in situ* measurement of porewater concentrations is the uncertainty in the time required for equilibration. The equilibrium time is largely defined by the time required to replenish the zone that is depleted of the contaminants by sampler, which is controlled by the hydrophobicity of compounds, sorption capacity of the sorbents, and the dynamic conditions at the sampling sites. Different methods have been used to correct the disequilibrium of passive samplers. A common method is preloading the sorbent with performance reference compounds (PRCs), such as deuterated PAHs or C-13 labeled versions of the contaminants of interest, that desorb (Huckins et al., 2002; Fernandez et al., 2009b) that desorb and indicate the rate of sorption of a similarly hydrophobic compound. This approach requires that sorption in the surrounding sediments is linear and reversible. An alternative means is through using two different size sorbents (with different intrinsic kinetics) or measurement of concentrations over at least two different time periods. In either case, the ratio of the two concentrations can be used to fit a model of sorbent uptake. If the sorbent in the thin layer is assumed two dimensional and if the kinetics of exchange are controlled by the surrounding medium rather than internal diffusion in the polymer sorbent, the loss of PRCs can be predicted by the first of Equation 7.6 and the uptake of HOCs can be modeled by the second of Equation 7.6.

$$\begin{aligned} M_{PRC}(t) &= M(0)\left[\exp\left(\frac{RDt}{L^2K^2_{sorbent-water}}\right)\operatorname{erfc}\left(\frac{\sqrt{RDt}}{LK_{sorbent-water}}\right)\right] \\ M_{ads}(t) &= K_{sorbent-water}C_{pw}L\left[1-\exp\left(\frac{RDt}{L^2K^2_{sorbent-water}}\right)\operatorname{erfc}\left(\frac{\sqrt{RDt}}{LK_{sorbent-water}}\right)\right] \end{aligned} \tag{Eq. 7.6}$$

Here L is the volume-to-surface ratio of the sorbent, t is time, and RD is an effective transport parameter (product of retardation factor and diffusion coefficient) for the medium surrounding the sorbent. RD would normally have to be fit to data whether it is desorption of PRCs, a time series of uptake, or the ratio of uptake in sorbents with two different volume-to-surface area ratios. The effective diffusion coefficient is only a weak function of compound if molecular diffusion controls (e.g., inversely proportional to the square root of molecular weight) and independent of compound if an effective diffusion process such as tidal motion or advection controls mixing external to the sorbent. Since the retardation factor is generally linear with octanol-water partition coefficient, RD should be linearly related to K_{ow}.

Besides predicting bioaccumulation through porewater concentrations, passive sampling has also been used as a direct biological surrogate since tissue concentrations show strong linear correlation with sorbent concentrations (You et al., 2006; van der War et al., 2004; Friedman et al., 2009). Hydrophobic organic contaminant accumulation by *Lumbriculus variegatus* (C_b, nanograms per gram [ng/g] lipid) correlated well with the matrix-SPME fiber concentrations (C_f, nanograms per milliliter [ng/mL] PDMS) accounting for 92% of the variation in the data (You et al., 2006). With well-designed samplers that can be successfully deployed in the field (Lampert et al., 2013; Reible and Lu, 2011; Maruya et al., 2009), passive sampling with SPME can be used to assess *in situ* bioavailability of HOCs.

7.5.2 Passive Sampling for Metals

Centrifugation, dialysis, suction filtration and other methods have also been traditionally used to collect porewater for dissolved metals analysis, although these methods have suffered from various sources of errors, such as operator inexperience, insufficient sample size and change of oxidation states during processing (Bufflap and Allen, 1995; Mason et al., 1998). More difficulties arise from extremely low metals concentrations on the order of ng/L as well as from sharp porewater metal concentration profiles, which may vary on the scale of millimeters due to complex biogeochemical redox reactions (Zhang and Davison, 1995).

To overcome these difficulties, passive sampling techniques have also been widely used for metals (Greenwood et al., 2007). Diffusive gradient in thin film (DGT) devices are one alternative that determines labile metal concentrations in aquatic systems (Zhang and Davison, 1995). The DGT probe employs a series of layers including a filter membrane, a diffusive hydrogel, and a resin gel in a plastic unit. The filter side is exposed to the environment after which dissolved metals diffuse through the hydrogel and are accumulated in the resin gel, which acts as a sink. Assuming that steady-state diffusion in the hydrogel layer of thickness, ΔZ_{gel}, at diffusivity, D_{gel}, controls the rate of uptake into the sorbing resin at its base, the concentration in the porewater is given by the mass accumulated in the resin, m_{resin}, over a time, Δt, as shown in Equation 7.7:

$$C_{pw} = \frac{m_{re\sin} \Delta z_{gel}}{\mathrm{D}_{gel} \Delta t} \tag{Eq. 7.7}$$

This device can achieve millimeter resolution profiling of metals in sediments and low detection limits by concentrating metals in resin gel (Zhang et al., 1995). The technique has been used to detect various trace levels of ionic species by employing different types of resins and diffusive layers (Zhang and Davison, 1995; Dočekalov and Diviš, 2005; Clarisse and Hintelmann, 2005; Li et al., 2006, 2009). DGT probes have been applied to a variety of soil and sediment to measure porewater metal concentrations and to study remobilization kinetics of metals (Nowack et al., 2004; Ernstberger et al., 2005).

Figure 7.6 shows AVS/SEM and DGT measured porewater zinc (Zn) and Cd concentrations in Anacostia River sediment, which was exposed to aerobic salt water for 120 days in the laboratory (Hong et al., 2011b). The AVS profiles were characterized as decreased concentrations at the surficial sediments and relatively constant concentrations $\leq$2 cm. Based on the AVS/SEM model, the sediments <2 cm are expected to be nontoxic and dissolved metals concentrations should not be detected. In the upper centimeter, the segment averaged AVS was approximately equal to SEM and so dissolved metals and increased metal toxicity might be present. The vertical profiles of $Zn_{(aq)}$ and $Cd_{(aq)}$ measured by DGT probes reflected this and were characterized by elevated concentrations in the surficial sediments followed by <1 microgram per liter (μg/L) concentrations in the deeper anoxic sediments. These observations

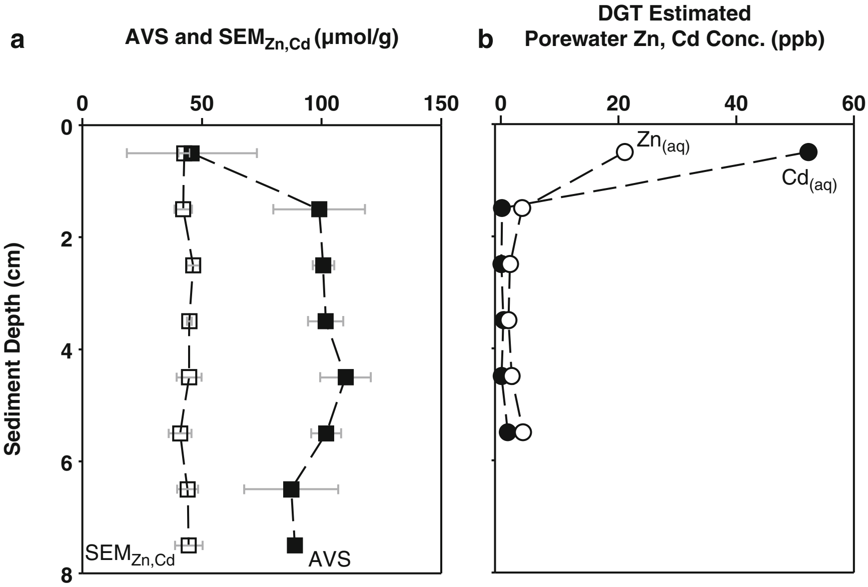

Figure 7.6. Vertical profiles of (a) AVS and SEM in sediments and (b) porewater Cd and Zn concentrations measured by DGT probes (Hong et al., 2011b).

suggested that a bulk measurement of AVS and SEM would not capture the potential metals' availability due to poor resolution in the surficial sediments (Chapman et al., 1998) but that the higher resolution *in situ* passive sampling techniques would better capture the bioavailable fraction of metals in sediments.

DGT is a robust *in situ* passive sampling technique; however, care should be taken when deploying the probe in sediments. In well-mixed bodies of water, the concentration of metals in the aqueous phase can be directly estimated from the mass of metals accumulated in the resin (Zhang and Davison, 1995). However, in soil and sediments, DGT perturbs the local concentration and thus reduces porewater metal concentrations below the equilibrium value near the probe (Nowack et al., 2004; Ernstberger et al., 2005). To overcome these limitations, a modeling approach – the DGT induced fluxes in soil and sediments (DIFS) model – has been used to estimate porewater metal concentrations and to understand the dynamic response of soil and sediment during DGT deployment (Harper et al., 1998, 2000; Lehto et al., 2008). The DIFS model requires a relatively complex numerical simulation for assessing porewater metals kinetics in solid matrices and contains several parameters that must be assessed for interpretation of experimental data.

7.6 SUMMARY

Bioavailability of contaminants is an important factor in sediment and soil remediation and risk assessment. Bulk sediment concentration is not a reliable predictor of exposure and risk; sediment porewater concentration, however, provides a good indicator of readily available contaminants and often describes bioavailability quantitatively. There are several ways to assess bioavailability of HOCs and metals in sediment including equilibrium partitioning predictive methods, extractive methods, and direct porewater concentration measurement. Direct measurement of freely dissolved porewater concentrations are better correlated to bioassays, such as bioaccumulation and toxicity testing. Passive sampling techniques with SPME for HOCs and the DGT probe for metals are efficient tools to measure freely dissolved porewater concentrations because they eliminate the problems associated with colloidally-associated contaminants and the analytical problems associated with detection of low porewater concentrations. Such passive sampling methods are expected to become increasingly helpful in better characterizing the bioavailability and toxicity of HOCs and metals in contaminated sediments. Although passive samplings are less helpful in assessing future conditions, they help improve the predictive capabilities for bioavailability in sediment.

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CHAPTER 8

RISK MANAGEMENT FOR CONTAMINATED SEDIMENTS

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8.1 RISK MANAGEMENT CHALLENGES

Contaminated sediments present a serious and vexing problem. The legacy of poor environmental practices related to industrial, agricultural, and residential uses of chemicals, waste water treatment, storm water management, as well as numerous other activities affecting water quality are evident in the current challenges facing public and private organizations addressing the risks posed by contaminated sediments. Managing these risks involves detailed consideration of a complex set of processes (e.g., physical, chemical, biological, socioeconomic) operating over broad spatial and temporal scales. Large uncertainties related to these processes cloud projections about the future performance of remedies. The number of technologies that are currently available for application at contaminated sediment sites is limited to a small number of variations of dredging, capping, treatment (both *in situ* and *ex situ*) and monitored natural recovery (MNR). The economic and environmental costs of managing contaminated sediment risks are large (e.g., project costs for each of the Fox and Hudson River cleanup projects in the United States are pushing $1 billion). Sediment cleanup projects are further complicated by the diverse range of policies, perspectives, risk attitudes and personal values that pertain to risk management decisions. Government institutions, private organizations and local communities face a number of difficult problems connected to risk management for contaminated sediments. Our purpose here is to analyze the risk management problem posed by contaminated sediments, present a series of guidelines for advancing risk management practice, and describe the path toward more effective risk management solutions.

8.1.1 The Problem Setting

The setting for contaminated sediment projects in the United States serves to illustrate the considerable range of conditions found at such projects. While chlorinated organic compounds (e.g., polychlorinated biphenyls [PCBs], dioxins) are driving risk management decisions at some of the most challenging projects (e.g., Hudson River, Fox River, Tittabawassee River), the range of contaminants contributing to risks at cleanup sites includes polycyclic aromatic hydrocarbons (PAHs), various metals, and a range of pesticides. The physical setting for these sites varies and includes projects in open-coast environments (e.g., Palos Verdes Shelf in Southern California); bays, estuaries, and tidal habitats (e.g., Hunters Point and Alameda Naval Air Station in San Francisco Bay); and inland rivers and lakes (e.g., Saginaw River and Bay). Contaminated sediment projects encompass a broad range of spatial scales, including sites of a few acres (United Heckathorn in Richmond Harbor, California) to those encompassing more than 50 river miles (Tittabawassee River, Michigan). The surrounding landscape for these projects includes highly industrialized/urbanized environments (e.g., Passaic River, New Jersey) as well as those

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occupying relatively undeveloped/rural landscapes (e.g., Upper Columbia River, Washington). This diversity in setting and conditions contributes to the complexity involved in managing the risks posed by contaminated sediments.

8.1.2 Technical Aspects of the Risky Business of Sediment Management

From a risk management perspective, the objective of contaminated sediment remediation is to reduce the risks posed to human health and the environment (e.g., fish, wildlife and other organisms). Remediation is intended to interrupt the contaminant exposure pathways between sediments and these organisms. Exposure pathways can be direct; for example, the direct exposure of benthic invertebrates to metals-contaminated sediment. Or, the exposure pathway can be indirect; for example, human exposure to PCBs from consuming fish which contain sediment-derived contaminants. A variety of media (water, dissolved and particulate organic carbon [DOC and POC], sediments, dietary constituents) and sources (current or historic discharges of contaminants via surface waters, groundwater, or nonaqueous phase liquids [NAPL]) feed those exposures. The contaminants themselves can be present in various phases (freely dissolved, colloidal, or tightly bound to sediment particles). The bioavailability of those contaminants to organisms can also vary across media and exposure routes. As a result, determining which contaminated media, source areas, and processes are responsible for the exposures driving adverse effects is critical to implementing effective sediment remediation. For example, a common objective for remediation at PCB-contaminated sites is to reduce PCB levels in fish tissue (which are a source of exposure and risk to humans). Thus, the critical question is: What processes are contributing to exposures and uptake of PCBs in fish? Answering this question is key to the effective design and implementation of a remedy that reduces exposures and risks.

There are many challenges to determining the exposures that drive risk and then implementing an effective remediation. These challenges are generally associated with (1) understanding which environmental media are contaminated, where they are located, and when they are present (e.g., transient discharge in surface waters compared to ongoing exposures from sediment); (2) understanding which of those media and locations are driving adverse effects in receptors of concern; (3) remediating those areas to reduce or eliminate contaminant exposures; and (4) ensuring that remediated areas are not recontaminated after remediation.

8.1.2.1 Transport Phenomena and Future Exposures

Overall, transport processes represent the physical blueprint by which the magnitude, duration and spatial extent of future contaminant exposures is determined. Most of the sediment contaminants targeted by remediation, such as PCBs, heavy metals, and chlorinated pesticides, are legacy contaminants that were introduced through releases that occurred decades or even a century ago. These persistent contaminants often strongly associate with sediments and either do not degrade (in the case of metals), or degrade only slowly. These contaminants will associate preferentially with sediments. For example, organic contaminants have a strong affinity for sediments that are enriched with organic carbon. As those sediments are transported over time, the contaminants can spread far from their point of release – in some systems hundreds of miles. Contaminated sediments will settle when buoyancy and turbulent forces are no longer sufficient to keep them suspended. Sediments can then be buried by further deposition, buried but later eroded and transported during routine or severe flows, or deposited and intermixed with older and newer sediments through bioturbation.

Transport phenomena play a large role in determining the pattern and magnitude of future exposures to contaminated sediments. The processes contributing to sediment erosion and deposition, and the rates of these processes, are the subject of intensive study and modeling (Lick, 2009). Deposited sediment can serve as both a source and a sink for contaminants in the environment. Contaminant exposures can be reduced through mixing, i.e., dilution with clean sediment, and burial or sediments can produce ongoing exposure and risk as organisms interact with the deposit.

8.1.2.2 Uncertainty in Site Characterization

Over time, transport processes result in substantial heterogeneity in the horizontal and vertical pattern of contamination throughout aquatic systems. Years of variation in contaminant releases and changes in water body morphology, hydrodynamics, and environmental conditions further increase that heterogeneity. As a result, surface sediment concentrations can vary substantially over a distance of several meters. Characterizing this heterogeneity presents a major challenge that can require multiple, high-resolution sampling events. Even sediment sampling technologies contribute to the uncertainty in site characterization. For example, coring is one of the best approaches for understanding the vertical distribution of contamination (USEPA, 2001), but core compression (Glew et al., 2002), refusal of cores by debris (e.g., see USEPA, 2010a), and core loss represent significant sources of uncertainty that can lead to inaccurate depictions of the depth of contamination.

Overall, an understanding of the location and magnitude of sediment contamination is a critical component of developing a conceptual site model. Incomplete characterization of contamination is a major factor contributing to remedial operations that do not achieve their intended objectives or inadvertently produce adverse effects (NRC, 2007). However, the size of many sites and their heterogeneity make robust characterization a significant challenge.

8.1.2.3 Uncertainty in Exposure and Effect Assessments

The physical and geochemical characteristics of contaminated sediments vary, and these attributes can play a significant role in the magnitude of contaminant exposures and uptake experienced by organisms. The types of organic carbon in sediments vary and differences in the nature of that carbon and its properties play a significant role in contaminant partitioning and, ultimately, food chain transfer (Ghosh et al., 2003; Ghosh and Hawthorne, 2010). It is known that contaminant hydrophobicity is a primary driver of partitioning to organic carbon phases (Tanford et al., 1980) and that hydrophobicity drives bioaccumulation in organisms, although not in a linear fashion (Evans et al., 1991). However, even within a group of contaminants, such as PCBs, there can be differential bioaccumulation of congeners both relating to as well as being independent of hydrophobicity (Niimi, 1996).

Further complexity is introduced by organism behavior. Large piscivorous fish are a primary concern at sediment sites because they are fished for and consumed by humans. However, their uptake of highly hydrophobic contaminants does not stem directly from sediments; rather it is primarily from dietary exposures (Bruggeman et al., 1981; Oliver and Niimi, 1988; Thomann et al., 1992). Thus, inter- and intra-species differences in behavior, diet and health status introduce further uncertainty into defining the cause and effect relationship between sediment concentrations and bioaccumulation.

8.1.2.4 Uncertainty in Predicting the Effect and Effectiveness of Remedial Actions

Understanding and predicting the effect of remedial actions on contaminant conditions in the environment and biota presents an ongoing challenge (NRC, 2001, 2007; Bridges et al., 2010a). Even after 40 years of remediation, it is generally not known whether active sediment remediation has resulted in decreases in fish tissue contaminant concentrations beyond what would be expected in its absence (NRC, 2001, 2007; Bridges et al., 2010b). Dredging may not reduce exposures as anticipated (NRC, 2007), sediment caps may not prevent contaminant flux to overlying water (e.g., USEPA, 2006a), and MNR may not reduce contaminant levels in receptors to anticipated levels (e.g., USEPA, 2009a). Ongoing contaminant sources may recontaminate remediated areas (e.g., USEPA, 2006b). A wide variety of operational and environmental conditions can influence remedial effectiveness (Palermo et al., 1998, 2008); these conditions may not be known prior to implementation and they can be highly variable over time and space. As a result, the practice of predicting future environmental conditions – over decades or even centuries – is fraught with uncertainty; yet, predictions, whether formal or informal, provide the basis of remedial decisions.

8.1.2.5 Compounded Uncertainty

When we combine uncertain operational outcomes with heterogeneous contamination, complex environments, and a diverse and wide-ranging resource such as fish, the depth of our uncertainties and the challenges associated with modeling and predicting remedy outcomes over a period of decades quickly becomes apparent. Mathematical models, taking a variety of forms, are used to predict area-wide concentrations of contaminants in sediment and water, transfer of contaminants between environmental media, transport of sediments and contaminants over space and time, the bioaccumulation and transfer of contaminants into and among organisms, and the effect of remedial actions on those processes. The outputs of all models, to varying degrees, are uncertain, owing to intrinsic uncertainty in their structure and parameters. The models used in contaminated sediment projects are frequently applied in series with results from one feeding into another, a process that propagates and compounds the uncertainty. While specific sources of uncertainty can be targeted, refined, and reduced, the magnitude and implications of the residual uncertainty associated with model outputs represents one of the most significant challenges faced by risk management.

8.2 THE RISK MANAGEMENT PROCESS

The complexity of contaminated sediment projects has motivated both critical reviews (NRC, 2001, 2007) and the development of technical guidance for managing contaminated sediments (e.g., Palermo et al., 1998, 2008; USEPA, 2005). Concurrent with these activities, a consensus has been growing within the United States for the use of "risk-based" approaches to inform decision making, in recognition of the uncertainties associated with managing contaminated sediments (NRC, 2001, 2007; Horinko, 2002; Bridges et al., 2006, 2010b). In other parts of the world, increasing attention is being given to the problem of contaminated sediments, as reflected by the activities of such organizations as the European Union-funded Sediment Research Network (SedNet, http://www.sednet.org/, accessed March 31, 2013) and many other efforts (Wenning et al., 2005, and examples therein). While in some cases the use of prescriptive, single-solution approaches to sediment management are still evident, increasing attention is being given to the use of concepts and analytical methods supportive of risk-based approaches (e.g., PIANC, 2006; Sparrevik et al., 2011). In order to translate the growing interest in risk analysis into implementable

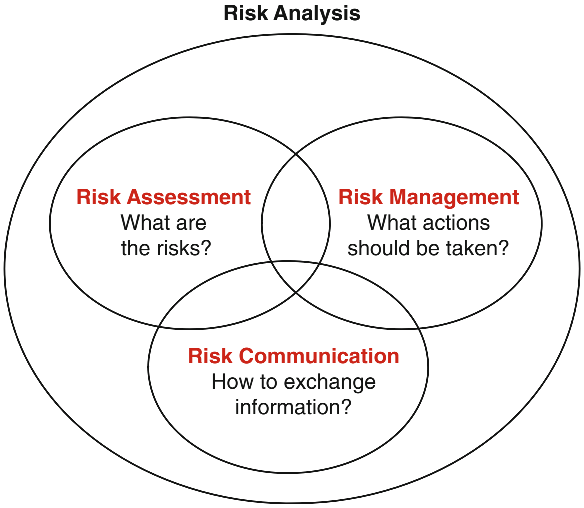

Figure 8.1. Conceptual representation of risk analysis as the integration of risk assessment, risk management and risk communication.

practice, we must first reach a common understanding of the concepts and methods integral to risk-based management.

Risk is defined as the probability of an undesirable outcome or consequence. The concepts associated with risk management are applicable to a wide set of decision problems: disease transmission and infection, the probability of losses associated with a flood event, or the likelihood for human health injuries and environmental harm caused by exposures to sediment-associated contaminants.

Risk analysis refers to a collection of techniques, methods, and approaches for developing an understanding of the processes shaping the scope and magnitude of risks that is sufficient to support decisions about how to manage and communicate in regard to those risks. As an approach to problem-solving, risk analysis comprises three inter-related spheres of activity: risk assessment, risk management and risk communication (Figure 8.1). Risk assessment is concerned with developing evidence for characterizing the nature of the risks, including an understanding of the processes (e.g., physical, chemical, biological) producing the risks. Risk management refers to developing and implementing actions or interventions for reducing risks. Risk communication involves the exchange of information related to characterizing and managing risks. While Figure 8.1 presents risk analysis as the integration of three related groups of activities, many of the gaps and challenges in risk analysis practice are due to a lack of integration across these three areas, i.e., disconnects between risk assessment, risk management and risk communication.

Our focus here is on risk management, which we define as a *structured process through which actions for reducing risks are identified, evaluated, selected, and implemented.*

Risk management actions are *identified* by developing a list of actions that have potential relevance for the site in question, given an understanding of the processes ongoing at the site that are contributing to the risks. This task is simplified by the fact that there are relatively few options available for reducing exposures at contaminated sediment sites. Institutional controls can be employed to modify human actions or behaviors that contribute to exposure (e.g., fishing bans or limits). Engineering actions include efforts to address ongoing sources (e.g., on land or within groundwater), *in situ* approaches (e.g., MNR, capping, and treatment), and *ex situ* approaches (e.g., dredging or excavation followed by disposal and/treatment).

Once identified, the risk management actions are *evaluated* with respect to their ability to satisfy the project's objectives. In most cases, the list of project objectives will involve a range of interests, including the desire for risk reduction over some defined period, preserving future uses of the water body, minimizing remedy implementation costs, etc. The evaluation process involves establishing metrics for gauging progress towards each of the project's objectives and collecting data for those metrics. An example risk reduction metric would be contaminant concentration in fish tissue 20 years after implementation of the remedy. For this example, data collected during site characterization and the baseline risk assessment could be used to model the future trajectory of fish tissue concentrations under alternative remedial actions or combinations of actions.

Risk management actions are *selected* through a deliberative process that involves comparing the relative performance of the identified and evaluated risk management actions, or combinations of actions, across all of the project's objectives. The selection process employed by a project team or organization must satisfy the need to employ understandable and credible reasoning in evaluating the multiple trade-offs relevant to a set of project objectives. An example trade-off would be the case where the risk management action expected to produce the lowest fish tissue concentration at 20 years post implementation (one measure of risk reduction) would also impose the largest constraint on future uses of the water body (e.g., restrictions on recreational and commercial uses).

Risk management actions are *implemented* through the process of engineering design, construction, and operations and maintenance. What has become increasingly apparent through recent experience with contaminated sediment remediation projects is that uncertainties related to heterogeneity in the physical and chemical properties of the sediment (e.g., vertical and horizontal distribution of contamination) and encompassing water body (e.g., temporal variation in hydrology and hydrodynamics) seriously complicate the transition from design to construction and from construction to operations and maintenance. Effectively managing these uncertainties and their consequences presents a formidable challenge that should motivate the development and use of new approaches for accomplishing risk management for contaminated sediments.

In 2002, the U.S. Environmental Protection Agency (USEPA) published a set of 11 management principles to "help EPA site managers make scientifically sound and nationally consistent risk management decisions at contaminated sediment sites" (Horinko, 2002). The 11 management actions and approaches are:

1. Control sources early.
2. Involve the community early and often.
3. Coordinate with states, local governments, tribes and natural resource trustees.
4. Develop and refine a conceptual site model that considers sediment stability.
5. Use an iterative approach in a risk-based framework.
6. Carefully evaluate the assumptions and uncertainties associated with site characterization data and site models.
7. Select site-specific, project-specific and sediment-specific risk management approaches that will achieve risk-based goals.
8. Ensure that sediment cleanup levels are clearly tied to risk management goals.
9. Maximize the effectiveness of institutional controls and recognize their limitations.
10. Design remedies to minimize short-term risks while achieving long-term protection.
11. Monitor during and after sediment remediation to assess and document remedy effectiveness.

While progress in applying the management principles and approaches presented in Horinko (2002) has been made over the last 10 years, gaps in practice continue to challenge both the technical community and decision makers.

8.3 ADVANCING RISK MANAGEMENT PRACTICE

The complexity, uncertainty, and current challenges confronting sediment remediation projects point to the need to develop more robust risk management practices.

The need for improving risk management practices and environmental decision making, generally, is evident in appeals for using "sound science" and the need for "scientific integrity" in government decision making. On March 9, 2009, President Barrack Obama issued a "Memorandum for the Heads of Executive Departments and Agencies" in the Federal government on the subject of "scientific integrity" (Obama, 2009). This memorandum was followed by guidance issued by John Holdren, Director of the Office of Science and Technology Policy, on December 17, 2010 (Holdren, 2010). In his memorandum, President Obama makes the following statements:

> *Science and the scientific process must inform and guide decisions of my Administration on a wide range of issues, including improvement of public health, protection of the environment, increased efficiency in the use of energy and other resources, mitigation of the threat of climate change, and protection of national security.*
>
> *The public must be able to trust the science and scientific process informing public policy decisions.*
>
> *Political officials should not suppress or alter scientific or technological findings and conclusions.*
>
> *To the extent permitted by law, there should be transparency in the preparation, identification, and use of scientific and technological information in policymaking.*
>
> *When scientific or technological information is considered in policy decisions, the information should be subject to well-established scientific processes, including peer review where appropriate…*

Key attributes of "scientific integrity," as applied to decision making, include, (1) the importance of defining "well-established" scientific processes, (2) the use of peer review, (3) the importance of establishing trust with the public, (4) the need for transparency in the development of science-based evidence and (5) the importance of ensuring that the scientific process of building evidence for conclusions and inferences is not manipulated to bring about predetermined or politically favored outcomes. The need for transparency is critical to achieving scientific integrity as transparency touches upon all of the other attributes. Transparency will ensure that the methods, models and analytical results used in risk management are sufficiently described so that they can be subjected to critical examination, validation and falsification, which are essential qualities of the process of scientific inquiry. This need for transparency extends to the full range of technical activities that must be undertaken within risk management, including the development of project objectives (e.g., remedial action objectives) and the logic that will be used to compare and select remedies. Quality science is integral to quality risk management.

In the remainder of this chapter we elaborate on ten guidelines for robust risk management (Table 8.1) that relate fundamental concepts and methods from the field of risk analysis to needs regarding sediment remediation. Our objective is to establish a foundation upon which further progress can be achieved in the form of more effective and efficient risk management outcomes for contaminated sediment projects in the United States and elsewhere. We recognize the impracticality of trying to develop a uniform risk management "recipe" for all government agencies and private organizations. However, we do believe that substantial improvement can be achieved by applying these guidelines to develop improved standards and protocols that support good risk management practice.

Table 8.1. Ten Risk Management Guidelines Relevant to the Management of Contaminated Sediments

Guidelines for Robust Risk Management	
1	Risk management is undertaken through credible, scientific processes.
2	Risk management assumes a forward-looking posture.
3	Specific and measurable objectives are developed in a transparent and rigorous manner.
4	Risk management is accomplished through open, transparent and deliberative processes.
5	Uncertainties are acknowledged and addressed through quantitative analysis.
6	Risk management investments are commensurate with the magnitude of risks and uncertainties.
7	Risk management is a system-scale activity.
8	Risk reduction is most reliably achieved through the use of an integrated network of multiple remedial technologies and actions.
9	Risk communication is integral to effective risk management.
10	Risk management is achieved through formal application of adaptive management.

8.3.1 Ten Guidelines for Robust Risk Management

1. *Risk management is undertaken through credible, scientific processes*

In stating that risk management employs scientific processes, we mean that decisions and actions taken to reduce risks are based upon objective analyses of scientific inferences, quantitative evidence, and conclusions regarding the nature and magnitude of risks.

The fundamental question that should guide all risk management data collection and analysis is: How will this information/study/analysis contribute to our ability to distinguish among and select from the risk management alternatives under consideration? The need to assemble evidence to support the selection of a remedial action, or a sub-set of actions, from a list of competing, alternative actions is the basis for this question. Risk management is concerned with identifying, evaluating, selecting, and implementing actions to achieve risk reduction goals. This sequential process uses information to distinguish and compare an action or remedy with alternative actions and remedies. Relevant information in this regard would include quantitative data and descriptions of the physical (e.g., sediment transport), chemical (e.g., contaminant partitioning and fate), and biological (e.g., toxicology) processes contributing to risks and how those risks can be managed (e.g., how a particular cap design would reduce exposure rates to benthos and fish over time). In view of all the possible data that could be collected, an example, fundamental question to ask would be: What information would be needed to distinguish whether dredging or capping could be used as the predominant means for achieving risk reduction for site X? By developing, from this question, a detailed hierarchy of specific questions and associated data quality objectives (USEPA, 2006c), the structure to guide focused data collection and evidence building can be developed. In general, the sooner the fundamental risk management questions are identified within a project (even within remedial investigation and baseline risk assessment) the more expeditious the path to achieving the project's risk management objectives.

Risk management using scientific processes incorporates the formal and disciplined use of hypotheses. The central hypothesis for contaminated sediment remediation is that *the remedial* *actions are having their intended effect on risk reduction*, and data collection and evaluation throughout the project are structured to support the testing of that hypothesis. While some activities in risk assessment and risk management can be pursued through the use of formal hypothesis testing (e.g., sediment toxicity testing), many activities do not completely conform to this form of inquiry (e.g., modeling to predict remedy performance over time). However, all data collection, analysis and modeling should be guided by the use of an explicit set of rigorously developed questions.

2. ***Risk management assumes a forward-looking posture and employs an analytical approach to developing robust remedial plans***

Risk management is primarily concerned with defining future actions to reduce risks, evaluating results from those actions, and managing the trajectory of risk reduction over time. On this basis, risk management can be distinguished from site characterization, baseline risk assessment, and remedial investigation, which are primarily concerned with characterizing the current status of a site and past events that contributed to current adverse conditions. Risk management is concerned with future actions taken to realize a project's objectives, i.e., improving conditions and reducing risks. Clearly, one must first develop an understanding of *what has happened* and *what is happening* at a site before setting about to design a plan to affect a change in the future. However, the transition from a past/current focus to developing a plan for achieving specific objectives in the future is a significant change in posture – a shift from description to prediction. In fact, the failure of a remedy to meet a project's risk reduction objectives is a consequence of the challenge of using knowledge about current conditions (and the uncertainties associated with that knowledge) to develop a plan to address uncertain, future conditions. The need in this regard is to develop robust plans for managing risks that incorporate approaches for addressing large uncertainties related to process drivers and future conditions. Robust plans manage uncertainties (in contrast to the idea of resolving them), preserve options for adapting over time, and address the broad-ranging conditions associated with alternative future scenarios (e.g., Lempert and Collins, 2007). Developing robust plans will require more analysis than is currently being deployed, effort that combines elements of scenario planning with mathematical modeling and simulation.

The relevance of scenario planning for contaminated sediment risk management emerges from the long time scales associated with contaminated sediment projects. The investigation/study phase alone for some of the most challenging sites can take several years to multiple decades (e.g., New Bedford Harbor, Hudson River, Passaic River, etc.). The recalcitrant nature of many of the contaminants driving risk management decisions (e.g., PCBs, dioxins, heavy metals) contributes to long recovery periods following remedy implementation (several decades in some cases). These long time scales emphasize the need for considering how future conditions and processes will affect the performance of engineering actions and remedies. Examples that illustrate the potential significance of future conditions in achieving risk reduction include questions related to (1) changes in upland, atmospheric, and upstream contaminant transport and delivery, (2) the effect of climate change on hydrology and water quality, (3) how future land use and development will affect water use and exposure rates, (4) how economic trends will affect the funding streams needed to execute long-term remedy implementation and operations and maintenance (O&M), as well as many other processes and conditions. Scenario planning has been used for many years in a variety of fields to help address the complexities associated with long-term planning in the face of uncertain future conditions (Lindgren and Bandhold, 2003). The opportunity with respect to contaminated sediment risk management is to use scenario planning to develop more robust and resilient remedies. The basic approach to scenario planning is that multiple alternative futures (i.e., scenarios) are developed and alternative risk management plans (or proposed remedies) are quantitatively evaluated for each of the developed scenarios. The information produced from this analysis is used as input to selecting actions, or combinations of actions, which perform well for the most likely or the broadest range of future conditions. Used in this manner, scenario planning provides the means for identifying robust and resilient risk management plans.

Mathematical modeling and simulation at contaminated sites has presented a number of challenges for project teams, a fact that has motivated the development of guidance to inform modeling practice (USEPA, 2008, 2009b) and the publication of commentaries on the use of modeling to inform decision making (Glaser and Bridges, 2007). What is equally clear is that making improvements in the quality of risk management for contaminated sediments is closely tied to advancing the use of mathematical models to inform decision making. Models are used to synthesize understanding about processes through the integration of empirical data. They are essential to informing remedy design and are critical to the process of evaluating the performance of alternative remedies with respect to future conditions. They also provide the means for interpreting and responding to data that are collected as a part of monitoring programs, whether that monitoring is being conducted to optimize operational aspects of remedy implementation or to gauge the performance or effectiveness of the remedy over time. Models enable the forward-looking posture of risk management.

One of the benefits that will be realized through the enhanced use of scenario planning and mathematical modeling is more efficient and effective treatment of residual risks. The term residual risk has generally been used to refer to the level of targeted risk, attributable to site conditions, that remains after a remedy has been implemented. For example, cancer risk resulting from the ingestion of contaminated fish at the site will not instantaneously decline to acceptable levels the day after dredging or capping is completed. The expected and desired result would be for cancer risk to decline toward an acceptable target level over some period of time. One of the goals of a risk management plan should be to minimize residual risk, within relevant constraints.

3. *Specific and measurable objectives are developed in a transparent and rigorous manner*

Structuring a remediation project, first and foremost, as a decision problem will elevate the requirements of sound decision making within remediation projects. Chief among these requirements is a coherent listing of project objectives that supports decision making. The development of a robust set of project objectives is critical to establishing and maintaining a decision-focus within the project, whereby all of the activities comprising the project are structured to support decision making. Information is collected, analyzed and organized for the purposes of:

1. Distinguishing alternative risk management actions (e.g., remedies) in terms of their ability to satisfy the project's objectives. The key question that informs all information gathering is: How will this information be used to distinguish among alternative actions?
2. Establishing whether the remedial action has achieved the project's objectives within the desired timeframe.

In the case of the U.S. Superfund Program, the National Contingency Plan (NCP) calls for the development of "Remedial Action Objectives, specifying contaminants and media of concern, potential exposure pathways, and remediation goals." Those Remediation Goals "shall establish acceptable exposure levels..." (40 CFR 300.430[e][2][i]). The Remediation

Table 8.2. The Nine National Contingency Plan Criteria Used by the USEPA in the Superfund Program to Evaluate Remedy Options

National Contingency Plan (NCP) Criteria	
Threshold criteria	
1	Overall protection of human health and the environment
2	Compliance with applicable or relevant and appropriate requirements (ARARs)
Balancing criteria	
3	Long-term effectiveness and permanence
4	Reduction of toxicity, mobility, and volume through treatment
5	Short-term effectiveness
6	Implementability
7	Cost
Modifying criteria	
8	State (or support agency) acceptance
9	Community acceptance

Goals and associated Cleanup Levels should satisfy the NCP's threshold criterion for protection of human health and the environment (Table 8.2) (USEPA, 2005 and references cited therein). It can be argued that deficiencies in current practice in regards to the use of decision-making objectives has less to do with the adequacy of existing guidance and more to do with how the guidance is being implemented.

In order for decision-making objectives to guide the process of identifying, evaluating, selecting, and implementing remedies, the objectives must be developed in sufficient detail so that they can support a rigorous analysis that is able to identify meaningful distinctions among competing risk management alternatives. In regards to the detail that is necessary, decision-making objectives should possess several key attributes that are represented in the acronym SMART (adapted from Doran, 1981). Objectives should be:

- **S**pecific. Decision-making objectives should identify specific qualities and goals in regard to the risks that are to be managed.
- **M**easureable. Objectives should be formulated such that progress toward achieving those objectives can be measured through monitoring.
- **A**ligned. The intention embodied by the objective should be aligned with the scope and nature of the problem, existing statutory/regulatory requirements, the values of interested and affected parties, etc.
- **R**ealistic. The objectives should establish targets that are achievable. Doing otherwise will not provide effective guides for decision making nor serve the long-term interests of the public.
- **T**imed (time-bound). Decision-making objectives should identify the timeframe within which the objectives are to be achieved so that accountability is assured.

In following such an approach, an example decision-making objective for a site where bioaccumulative contaminants are contributing to site risks would be:

> *Reduce to acceptable levels, by the year 2025, cancer risks for vulnerable subpopulations of adults and children exposed through ingestion of contaminated fish and shellfish taken from the site.*

This example objective contains specific information about the nature of the risks (the population at risk and the target exposure pathway), it includes opportunities for measuring progress (e.g., through monitoring fish tissue concentrations), and it is aligned with the intent of laws and policies governing the protection of human health. This objective should be supported by relevant metrics to evaluate progress, e.g., risk-based tissue concentrations established for different fish or shellfish species, specific collection areas that delineate "the site," and other collection guidelines. While a judgment about whether the objective sets a realistic goal is dependent on a number of project-specific considerations, including a specific time in the future when the objective is to be achieved provides a clear basis for quantifying progress and enforcing accountability with respect to the stated goal.

While the fundamental basis for decision-making objectives may be established by law and regulation, the specification of those objectives for a particular project will be determined, in large measure, by how the site-specific problem is framed in terms of risks and the values that stakeholders associate with the project's opportunities and constraints. As a part of our democratic institutions and processes, engagement with interested and affected parties is critical to ensuring that the problem is adequately framed, project objectives are aligned with the interests of those being affected by the risks, and trade-offs among the objectives can be adequately explored. Because values and interests vary among organizations and individuals, the sufficiency of the engagement will be related, to a significant degree, to ensuring broad representation from interested and affected parties. For the objectives and resulting decisions to be viewed as credible, the processes used to establish objectives and make decisions must be open, accessible, and understandable (i.e., the rules and logic employed must "make sense").

4. *Risk management is accomplished through open and transparent deliberative processes*

Deliberation refers to the processes used by the parties involved in a decision to communicate, consider issues and develop understanding (NRC, 1996). Deliberation is an essential component of risk-informed decision making. The number of interested and affected parties germane to risk management decisions concerning sediment is large. The diversity of values, attitudes and perspectives evident among these parties affects every aspect of the decision problem – conceptualizing what the problem is, how the problem should be analyzed, and what constitutes a successful solution. While there are many complex technical aspects to assessing risks and evaluating risk management alternatives, this fact does not justify the use of a technocratic approach, where a small, elite group of individuals drives decision making. That said, public meetings, by themselves, do not constitute proof that effective deliberation has occurred within a project, that information is being exchanged, and that the developed understanding is being incorporated into decision making.

The National Research Council (NRC) has produced an extensive series of reviews and recommendations regarding the practice of risk analysis within the Federal government that are germane to our consideration of deliberative processes. The NRC's *Understanding Risk: Informing Decisions in a Democratic Society* (NRC, 1996) states:

> *The analytic-deliberative process leading to a risk characterization should include early and explicit attention to problem formulation; representation of the spectrum of interested and affected parties at this early stage is imperative. The analytic-deliberative process should be mutual and recursive. Analysis and deliberation are complementary and must be integrated throughout the process leading to risk characterization: deliberation frames analysis, analysis informs deliberation, and the process benefits from feedback between the two.*

Among the many findings and recommendations made by the National Academies' Committee on Improving Risk Analysis Approaches Used by the USEPA (NRC, 2009), a number relate to the need for substantive improvements in the use of deliberative processes in risk analysis. On this point, the Committee's report entitled *Science and Decisions: Advancing Risk Assessment* states that:

> *Decision-making based on risk assessment is also bogged down. Uncertainty, an inherent property of scientific data, continues to lead to multiple interpretations and contribute to decision-making gridlock. Stakeholders – including community groups, environmental organizations, industry, and consumers – are often disengaged from the risk-assessment process at a time when risk assessment is increasingly intertwined with societal concerns. Disconnects between the available scientific data and the information needs of decision-makers hinder the use of risk assessment as a decision-making tool.*

The need for bolstering deliberation processes in connection to risk assessment and management is supported by the Committee's recommendation that USEPA "establish a formal process for stakeholder involvement in the framework of risk-based decision-making."

Decision making for contaminated sediment risk management is a complex undertaking. There is no single, authoritative decision maker for such projects. Many individuals and parties contribute to decision making and the roles, responsibilities and authorities of those individuals differ. While it is clear that decision making has become increasingly complex over time, the approaches and technology we apply to decision making has not kept pace with that complexity. Achieving effective deliberation will require more purposeful investment in "infrastructure" to support decision making, including appropriate governance structures, more sophisticated communication processes within and across the communities engaged within a project (different technical teams, agencies/organizations, public groups, etc.), and the analytical capability required to organize, evaluate and use information within deliberation.

5. *Uncertainties are acknowledged and addressed through quantitative analysis*

Confidence in the results of risk assessments, as well as the risk management plans based upon those results, is established through analysis and actions taken to address uncertainty and variability. *Uncertainty* refers to incompleteness of knowledge and *variability* refers to the heterogeneity associated with a particular attribute or quantity. As a simple example, the level of confidence in the results of a risk assessment for a PCB-contaminated sediment will be related to judgments regarding how complete the characterization of the relevant exposure pathways is (related to uncertainty) and how variability in key inputs (e.g., the amount of fish being ingested within the exposed population) is addressed within the assessment. Similarly, confidence in a risk management design or plan will be related to how knowledge of key processes affecting remedy performance is applied (e.g., how resuspension of sediments will affect the efficacy of a dredging remedy, how a particular storm event will affect a cap, etc.) and how variability in those processes is incorporated into the ultimate design and long-term management plan (e.g., variability in resuspension rates as a function of the distribution of debris or other impediments to dredging, variability in the hydrograph as a function of storms of different intensities, etc.). Recent experience has shown that uncertainty and variability can result in the need to make major modifications in risk management plans and remedy designs over time (e.g., United Heckathorn, Fox River, Hudson River).

Increasing confidence in the conclusions of risk assessment and the reliability of its products for use in decision making will be achieved by addressing uncertainty and variability in a quantitative manner, rather than relying upon the use of defaults, assumptions, or the adoption of "precautionary" measures or actions.

Quantitative uncertainty analysis encompasses methods for analyzing and propagating uncertainty and variability within an analysis (e.g., through the use of one- and two-stage Monte Carlos simulation) (NRC, 2009). While acknowledging that the USEPA has developed guidance for conducting uncertainty analysis within its programs, NRC (2009) states that "EPA does not have a consistent approach to determine the level of sophistication or the extent of uncertainty analysis needed to address a particular problem." NRC (2009) further recommends that "EPA should encourage risk assessments to characterize and communicate uncertainty and variability in all key computational steps in risk assessment..." and that "Uncertainty and variability analysis should be planned and managed to reflect the needs for comparative evaluation of risk-management options."

In some cases, more data and time will be required to quantitatively address the uncertainties confronting a project. An example of this would be cases where there is a need to replace qualitative arguments with quantitative arguments. One of the major focal points of conflict in regards to remedial decision making is determining the extent to which removal and in-place technologies will be used to achieve the project's decision-making objectives (e.g., dredging vs. capping). In many cases, the position against the use of capping is based upon qualitative arguments related to uncertainty in the performance of caps over time, e.g., that the cap would be vulnerable to disruption by a future storm/flooding event. The need to consider such physical processes in regard to the performance of capping is certainly justified. However, raising a question (Could the cap be compromised by a future storm?) is *not* equivalent to quantitative evidence against capping. Performing a quantitative analysis of performance in which alternative cap designs are subjected to different hydrodynamic conditions to determine effects on contaminant exposure and risk is well within the bounds of currently available methods. Performing such an analysis would reduce uncertainty regarding the performance of capping and would itself include opportunities to give careful attention to the treatment of variability (e.g., in future hydrodynamic conditions). It is also necessary to point out that *informed* decision making is not being served when the treatment of uncertainty is focused only on a subset of risk management alternatives, rather than all of the alternatives under consideration. It is clear from the complications experienced at some dredging projects that insufficient consideration has been given to uncertainty and variability in respect to dredging (Bridges et al., 2010a, b). Failure to give equivalent attention to the handling of uncertainty and variability across the range of alternatives under consideration will not "...reflect the needs for comparative evaluation of risk-management options" (NRC, 2009) nor produce satisfying risk management outcomes.

The ultimate "pay-off" for investing analytical effort in quantitatively addressing uncertainty and variability is increased confidence in remedial investigations and feasibility studies and, ultimately, remedial decisions that produce better outcomes.

6. *Risk management investments are commensurate with the magnitude of the risks and uncertainties*

To state it simply, bigger problems justify larger costs to solve those problems. The magnitude of risks posed by contaminated sediments at a site will be a function of the size of the contaminated area (and the total area that the contaminated zone influences), the size of the exposed populations (human or ecological), the vulnerability of the exposed populations (e.g., sensitive sub-populations of people, threatened or endangered species), the magnitude of adverse effects caused by site-related exposures (e.g., low vs. high toxicity), and the duration over which the adverse effects are expected to persist. The nature and magnitude of risks associated with contaminated sediment sites in the United States and elsewhere varies broadly, from those imposing large risks on human health and the environment to those whose influence is felt largely through an incremental contribution to impaired water body conditions caused by a range of factors (e.g., nutrient loading, pathogens, habitat loss, etc.).

The costs that are incurred in efforts to reduce risks can take a variety of forms. There are the direct monetary costs of funding the design, construction, and maintenance of remedies such as dredging and capping. Indirect monetary costs could include restrictions on future uses of the waterway (e.g., recreational or commercial uses) and effects that management actions could have on property values. An example of costs imposed in the form of constraints on future uses would be a case where the use of capping at a site imposes restrictions on future navigation dredging, which could result in the loss of opportunities to pursue local economic development. The costs associated with implementing a remedy may also take the form of direct damage to the environment. For example, the act of dredging disturbs sediment habitat. The resulting damage may be mitigated through actions that occur after dredging (e.g., passive habitat construction through natural processes and recruitment or active construction through engineering); however, mitigating the damage to some habitats can be difficult to accomplish (e.g., sub-aquatic vegetation, wetlands, etc.). Direct and indirect costs can also be mitigated by economic benefits associated with cleanup, such as redevelopment and increased recreational usage (e.g., Stoll et al., 2001).

The need to consider, weigh and balance the benefits to be achieved by actions taken in the name of risk management against the costs associated with those actions has been an active topic of discussion within the sediment community (e.g., Pavlou and Stansbury, 1998; Wenning et al., 2006). This discussion has been a response to experience implementing remedies and the complexities those experiences have revealed. These experiences provide additional emphasis for the need to give careful attention to developing and updating a project's decision-making objectives (risk management principle #3) and the importance of the processes needed to facilitate effective deliberation (risk management principle #4). The simple economic principle at play in these considerations is that it is inefficient to accept more costs than necessary to achieve your objectives. If you can achieve your decision-making objectives by spending \$10 million, then it would not be rational to spend \$20 million to accomplish the same objectives (irrespective of whose money is being spent or whose "ox is being gored" in the case of indirect costs). One response that can be expected to this simple argument would be that decision makers may be willing to spend more (the \$20 million) if they had reason to believe that the additional costs would produce compensating benefits (e.g., greater confidence in the ultimate success of the risk management plan). However, this response merely serves to further emphasize the importance of developing a comprehensive and robust set of decision-making objectives to guide analysis and deliberation. When undeclared or hidden objectives are imposed upon decision making, the process loses credibility, which can result in bad outcomes (e.g., litigation, project delays, remedy failures, disputes over the definition of project success, etc.).

In developing risk management plans, costs are also incurred in the process of addressing uncertainties. Risk management is a scientific enterprise (risk management guideline #1) and is therefore based upon evidence produced from data and analysis. If the costs of making the wrong decision are high, either for the environment or for the organization providing the capital to execute the decision, then there should be less tolerance for uncertainty, in comparison with cases when the costs of being wrong are lower. In relation to this point, we note that not all uncertainties "are created equal," i.e., some uncertainties matter more than others because they are expected to have a greater effect on the decision under consideration. In general, the greater and more consequential (for decision making) the uncertainties are, the greater the investment that should be made to address those uncertainties. Much time and effort is expended by project teams in wrestling with the problem of prioritizing investments in data collection and analysis to address uncertainties prior to remedy selection. However, given that it is not possible to completely resolve or eliminate uncertainties associated with the performance of remedies, developing more formal processes for managing uncertainty throughout the lifespan of a project will increase the likelihood of achieving the project's objectives in a timely manner. The review of past and current sediment projects described within NRC (2007) reveals the need for much greater investment in monitoring as a component of managing uncertainties after a remedy is selected and implemented.

One final point to be made concerns the nature of the analyses that are conducted relative to costs and benefits. Much of the evidence or argumentation that is developed on costs and benefits in the context of contaminated sediment projects is qualitative and uncertain. The use of quantitative approaches and analyses in support of considering, weighing and balancing costs and benefits will strengthen risk management decision making (e.g., Efroymson et al., 2003; ASTM, 2006; Sparrevik et al., 2011).

7. *Risk management is a system-scale activity*

Sediments are part of a complex system. The physical domain of the system includes the water body, the adjoining land and the activities occurring on the water and land, the hydrology of the system, the physical and chemical processes affecting contaminant fate and transport, and the physical components of ecological habitats and ecosystems. The biological domain of the system includes the ecological and human receptors within the system, the biological processes affecting exposure to contaminants (e.g., the movement and feeding behavior of receptors, contaminant degradation processes, etc.), and the processes giving rise to adverse effects and impacts (e.g., toxicology). The socioeconomic domain includes a variety of uses and services supported by the water body including drinking water supply, transportation, recreation, food supply (commercial, recreational, subsistence, cultural), other ecosystem services connected to economic activity (e.g., removal of waste products); and the laws and regulatory processes relevant to the system. The processes and interactions occurring within each of these domains represent one level of complexity. Interactions occurring across the domains give rise to higher orders of complexity.

Evidence of the growing importance of "systems thinking" in the context of environmental risk assessment and management can be found in the attention being given to cumulative risk and cumulative risk assessment (USEPA, 2003; NRC, 2009). Cumulative risk refers to the combination of risks posed by exposure to multiple stressors from all routes, pathways and sources (NRC, 2009). This definition is understood to include both chemical as well as non-chemical stressors, including biological (e.g., disease organisms), psychological, and social stressors. In the context of managing risks posed by contaminated sediments, the consideration of cumulative risks could include chemical exposures originating outside the site in question (e.g., through industrial air emissions), the psychological stress associated with living near a hazardous waste site, and adverse effects attributable to living in an economically depressed community. The value of broadening the scope of adverse effects considered in the context of Superfund "mega-sites" has been noted by previous reviews (NRC, 2005).

The system under consideration contains numerous processes, many significant interactions, and a whole series of dependencies that enable effects or actions taken in one domain to propagate across the system, giving rise to expected as well as unexpected effects. The relevance of these points to risk management is that decisions taken to reduce risk must take into account not only the benefits sought with respect to the specific targeted risks, but also the countervailing risks that may be created by the risk management action itself. The desire to view problems and solutions in simple terms, outside of a system context, has led to many unsatisfying risk management outcomes.

Countervailing risks occur when actions taken to reduce one risk result in increasing other risks. The reality of countervailing risks has given rise to a long-standing discussion of risk-risk trade-offs in the context of human health and environmental policy, regulation and decision making (Graham and Wiener, 1995). Simple examples of countervailing risks include side-effects in medicine, collateral damage in military engagements, and unintended consequences in policymaking (Graham and Wiener, 1995). This discussion has produced a typology that can be used to inform analyses of risk-risk trade-offs (Graham and Wiener, 1995; for a specific example see Gray and Hammitt, 2000). When the countervailing risk affects the same population and generates a risk of the same type it is referred to as a risk offset; if it generates a risk of a different type it is referred to as a risk substitution. When the countervailing risk affects a different population and produces a risk of the same type it is called a risk transfer; if it produces a risk of a different type it is called a risk transformation.

Examples of countervailing risks for contaminated sediment sites can be used to illustrate the nature of risk-risk trade-offs. A risk offset or risk transfer can be produced when the risk management action involves the transport of contaminants, giving rise to new exposure pathways. Resuspension during dredging can result in redistributing contaminants and exposures within the same population or to different populations (e.g., in the case of rivers where contaminants mobilized through dredging can be transported many miles from the removal location). Relocation of contaminated sediments to upland management sites poses risks to populations in the vicinity of the disposal location, e.g., through volatile emissions, dust, contact as a result of trespassing, a future engineering failure at the site resulting in release of the contaminated material, etc. (specific examples of all of these could be cited to substantiate the reality of these scenarios). Institutional controls in the form of fishing restrictions and bans, which are intended to deflect fishing activity away from the site in question, could lead to fishing at other contaminated sites that are not currently subject to fishing restrictions. Examples of risk substitution and transformation would include accidents and fatalities associated with implementing the remedy (which can take many years to complete), negative effects that management actions may have on the local economy through restrictions on future uses of the water body and/or negative effects on property values (the positive relationship between personal wealth and health is well established), negative effects on ecological receptors due to structural changes in habitats and ecosystems caused by remedial actions (e.g., through dredging and/or capping), and negative effects on human quality of life and well-being associated with degraded ecosystems.

Informed decision making for contaminated sediments should include formal analysis of risk-risk trade-offs. Doing so will entail developing an expanded notion of remedy effectiveness within a systems context. It is certainly possible to develop a simplistic definition of remedy effectiveness by taking a narrow view of law, regulation and policy that constrains the definition of the problem and the scope of the solution. However, the purpose of risk management is to seek improvements that optimize outcomes within the system as a whole, rather than simply moving risks and impacts across the domains of the system.

8. *Risk reduction is most reliably achieved through the use of an integrated network of multiple remedial technologies and actions*

In the “early days” of contaminated sediment remediation, it was (naively) thought that the desired level of risk reduction could be routinely achieved by simply removing the offensive material from the water body through dredging. Experience and less-than-satisfactory outcomes are reshaping this attitude within the regulatory and technical community. Dredging has proven itself to be a complicated engineering activity that includes many uncertainties (Bridges et al., 2010b) and moving parts that must be intensively coordinated and managed (Palermo et al., 2008). In fact, despite widespread application of dredging to address contaminated sediments, its effectiveness as a remedial technology has yet to be firmly established (NRC, 2007). While pockets of intellectual resistance may still exist in some quarters, the emerging consensus is that effective risk management at the vast majority of contaminated sediment sites will involve a combination of MNR, capping and dredging applied to match site-specific conditions.

The technical problem confronting risk management is determining what the most effective combination of technologies will be for a particular project or site. Technical guidance and policy regarding remedy selection for contaminated sediments sites has been published by USEPA (2005) and numerous feasibility studies have been completed and many are underway. While current experience demonstrates that best practice for integrating a combination of remedies is still evolving, there are some germane facts and principles that should be considered.

What worked for one site may not work for another site. That is not to say that experience and knowledge are not transferrable. However, given the dominant role that site-specific factors and processes play in shaping risks at contaminated sediment sites, the strategies and technologies that "worked" at one site may not work at another. USEPA policy is that there is no "preferred" remedy or technology for contaminated sediments sites, and that remedy selection is site-specific (USEPA, 2005).

The processes contributing to MNR are operating at all sites. MNR achieves risk reduction through the influence of natural processes, specifically (1) contaminant transformation, (2) changes in contaminant mobility/bioavailability through sorption and binding processes, (3) changes in exposure through sediment deposition, erosion, mixing and contaminant burial, and (4) contaminant dispersion, diffusion, and transport (Magar et al., 2009; Chapter 9 in the current volume). These processes, the rates of these processes, and their effect on risk reduction over time represent the baseline condition, in the absence of any engineered intervention. As a means of defining an integrated remedy for a site, the logical questions to ask, in sequence, are:

1. How much progress toward the project's objectives can be achieved through MNR?
2. What engineering interventions should be added to MNR in order to realize the project's objectives?
3. What is the most efficient and effective combination of those interventions?

Efficient technology integration will seek to achieve the project's objectives in a way that minimizes overall costs. The costs that we are considering here include the monetary costs of implementing the remedy, the costs (both monetary and nonmonetary) associated with countervailing risks associated with the remedy, as well as costs in the form of lost opportunities. Efficiency, in this sense, provides the impetus for beginning a remediation with less invasive approaches or technologies that can be more easily modified, or even undone, if the desired risk reduction trajectory is not being met. Such an approach would be analogous to a treatment regime that a physician may prescribe for a patient experiencing severe back pain, where pain relief is sought through a combination of medication and physical therapy before a commitment is made to surgical intervention. The monetary and non-monetary costs (including countervailing risks) of invasive intervention warrant first exploring the efficacy of less invasive measures.

9. *Risk communication is integral to effective risk management*

Risk communication, fundamentally, refers to an exchange of information that supports making informed judgments about risks. In practice, the term *risk communication* is commonly used in reference to efforts to communicate about risks with stakeholders, laypersons, and other interested or affected parties. The field of risk communication has grown considerably over the last 20 or more years and includes many active areas of research that have provided useful insights and tools related to the psychology of risk perception, cognitive heuristics,

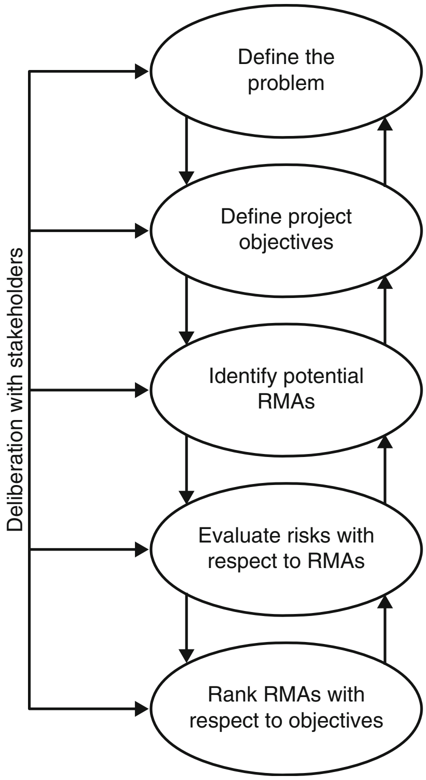

Figure 8.2. Simplified decision-making framework based on NRC (2009). RMAs – risk management alternatives.

mental modeling, etc. that are being applied to a range of different risk problems (NRC, 1989; Morgan et al., 2002; Lundgren and McMakin, 2009). The depiction of risk analysis as the integration of risk assessment, risk management and risk communication in Figure 8.1 more accurately reflects the aspirations of the technical community within risk analysis rather than the *current* state of practice within government agencies and programs. Many of the criticisms and recommendations addressing weaknesses in current practice relate directly to deficiencies in risk communication.

NRC (2009) proposes a framework for risk-based decision making that is composed of three phases: (1) problem formulation and scoping, (2) planning and conduct of risk assessment and (3) risk management. The framework is organized to emphasize two critical points.

First, the framework is focused on the central purpose of evaluating and comparing risk management options: Phase 1 frames the problem and identifies the risk management options for reducing unacceptable risks; Phase 2 evaluates the risks under baseline conditions as well as the effect that each identified risk management option would have on those conditions; and Phase 3 includes a comparison of the relative benefits, costs and uncertainties associated with each risk management option. The framework is organized in this fashion to ensure that the products of risk assessment serve the purposes of decision making, i.e., by providing information to distinguish alternative risk management actions from each other in terms of the degree to which they satisfy the project's objectives. These activities are represented in the simplified framework depicted in Figure 8.2.

Second, the framework emphasizes that communication with stakeholders is critical to the integrity of the decision-making process. On this point, NRC (2009) states the following:

> *A critical feature of the framework is related to stakeholder involvement. A continuing theme in earlier National Research Council and other expert reports on risk assessment, and loudly echoed in opinions offered to the present committee by many commenters, concerns the consistent failure to involve stakeholders adequately throughout the decision process. Without such involvement, the committee sees no way to ensure that the decision process will be satisfactory; indeed, without such involvement, it is inevitably deficient.*
>
> *It is time that formal processes be established to ensure implementation of effective stakeholder participation in all stages of risk assessment.*

While acknowledging that USEPA has many programs and guidance documents related to stakeholder engagement and in many cases makes a substantial effort to engage the community (e.g., NRC, 2005), the recommendations made within NRC (2009) represent a call to stretch beyond current practice in regard to risk communication. An example in this regard is USEPA Superfund's Community Involvement Toolkit. The Toolkit was first published in 2001 (with updates in 2005) with the intent of providing Superfund project teams "with a practical easy-to-use aid for designing and enhancing community involvement activities" (USEPA, 2010b). However, the Toolkit is a collection of over a 100 separate documents, templates, and brochures that are intended to be "adopted, combined, or reinvented, as needed..." (USEPA, 2010b). One of the documents included in the Toolkit is entitled "Risk Communication" (USEPA, 2002). This document includes six pages of descriptive text about risk communication followed by a listing of related resources. In asking whether risk communication is a "required activity" within Superfund, the documents states "No. Although the specific communication techniques contained in this tool are merely suggested, the general process of risk communication can be construed as implied by the NCP" (USEPA, 2002).

The "decide and defend" model of public engagement, whereby a government authority independently decides what needs to be done then crafts a message to convince the public that it has made the correct decision, is no longer viewed as sufficient or acceptable practice. Current practice in risk communication is built upon a two-way model of communication between government and the interested and affected parties to a decision. Drawing upon and applying risk communication science is essential to making progress toward the goal of informed decision making that seeks optimal risk management outcomes. Such an approach will ensure that risk management problems are adequately framed, the assessment of risks is sufficient to the needs of decision making, and that the risk management options are evaluated and compared in a manner that is consistent with the values and objectives of the parties the decision is intended to serve.

10. *Risk management is achieved through formal application of adaptive management*

Risk management of contaminated sediments is a complicated undertaking. The relevant systems and processes are complex. Deliberation concerning risk management actions involves a diverse range of interests, values and stakeholders. Uncertainties limit the accuracy of predictions about risk management outcomes. These facts argue for the need to develop and apply a formal adaptive management process to contaminated sediment projects.

Much has been written on the topic of adaptive management, including its application to water resources planning and contaminant remediation activities (NRC, 2003, 2004; Linkov et al., 2006a, b; Satterstrom et al., 2007); however, it is arguably the case that relatively little progress has been made over the last 10 years with regard to the application of formal adaptive management to sediment remediation activities. The basics of the adaptive management process are straightforward enough: objectives for an action are established, monitoring

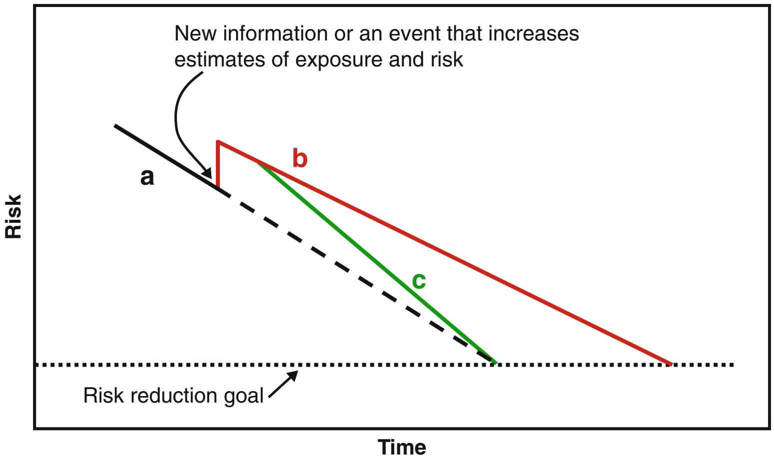

Figure 8.3. Simple illustration of adaptive management. (a) represents the desired and expected risk reduction trajectory at the point when the original remedy is implemented. (b) is a revised risk reduction trajectory that is developed from monitoring data that indicates higher exposure rates and risk based on new information or an event (e.g., a storm uncovers contaminated sediment). (c) is the expected trajectory after the remedy is adapted in order to meet the risk reduction goal.

is planned to evaluate attainment of the objectives, the action is taken, monitoring is implemented, monitoring results are evaluated to ascertain attainment or progress toward the objective, and those evaluations provide the foundation for learning and adaptation in the form of future actions. A simple case illustrating the need for adaptive management is presented in Figure 8.3. In this example, monitoring effort is critical to detecting the change in conditions that allows the remedy to be adapted so that the risk reduction target can be met (i.e., an acceptable risk level at a specified point in the future). The earlier the elevated risk condition is detected through monitoring, the greater the opportunity to minimize risk over the recovery period. In the absence of adequate monitoring, the elevated risk level would persist.

One of the chief impediments to progress with respect to adaptive management is the long (in duration) and predominantly linear decision process applied to cleanup projects, whereby a remedial investigation and baseline risk assessment leads to a feasibility study and ultimately a decision to select a remedy. Notwithstanding the requirement to review a project's remedy every 5 years, there is relatively little in the way of incentive or formal mechanics to promote learning at the project or programmatic level. Evidence for this assertion is found in the lack of investment that has been made in performance monitoring of remedies. The NRC committee charged with evaluating the effectiveness of remedial dredging reviewed existing documentation for 26 dredging projects. Due to the inadequate state of past monitoring investments and practice, the committee "could not generally establish whether dredging alone is capable of long-term risk reduction" (NRC, 2007). Performance monitoring data represents the energy that fuels adaptive management; without that energy there is no adaptive management.

Previous reviews and analyses have identified six key elements of a formal adaptive management process that embodies the risk management guidelines put forward in this chapter (Linkov et al., 2006a, b; Satterstrom et al., 2007).

1. Specific risk management objectives are established. Stakeholders are actively engaged in the development of the project's objectives. These objectives are reviewed and can be

updated as new information is generated over the course of the project, per an agreed upon adaptive management plan.

2. A model of the system(s) being managed is developed to integrate current knowledge of the system, to evaluate risk management options, and to provide the basis for interpreting the results of performance monitoring of the management options. The model is updated as new information and understanding about the system is developed. Model updating provides immediate benefits from learning.
3. A range of management options for reducing risks is developed through active engagement with stakeholders. Most contaminated sediment sites will make use of multiple remediation approaches (e.g., MNR, capping, dredging). Early implementation of these approaches will enable the testing of hypotheses and the development of conclusions that can be used to optimize the integrated network of remedial technologies over time.
4. A performance monitoring program is designed and implemented for the array of deployed technologies. The data developed from this monitoring are interpreted using the developed system model. An evaluation of the remedies is conducted by comparing monitoring results with the project's objectives and the metrics that were established to gauge progress toward those objectives.
5. A formal process is developed and used to incorporate the products of learning into project decisions, as well as the decisions of other projects in the program. The process is developed by defining the logic, relevant decision thresholds, and contingent actions that are to be taken in relation to monitoring results. This process provides structure and transparency for future decision making (Satterstrom et al., 2007). It also provides the means for transferring the knowledge gained to other projects within the overall program.
6. A collaborative structure and process for engaging stakeholders is used to foster broadly based participation, learning and risk communication. Optimizing the network of remedial technologies, while resolving uncertainties over time, is a dynamic process that requires active and sustained dialogue regarding the complex array of trade-offs that are germane to such projects.

Some key distinctions can be made by comparing the three management models depicted in Figure 8.4 (Linkov et al., 2006b). Following the traditional management scheme, broadly framed project objectives may be established (in contrast to SMART project objectives). The risk management plan is developed from information provided by site investigations and studies. The implemented remedy may or may not be closely monitored (represented by the dotted-line box) and the remedy is evaluated at some point in the future (e.g., 5-year review) using a pre-defined or ad hoc process. The remedy is subject to modification only if there is evidence indicating that the remedy has failed. Following *passive adaptive management,* only one risk management approach is deployed. The formalism and structure of a system model plays a large role in formulating that approach and in evaluating the results of monitoring. The performance of the strategy is closely and continuously monitored for the purpose of conducting a formal evaluation that uses a pre-defined process and set of performance metrics. Early opportunities to adapt and optimize the performance of the strategy are identified. *Active adaptive management* involves the simultaneous deployment of multiple approaches or remedial strategies (e.g., MNR, capping and dredging, or different combinations of these) in association with close and continuous monitoring for the purpose of identifying distinctions and insights that can be used to adapt, optimize and learn. Following an adaptive management

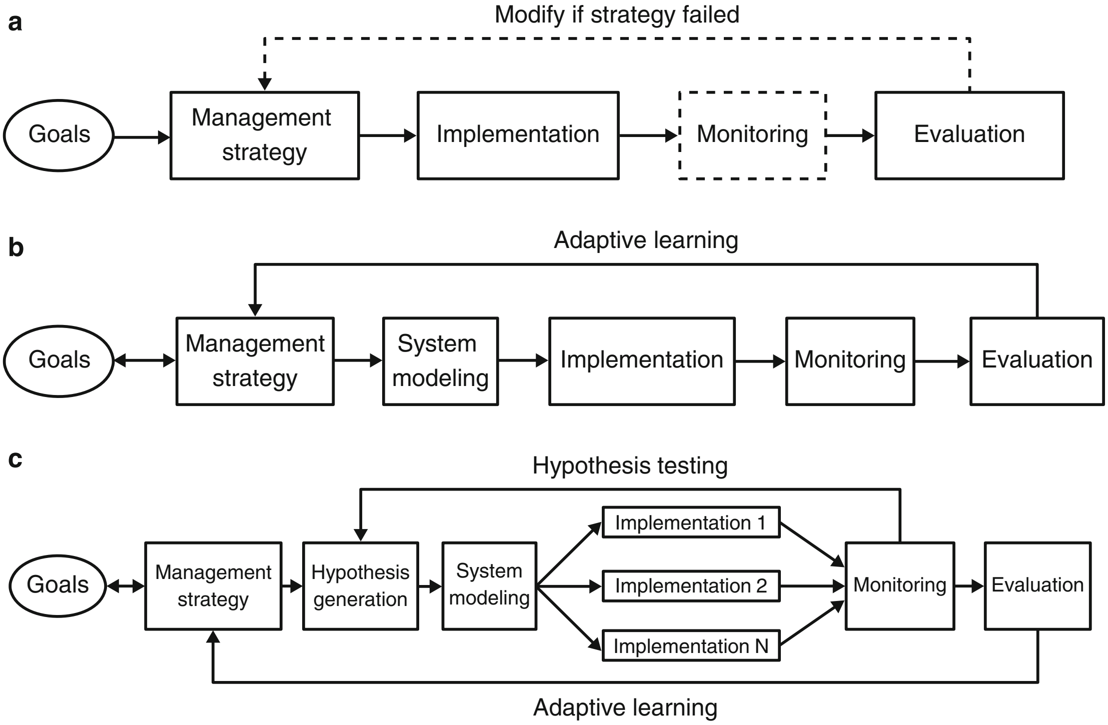

Figure 8.4. Three management models illustrating the distinctions between (a) traditional management, (b) passive adaptive management, and (c) active adaptive management (adapted from Linkov et al., 2006b).

model, in contrast to traditional management, changes are expected and discussed, learning is emphasized, and project objectives are updated based on monitoring results, changing societal values, or institutional learning.

Adaptive management offers the means for accelerating the delivery of risk reduction benefits. It is not uncommon for many years or decades to transpire between the point at which a site is identified and the construction of a remedy begins, where significant portions (if not all) of that time is consumed by one or more rounds of remedial investigation and feasibility study. The complexity and uncertainties associated with these projects certainly contributes to this protracted schedule. However, more rapid progress could be achieved by adopting a decision framework like the one recommended by NRC (2009) that pushes the identification of potential risk management options to the front of the process. Once sufficient evidence is accumulated to support a conclusion that the contaminated sediments pose an unacceptable risk, there will come a point at which a threshold of diminishing returns is reached in efforts to resolve uncertainties through the collection of additional baseline data or bench-level investigations. We argue here that promising remedial approaches should be deployed during the early stages of the project (i.e., before or as a part of remedial investigations and feasibility studies), at field-relevant scales (as contrasted with small-scale pilot studies or technology demonstrations), in order to address decision-relevant uncertainties regarding risk management alternatives in a manner consistent with active adaptive management. Obviously, logic and guidance must be developed to inform the timing and scope of such investments, but the benefits of pursuing such a course will be realized in terms of more rapid and cost efficient provisioning of risk reduction benefits.

8.4 THE PATH TO MORE EFFECTIVE RISK MANAGEMENT

Risk management is a process. As such, it is reasonable to consider how the process can be improved in order that decision making provides efficient and effective risk reduction. We propose three broad themes in respect to improving the process: structure, quantitation and innovation.

8.4.1 Structure

The risk management guidelines we have chosen to emphasize (any listing of ten guidelines cannot be considered exhaustive) point to the need for additional structure within the risk management process. The goal in this respect is to develop a more deliberate formalization of good practice that serves the purpose of implementing risk management principles and policy. The goal is not to develop an invariant recipe for risk management that ignores the diversity of conditions that exist. Rather, structure, in the sense espoused here, is provided by assembling and consistently applying a risk management framework that encompasses a set of rigorous methods, tools and procedures. The framework guides the implementation of a program's risk management principles and guidelines and provides the means for ensuring accountability. This structure provides the means for achieving consistent practice across a program that includes many individual projects across a local area, region or country. The goal is risk management practice that considers technologies in an objective and neutral fashion, while sustaining progress toward desired risk reduction outcomes.

The value of developing more structure within the risk management process can be illustrated by describing the use of decision analysis within risk management (Clemen, 1996; Kiker et al., 2005). One of the overarching challenges within risk management is organizing and maintaining progress in regards to decision making. Decision analysis represents a set of methods for structuring, guiding and informing decision making. Using these methods, the results produced by risk assessment and the evaluation of risk management options can be integrated, in a quantitative fashion, with data concerning stakeholder values and attitudes regarding the project's decision-making objectives. This integration enables the risk management alternatives to be quantitatively scored and ranked (e.g., through the use of utility theory) in terms of the degree to which they satisfy the project's objectives. This approach to analysis and deliberation supports the process of organizing deliberation among interested and affected parties, developing robust decision-making objectives, evaluating and comparing risk management options in terms of those objectives, and exploring trade-offs among the objectives and risks. One of the primary benefits that decision analysis offers is it provides the structure and means to explore issues germane to decision making in a systematic, rational, and efficient manner that supports more transparent and credible decision making. Examples of the application of decision analysis to environmental decision making includes a broad range of problem types (Linkov et al., 2004; Kiker et al., 2005), including sediment management (Linkov et al., 2006c; Yatsalo et al., 2007; Kiker et al., 2008).

8.4.2 Quantitation

The use of numbers and mathematics to define, explore and solve problems introduces a definitive set of rules and logic to problem solving. For example, all contaminated sediment projects make use of mathematical modeling; credible modeling requires conformation to a set of logical constraints, e.g., that $2 + 2 = 4$, conservation of mass, etc. For risk management to be a scientific enterprise, it must employ quantitative methods. However, the extent to which quantitation is used across the activities comprising risk management varies. Most of the activities within risk assessment involve the use of quantitative methods, including the measurement of contaminant properties, fate and transport modeling, toxicity testing, etc. The engineering studies supporting remedial design are highly quantitative. However, other critical aspects of risk management are less commonly treated in a quantitative manner, including: the development of decision-making objectives that fail to include quantitative targets; the use of defaults, safety factors and other devices in lieu of quantitative uncertainty analysis; qualitative and incomplete treatment of trade-offs in decision making; inadequate investment in performance or remedy effectiveness monitoring; etc. It makes little sense to require a high level of quantitative specificity for some tasks while pursuing other activities that have an equal or even larger affect upon decision making through the use of informal or qualitative approaches. Such disparities are partially the result of the disciplinary background and experience represented on project teams; for example, if project teams included social scientists in addition to physical scientists and engineers, then remediation projects could benefit from quantitative approaches in stakeholder engagement, risk communication and decision-making processes.

All projects confront the need to apportion investment across the numerous activities comprising the project, including the conduct of studies, data collection and modeling. The rationale that is used to guide such investments should be directly tied to the specific needs of decision making. The decision analytic methods discussed previously can be used to explore, quantitatively, the implications of uncertainty in terms of decision-making outcomes. Decision modeling supports decision making under uncertainty, where a choice must be made between multiple actions whose outcomes are uncertain (Schultz et al., 2010). Value of information (VOI) analysis can be used to optimize investments in data collection by identifying the uncertainties with the greatest influence on the choices to be made among multiple alternative actions. Given the numerous sources of uncertainty involved in assessing risks and evaluating risk management options, the benefit of VOI is that it provides the means for quantifying the expected benefit of reducing uncertainties so that data collection efforts can be targeted and prioritized for maximum effect. In the context of its recommendations for "advancing risk assessment" practice within USEPA, NRC (2009) provides a description of different VOI methods and makes specific recommendations on the use of these in relation to risk assessment and risk management decision making. VOI has been applied to a range of environmental management problems (e.g., Yokota and Thompson, 2004), including contaminated sediments (Dakins et al., 1996), and expanding its use would help support a quantitative, decision-oriented structure for informing planning for data collection and analysis.

8.4.3 Innovation

The complexity of contaminated sediment projects, the magnitude of the challenges they pose, and the environmental, social, and economic costs involved all point to the need for more innovation in risk management practice. Transforming practice requires a commitment to change, experimentation, and learning. Change is rarely easy. In fact, when it comes to changing long-held approaches and practices, organizational and individual resistance is to be expected. For these reasons, a commitment to transforming practice must be sustained over the long-term. We must be willing to experiment with new approaches, learn from those experiences, and carefully consider the lessons learned (both the failures and successes) as a part of establishing new standards of practice. The scope and current state of contaminated sediment risk management calls for innovation in technology and process.

It is arguably the case that sediment remediation presents greater challenges than traditional land-based cleanups. While it is true that our collective appreciation and understanding for these challenges has grown over the last 25 years, there has been relatively little innovation over this period in how risks from contaminated sediments are managed. Most projects over this period have relied upon dredging as the primary means for achieving risk reduction, a smaller number of projects have made use of capping, and an even smaller subset have made explicit use of MNR. More recently, focused energy has been directed to research and development of new technologies, including *in situ* approaches (e.g., see Chapter 11 and Chapter 12, in this volume). In our view, significant opportunities exist for developing and applying approaches that are consistent with the notion of *enhanced* MNR, such as thin-layer capping (Merritt et al., 2010; Chapter 9 in this volume) and treatment technologies that minimize disturbance to valued habitats and the environment as a whole. However, impediments to innovation exist.

The process leading to the successful introduction of a new technology into practice (the definition of innovation) begins with discovery – the emergence of new ideas and insights. Discovery is supported by investments in monitoring and subsequent analysis that identifies the scope of the problem as well as opportunities. Invention is the next step in the process whereby new ideas are further developed and converted into new science and technology. Invention is the primary domain of research and development. The transition from discovery to invention will be advanced in cases where organizations value the research enterprise and prioritize and focus investments accordingly. This transition will be impeded when extreme forms of an action-oriented posture give rise to attitudes that can be identified by the refrains “Don’t study the problem to death,” “Paralysis by analysis,” and “Don’t turn this into a research project.” The transition from invention to innovation has been called “The Valley of Death” in the context of commercialization (Auerswald and Branscomb, 2003). In our present context, the three most prominent hazards an invention faces in the “Valley of Death” are dedication to precedent, risk aversion, and uncertainty. The existence of these hazards speaks directly to the need for developing guidance on how to employ innovative approaches in the context of risk management. Clearly, a new technology or approach would have to offer some advantages in terms of greater or more rapid risk reduction, lower costs, conserved habitat, etc. compared with existing approaches. However, the decision to apply an inventive technology or process should be matched with a plan for managing the risks and uncertainties attendant to using a new approach. Addressing the large volumes of contaminated sediment that exist worldwide in a timely and effective manner will require a combination of innovation and guidance.

8.5 CONCLUSIONS

Our purpose here has been to present an overview of the challenges involved in managing the risks posed by contaminated sediments and to identify the elements of good risk management practice. Risk management is a collaborative undertaking. In the context of contaminated sediments, government, industry, and the numerous interested and affected parties involved will define the scope of the risk management problem and the objectives that will guide development of a solution to that problem. A team of professional scientists and engineers, guided by the decision-making objectives established for the project, will collect and analyze data in order to produce the scientific evidence needed to formulate answers to questions, reasoned conclusions, and, ultimately, a risk management plan. Developing and implementing that plan, along with the adaptive management process needed to manage residual risks and uncertainties, will be the product of a deliberative process that engages decision makers, stakeholders, scientists, and engineers. The challenges to be confronted in this collaborative undertaking are significant, but our hope is that the guidelines we have briefly discussed here will help inform the development of good risk management practice in the future.

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CHAPTER 9

MONITORED NATURAL RECOVERY

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9.1 INTRODUCTION

Monitored natural recovery (MNR) of contaminated sediments is a remedial approach that relies on natural physical, chemical, and biological processes to isolate, destroy, or otherwise reduce the bioavailability or toxicity of contaminants (USEPA, 2005a; NRC, 1997). Like other sediment remedies, MNR typically includes contaminant source control, site investigation, development of a conceptual site model (CSM), and long-term monitoring. Unlike other remedies, MNR does not include a construction phase; however, it is not a "no-action" approach. If monitoring indicates that recovery is not proceeding as predicted, site managers may implement enhanced MNR (EMNR, discussed later in this chapter), combine MNR with other remedies such as capping, removal, or institutional controls, consider alternate remedies, or adjust expectations of MNR recovery (Magar et al., 2009).

Site-specific evaluation of MNR as a candidate remedial approach entails refining the CSM by developing lines of evidence to demonstrate whether natural recovery is occurring (or would occur following adequate source control), estimating the recovery rate, and evaluating uncertainties associated with the remedy. If MNR is selected as a remedy or remedy component, monitoring is implemented to verify with adequate certainty the continuing effectiveness of natural processes and quantify the risk reduction trajectory (Magar et al., 2009).

Building a site-specific understanding of natural processes is worthwhile even at sites where constructed remedies are contemplated (Magar and Wenning, 2006; USEPA, 2005a; NRC, 2001). Environmental scientists and managers should recognize that natural processes are always ongoing; the overall success of remedial action may be enhanced by combining natural recovery processes with other engineering approaches.

MNR relies on four natural processes that act to reduce human health and ecological risks associated with contaminated sediments (Magar et al., 2009; USEPA, 2005a; Reible and Thibodeaux, 1999):

1. **Chemical transformation:** Changes in chemical structure or valence state achieve risk reduction to the extent that transformation processes eliminate, detoxify, or reduce the bioavailability of the contaminant. Mechanisms include abiotic or biological degradation or mineralization of organic compounds. Redox transformations are also included in this category, particularly if they are not readily reversible under reasonably anticipated environmental conditions.

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2. **Reduction in contaminant mobility or bioavailability:** Sequestration of contaminants via sorption or precipitation achieves risk reduction to the extent that it minimizes the potential for human or biological exposure.
3. **Physical isolation:** Natural sediment deposition segregates contaminated sediments from organisms through several mechanisms, including burial beneath cleaner surface sediment, dilution of contaminated surface sediment by mixing with cleaner sediment, consolidation and cohesion of the sediment bed, and natural sediment winnowing and bed armoring. The resulting physical isolation achieves risk reduction by reducing chemical exposures in surface sediment (where biological receptors come into contact with sediment) and by reducing the potential for resuspension and transport of contaminated sediments.
4. **Dispersion:** Chemical dispersion, through resuspension and transport of contaminated sediments or dissolution and transport of dissolved contaminants, achieves risk reduction to the extent that dispersion processes reduce biological exposures in the original contaminated area without resulting in unacceptable risks elsewhere. Because of the potential for dispersion to incur exposure over a wider area, these processes may require a more comprehensive effort to analyze downstream or offsite risks.

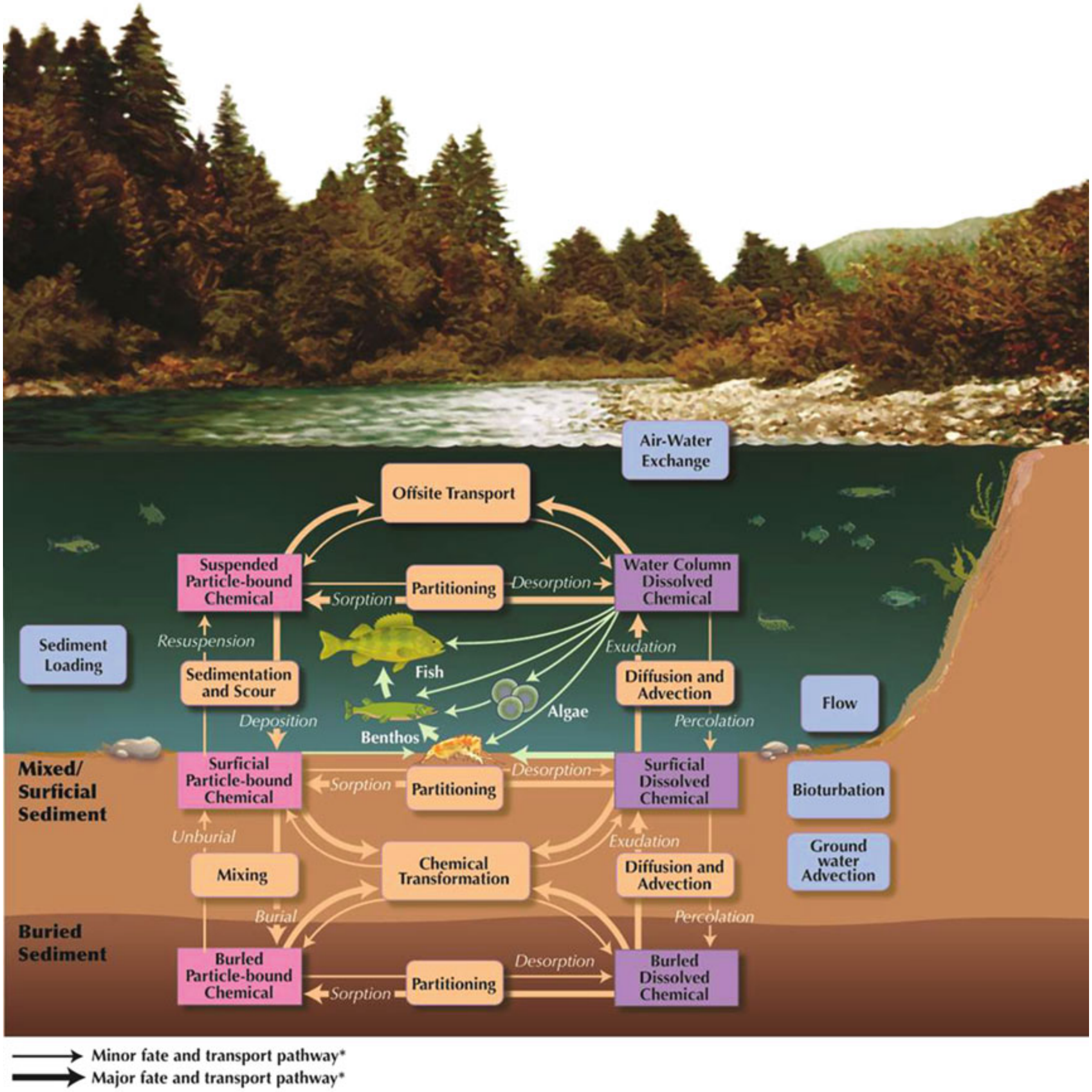
This chapter draws, in part, on information and approaches documented in *Technical Guide: Monitored Natural Recovery of Contaminated Sediments* (Magar et al., 2009), prepared for the U.S. Department of Defense Environmental Security Technology Certification Program. Below, we discuss development of the CSM as it relates to MNR, providing a brief background on an array of MNR-specific considerations. Subsequently, we describe lines of evidence for evaluating MNR feasibility, provide an overview of EMNR, and outline a framework for monitoring MNR progress and evaluating success.

9.2 MNR AND CONCEPTUAL SITE MODELS

Development of a CSM is the first step in considering the applicability of any remedy for a contaminated sediment site. Fundamentally, the CSM represents the site-specific state of understanding of contaminant sources, fate, transport, and potential exposure of receptors. By presenting this information in an organized framework, the CSM facilitates the development of risk reduction strategies, reveals key data gaps and uncertainties, supports development of investigation plans, and comprises a framework for quantitative evaluation of remedy performance, effectiveness, and permanence. CSM development is an iterative process; the CSM is continually refined by the incorporation of new information to reduce important uncertainties.

The CSM often includes a graphical element, which can take many forms. As one example, Figure 9.1 illustrates key contaminant fate and transport processes that may be relevant to exposures, risks, and natural recovery. Of course, this figure is an example only, and the significance of the different illustrated processes will vary among sites. Magar et al. (2009) provide additional examples of spatially and temporally explicit CSM graphics. Note that a CSM figure should not be mistaken for the CSM itself, since the CSM encompasses a greater variety and depth of information than a graphical representation can accommodate.

Every CSM should assemble knowledge of the nature and extent of contamination, risk drivers (in terms of key chemicals, exposure pathways, and receptors), baseline chemical exposure potential and risks under current conditions, contaminant sources, and the degree of source control. When determining MNR feasibility, the CSM must also address the effects of different natural recovery processes on the long-term fate of chemicals of concern, and how



*The significances (major/minor) of pathways shown in the above diagram are examples only, and will vary by chemical, by site, and through time. At some sites, pathways may be completely insignificant or absent. Determining the presence and importance of pathways is the focus of natural recovery performance monitoring.

Figure 9.1. Example graphical representation of a CSM, depicting fate and transport processes related to natural recovery.

future changes in site conditions may influence remedy effectiveness. As an aid to these considerations, chemical-specific and site-specific factors affecting natural recovery are reviewed below.

9.2.1 Contaminant Characteristics Affecting Natural Recovery Processes

For a contaminated sediment site, the CSM must take into account contaminant chemistry and the impact of natural processes on chemicals of concern. Below, we discuss some chemical-specific considerations as they relate to the four natural recovery processes identified in the introduction to this chapter. Additional chemical-specific information is available from Magar et al. (2009); however, knowledge about chemical characteristics is evolving continually. Thorough literature reviews should be conducted to identify the relevant considerations for specific sites and contaminants.

9.2.1.1 Contaminant-Specific Transformation Potential

Classes of chemical contaminants vary significantly in their susceptibility to detoxification through biological and chemical transformation. Figure 9.2 illustrates the continuum of transformation potential for several important chemical classes, focusing primarily on degradability of organic compounds. Radionuclides and hexavalent chromium (Cr[VI]) are also included, because relevant transformation processes (radioactive decay and reduction to Cr[III]) are irreversible or, in the case of Cr(VI), essentially irreversible in sediment under normal geochemical conditions (Magar et al., 2008; Martello et al., 2007). (The potentially reversible redox transformations of other metals are discussed in the context of bioavailability reduction, below.)

The chemicals most likely to exhibit natural recovery through chemical transformation over the timescale of an MNR remedy are those with rapid to moderately rapid transformation rates, such as organotins and low molecular weight petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). While biotic and abiotic transformation and degradation rates for these compounds are influenced by site-specific conditions, they have often been observed to transform significantly at a timescale of years (Atlas, 1981; Maguire, 2000). In the case of very rapid transformation (via either chemical or biological means), as for explosives or Cr(VI), the presumed chemical of concern may be absent by the time a sediment investigation is conducted; if not, source control rather than contaminated sediment management may be the more appropriate focus. Very slow or incomplete transformations, such as dechlorination of polychlorinated biphenyls (PCBs), that do not by themselves afford an acceptable rate of natural recovery may provide a supplemental recovery mechanism over the long term. For example, in sediments of Lake Hartwell, South Carolina, PCB dechlorination was found to be slow and limited to anaerobic subsurface sediments, thus contributing much less than physical

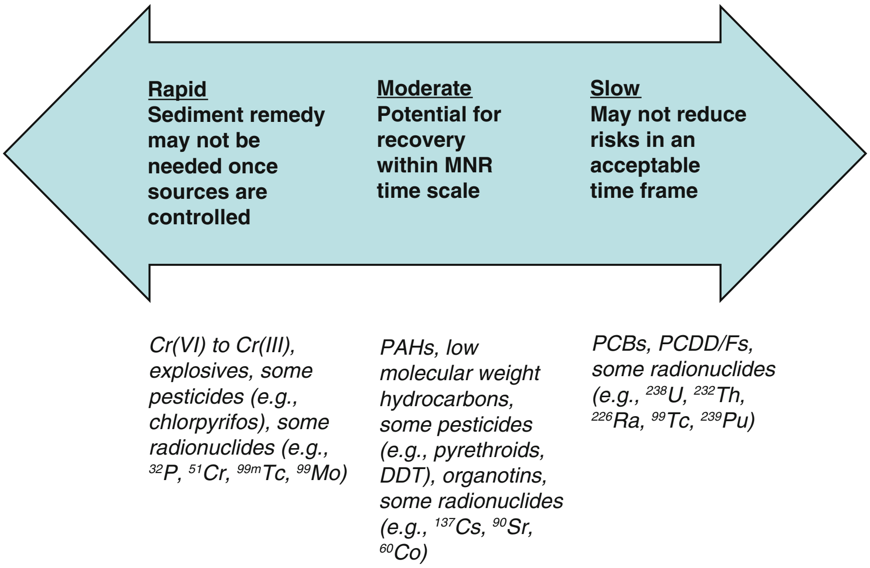


Figure 9.2. Relative transformation rates of various degradable chemical classes. Actual transformation rates vary depending on site-specific conditions.

isolation processes to short-term risk reduction. However, PCB dechlorination in Lake Hartwell sediments has reduced long-term risks associated with potential sediment resuspension at the site (Magar et al., 2005a, b, 2009). In 15 MNR case studies (Magar et al., 2009), transformation (biotic or abiotic) of chemicals of concern was a primary natural recovery process at one-third of the sites reviewed, although transformation was solely responsible for natural recovery only at one site (Table 9.1).

Biotic or abiotic transformation of chemicals is, however, not always a natural recovery mechanism. For example, environmental transformation of inorganic mercury to methylmercury increases mercury's bioaccumulation potential and toxicity. Also, degradation of the pesticide dichlorodiphenyltrichloroethane (DDT) to its major metabolites, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), results in the production of compounds that are environmentally persistent and toxic. Understanding the nature of such transformations is nevertheless important to contribute to the delineation of baseline risks, as well as the potential for risk reduction through other natural recovery processes.

9.2.1.2 Reduction in Contaminant Mobility or Bioavailability

By definition, all persistent sediment contaminants are susceptible to biotic and abiotic processes that reduce mobility and bioavailability. However, there are chemical-specific differences in the mechanisms, extent, and reversibility of these processes. The balance between available and non-available contaminant fractions (i.e., bioavailability) depends on site-specific sediment qualities (e.g., sediment mineralogy, redox conditions, organic carbon content, and organic carbon type) and chemical-specific partition coefficients. For example, organic compounds exhibit a wide range of sorption behavior depending on the contaminant type, molecular weight, and corresponding hydrophobicity, as well as the sediment matrix (e.g., whether sorbed to natural organic carbon or various forms of black carbon). Likewise, the bioavailability of metals is influenced by their solubility and speciation.

Progressive sorption and molecular diffusion into sediment pore spaces over years or decades increases sequestration of metals and organic compounds (Alexander, 2003; Locat et al., 2003; Schnoor and Zehnder, 1996); however, the outcome of such aging processes may already be largely reflected in current conditions at sites affected by legacy contamination. In other words, bioavailability/mobility reductions may have played a significant role in past natural recovery leading to current conditions; however, ongoing reductions in bioavailability and mobility are rarely a primary mechanism of continuing risk reduction at sediment sites impacted by aged, legacy contaminants.

If bioavailability has not been sufficiently addressed in the risk assessment, supplemental investigation may be needed for a more realistic estimate of risks that would occur during MNR implementation. Also, issues of bioavailability and mobility can be integral to understanding the effects of other natural recovery processes. For example, at Belews Lake in North Carolina, dispersion of selenium-contaminated sediment from near-shore to deep areas caused a reduction in selenium bioavailability due to differing geochemical conditions (Finley and Garrett, 2007).

9.2.1.3 Contaminant-Specific Differences in Relation to Physical Processes of Natural Recovery

Physical isolation of persistent sediment contamination is controlled by sedimentation processes and sedimentation rates, surface sediment hydrodynamic and biological mixing, sediment resuspension and transport processes, and chemical partitioning. In general, isolation

Table 9.1. Predominant Natural Recovery Processes at MNR Sites Reviewed by Magar et al. (2009)

Site	Hydrology	Remedy Drivers	Primary Recovery Processes				MNR Viewed as Success?
			Chemical Transformation	Bioavailability Reduction	Physical Isolation	Dispersion	
Belews Lake, North Carolina	Lake	Selenium		X	X	X	Yes
Bellingham Bay, Washington	Bay (marine)	Mercury			X		Yes
Bremerton Naval Complex, Washington	Bay (marine)	PCBs, mercury			X		TBD
Commencement Bay, Washington	Bay (marine)	Metals, PCBs, PAHs	X		X	X	Yes
Elizabeth Mine, Vermont	Stream	Metals			X	X	TBD
Fox River/Green Bay, Wisconsin	River and bay (freshwater)	PCBs			X	X	TBD
Hackensack River, New Jersey	Estuary	Chromium	X	X	X		TBD
James River, Virginia	River	Kepone			X	X	Yes
Koppers Barge Canal, South Carolina	Bay (marine)	PAHs			X		Yes
Lavaca Bay, Texas	Bay (estuarine)	Mercury, PAHs			X		TBD
Mississippi River Pool 15, Iowa	River	PCBs		X	X	X	TBD
Red Bank Creek, South Carolina	Stream and lake	Organotins	X				Yes
Lake Hartwell, South Carolina	Stream and lake	PCBs			X		Partially
Ward Cove, Alaska	Bay (marine)	Ammonia, sulfide, 4-methylphenol	X		X		Yes
Wyckoff/Eagle Harbor, Washington	Bay (marine)	PAHs, mercury	X		X		Yes

TBD – to be determined

of persistent sediment contaminants is dominated by sedimentation and mixing processes and is less affected by the types of contaminants present. However, for metals and metalloids, vertical cycling within the sediment commonly occurs as the result of mobilization at subsurface redox boundaries, followed by complexation with iron oxides and/or organic matter in surface sediment. Similarly, for radionuclides with radon in the decay chain, the high mobility of radon gas could potentially cause its decay product (lead) to accumulate in surface sediments.

Cycling of metals and metalloids can be further heightened by vertical fluctuations in redox boundaries, such as can arise from fluctuating water levels (e.g., seasonally, on a tidal cycle, or as the result of water level control in lakes or reservoirs) and/or ongoing sediment burial (Merritt and Amirbahman, 2007; Toevs et al., 2008; Widerlund and Ingri, 1995). For mercury, because the production of methylmercury in sediment is predominantly a microbial process and is dominated by sulfate-reducing or iron-reducing bacteria, vertical shifts in redox chemistry can also influence the production rate of methylmercury by altering microbial community structure, as well as control the geochemical stability of methylmercury in both sediment and porewater phases (Merritt and Amirbahman, 2009).

Dispersion encompasses a range of natural processes that tend to move contamination downgradient, from higher to lower concentration regimes. Dispersion of contaminants occurs as a result of physical sediment resuspension and the concurrent transport of sorbed chemicals, bioturbation, movement of dissolved chemicals via surface water currents, and simple chemical diffusion. Dispersion may involve contaminant transport from higher energy areas to depositional areas, where they may then undergo other recovery processes. Also, dispersion may be an important mechanism accounting for historical reductions in contaminant exposures. Chemical-specific properties can influence dispersion and transport. More soluble chemicals are diluted via dissolution, whereas hydrophobic chemicals tend to be more closely associated with particles and organic matter.

9.2.2 Site Conditions Affecting Natural Recovery Processes

Physical isolation is the most commonly cited recovery process at sediment MNR sites (as shown in Table 9.1). Key site-specific conditions that influence natural recovery through physical isolation include the extent and spatial pattern of depositional and erosional areas, sediment deposition rates, quality of newly deposited sediment, depth of surface sediment mixing (by burrowing organisms and physical processes), and physical stability of site sediment under frequent and infrequent high-energy conditions. Depending on the size and complexity of a site, it may be useful to construct multiple CSMs for physically distinct areas.

In addition, the CSM for a site where MNR is being considered should incorporate information about the interaction between chemical characteristics and site-specific conditions. Most chemical transformation and sequestration processes are affected by geochemical conditions, such as redox potential, the nature and quantity of organic carbon, pH, and salinity. Table 9.2 summarizes conditions favorable to biodegradation for various organic (and organometallic) chemical classes. Aerobic conditions favor oxidative biodegradation processes; anaerobic oxidation also occurs, generally at rates much slower than aerobic oxidation. Anaerobic conditions generally are required to support reductive dechlorination processes. Other conditions potentially favorable to biodegrading microbes include nutrient availability, warm temperatures, and chemical concentrations that are high enough to stimulate degradation but below microbial toxicity thresholds. Geochemical conditions that limit chemical bioavailability to macrofauna also tend to slow biodegradation because the chemical is not sufficiently bioavailable to microbes, but these same processes tend to reduce chemical bioavailability to ecological and human receptors.

Table 9.2. Site-Specific Conditions Conducive to Degradation of Organic Compounds

Chemical Class	Conditions Favorable to Degradation
PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)	Aerobic conditions favor microbial degradation of lower chlorinated congeners, whereas reductive dechlorination of more highly chlorinated congeners occurs (slowly) under anaerobic conditions (Field and Sierra-Alvarez, 2008; Magar et al., 2005a, b).
PAHs and petroleum hydrocarbons	Conditions favorable to biodegradation include availability of oxygen and nutrients, warm temperatures, and occurrence of hydrocarbons in a physical state with high surface-to-volume ratio (Atlas, 1981).
Pesticides	The diversity of pesticides and their degradation mechanisms precludes generalizations (Katagi, 2006); selected examples follow. Bifenthrin is moderately persistent across sediment conditions but degrades more rapidly in warm, anaerobic sediments (Gan et al., 2005). DDT degrades to DDE under aerobic conditions and to both DDE and DDD under anaerobic conditions, but this is not necessarily a natural recovery mechanism, because DDE and DDD are relatively persistent and toxic. However, DDE has been found to degrade significantly through reductive dechlorination under anaerobic conditions; this transformation is most rapid under methanogenic conditions and at warm temperatures (Eganhouse and Pontolillo, 2008).
Explosives	Degradation is relatively rapid under a range of conditions, but fine-grained, organic-rich sediments are particularly favorable (Lotufo et al., 2009).
Organotins	Aerobic conditions favor degradation to inorganic tin (USEPA, 2003d). Conditions associated with higher bioavailability may also tend to promote degradation.

Table 9.3 describes geochemical factors that affect the bioavailability of various chemical classes. Nearly all of the chemicals considered are affected by sediment organic carbon, which tends to reduce bioavailability with increasing organic carbon content for most chemicals. The nature and quantity of organic carbon are the most important factors determining bioavailability of hydrophobic organic compounds. Bioavailability of metals and organometals is also affected by a range of other conditions, such as sulfur availability (often measured as acid-volatile sulfide [AVS]), pH, redox potential and salinity.

9.2.3 Implications of Future Site Conditions

The CSM should include consideration of plausible non-steady-state events that would significantly influence site physical conditions. Examples include navigational dredging, major storm events, and habitat restoration. Concern that a large flooding event could uncover buried contaminated sediments is often cited in support of sediment removal, even if risks are low or manageable under current conditions. However, models and data have suggested that storm events may not necessarily cause significant sediment erosion or may result in net depositional conditions. The consequences of a reasonably plausible high-energy event should be evaluated on a site-specific basis, typically through application of sediment transport and stability models

Table 9.3. Site-Specific Geochemical Conditions Affecting Bioavailability of Selected Chemicals and Chemical Classes

Chemical	Geochemical Factors Affecting Bioavailability
Hydrophobic organic compounds	Bioavailability decreases with increasing sediment organic carbon (Di Toro et al., 1991). Sorption to soot, pitch, coke, and other black carbon forms can greatly decrease bioavailability of many hydrophobic organic compounds compared to amorphous organic carbon (Cornelissen et al., 2005).
Organotins	Bioavailability depends on pH, with lowest tributyltin bioavailability observed at pH 6–7. Salinity, organic carbon, and sediment mineralogy also influence bioavailability, with the direction and/or magnitude of effect depending in part on pH (Burton et al., 2004; Hoch et al., 2002). Sorption may not differ between black carbon and amorphous organic carbon (Brändli et al., 2009).
Divalent metals	Sulfide and organic carbon limit bioavailability of divalent metals, while bioavailability increases with decreasing pH (Di Toro et al., 2005).
Arsenic	Arsenic bioavailability is affected by the combination of pH and redox potential. Arsenic is most bioavailable in reducing environments at low pH and least bioavailable under oxic conditions (Drever, 1997; Harrison, 2007).
Chromium	Under even mildly reducing conditions, Cr(VI) is rapidly reduced to Cr(III), greatly reducing both its bioavailability and toxicity (Graham and Bouwer, 2010; USEPA, 2005b). Cr(III) remains stable under aerobic conditions (Magar et al., 2008; Martello et al., 2007). Cr(III) bioavailability is minimal due to solubility limitations, though it is greatest at low pH in freshwater sediments (USEPA, 2005b).
Mercury	The ecological and health significance of mercury depends primarily on its site-specific bioaccumulation potential, with methylmercury being much more bioaccumulative than inorganic forms. Factors that promote methylation include the availability of easily degradable organic matter (e.g., as in wetlands), moderately reducing conditions, and availability of appropriate terminal electron acceptors (e.g., sulfate or Fe[III]) (Merritt and Amirbahman, 2009). Also, pH and dissolved organic carbon influence mercury transfer into phytoplankton, thereby affecting bioaccumulation potential (though not methylation) (Pickhardt and Fisher, 2007). Sites that particularly favor mercury biomagnification include newly flooded reservoirs, acidic lakes, and coastal marshes, mudflats, and other sites of nearshore organic enrichment (Chen et al., 2008; Kelly et al., 1997). Sediment-associated mercury may be much less bioavailable than aqueous-phase mercury originating from upstream sources (Orihel et al., 2007; Southworth et al., 2002).
Radionuclides	Factors affecting bioavailability vary among radionuclides. For example, uranium bioavailability decreases under reducing conditions and with increasing organic carbon and pH. Technetium bioavailability decreases under reducing conditions and may also be affected by salinity, depending on its chemical form. Cesium bioavailability is determined by the prevalence and characteristics of mica-clay minerals (IAEA, 2006).

and/or relevant field data. For example, a modeling study of the Lower Duwamish Waterway (Seattle, Washington) indicates that the waterway is net depositional during large flood events, including the 100-year (yr) flood event (QEA, 2008). Modeling studies of Thompson Island Pool, Upper Hudson River (New York) and Lavaca Bay (Texas) have also indicated relatively minor and/or localized bed erosion following a 100-yr flood event and a Category 3 hurricane, respectively (Ziegler, 2002). Field data collected in the Gulf of Mexico in the aftermath of significant storm passage have documented localized sediment erosion to a depth of 8–9 centimeters (cm) (Swarzenski et al., 2007) and 19 cm (Allison et al., 2005), depending on storm force, location, water depth, and sediment bed characteristics.

Although valuable for constraining erosion versus deposition scenarios, some modeling studies have not captured the range of extreme events to which the sediment bed may be exposed. For example, as detailed by Merritt et al. (2010), results from on-going sediment sampling on the Grasse River (New York) documented significant erosion of a reactive material cap by extreme winter conditions in the vicinity of the capping test location. The design of this cap did not include consideration of forces that can be created due to an ice jam. A 1-acre armored cap designed to withstand ice jam-related scour forces was subsequently installed in the river near the original test location and remains stably in place. Although this example is more directly related to capping than to MNR, it highlights the need to appropriately characterize site conditions through data collection to confirm the likelihood of sediment bed stability during plausible events.

Habitat restoration also has the potential to affect natural recovery processes. Habitat restoration planning may be integrated with remedy analyses and decision making, or it may occur independently. Regardless, effects of future habitat restoration on site physical conditions merit consideration. For example, watershed-scale measures to control soil erosion could affect future sediment deposition rates. Where functioning habitats exist, MNR may be a restoration-friendly alternative, because it does not incur short- or long-term construction-related habitat damage. On the other hand, major restoration actions, such as dam removal or habitat re-engineering, may be incompatible with MNR, if physically isolated contaminants would become exposed and mobilized (Magar et al., 2009).

9.3 LINES OF EVIDENCE FOR EVALUATING MNR FEASIBILITY

In order to evaluate the suitability of MNR as a remedy, lines of evidence are developed to understand baseline risk conditions, identify and quantify trends toward reduced chemical exposures and risks, and characterize the long-term protectiveness of risk reductions. These lines of evidence are used to further refine the CSM, and so provide a more accurate depiction of the natural processes operating at the site and their impact on chemicals of concern.

A wide variety of investigative tools are available to develop the necessary lines of evidence, ranging from literature review to specialized analyses, such as radioisotope dating and sediment profile imagery. The selection of specific lines of evidence to investigate MNR feasibility is determined by application of the scientific method to address the key site-specific questions arising from the CSM. Site conditions, characteristics of the chemicals of interest, and the type and complexity of the site being evaluated all enter into this decision process. Larger, more complex sites generally warrant the development of multiple lines of evidence to address each of several key questions associated with MNR processes, process kinetics, and risk. For smaller, less complex sites, a reasonably conservative interpretation using more limited data may be sufficient to select a protective and cost-effective remedy. Table 9.4 identifies the types of evidence used to support remedy selection and implementation in 15 case studies reviewed by Magar et al. (2009).

In general, it makes sense to develop lines of evidence using a step-wise approach, beginning with less resource-intensive tools (such as literature review, aerial photographs, and historical data collection) to identify general concepts that apply to site-specific conditions, and then proceeding to more resource-intensive tools such as field and laboratory investigations and modeling. Further practices that can contribute to an efficient investigation include following the data quality objectives process, and integrating modelers and risk assessors into project planning (Magar et al., 2009).

Table 9.4. Lines of Evidence Used in MNR Case Studies (Magar et al., 2009) to Evaluate MNR Feasibility and Implement Monitoring

Process Investigated	Line of Evidence	No. of Case Studies	
		Feasibility (n = 13)	Monitoring (n = 15)
Physical isolation	Sediment core sampling and vertical profiling	5	2
	Radioisotope analysis and sediment age dating	5	1
	Bathymetric survey	4	4
	Sediment profile imagery	1	1
	Sediment trap analysis	1	
	Tide gauge monitoring		1
	Sediment bed stability studies	2	
	Hydrodynamic and sediment transport modeling	8	1
	Assessment of MNR success in similar sites	1	
	Visual documentation of physical changes of shoreline	2	2
Dispersion	Flow measurements	1	
	Streambed geology	1	
	Mass balance and sediment transport modeling	2	
	Assumed to occur in riverine environment during flood events	1	
Chemical transformation	Measurement of parent compounds and transformation products	2	2
	Laboratory studies of degradation in site sediment		1
	Contaminant fate and transport modeling	1	
Reduction in bioavailability and mobility	Indicators of redox conditions	1	
	Laboratory study of chemical release from resuspended sediment	1	
Risk reduction	Surface water chemistry		3
	Porewater chemistry		1
	Surface sediment chemistry	1	11
	Deep sediment chemistry		1
	Biota tissue chemistry		12
	Sediment toxicity analysis	2	2
	Characterization of benthic communities	2	3
	Characterization of fish communities		1

This section discusses the utility of temporal trend analyses, which is useful for establishing lines of evidence for source control as well as the full range of recovery processes, followed by discussions of lines of evidence for source control (important for all remedies, but especially critical for MNR), chemical transformation, reduced bioavailability, and physical isolation/ dispersion.

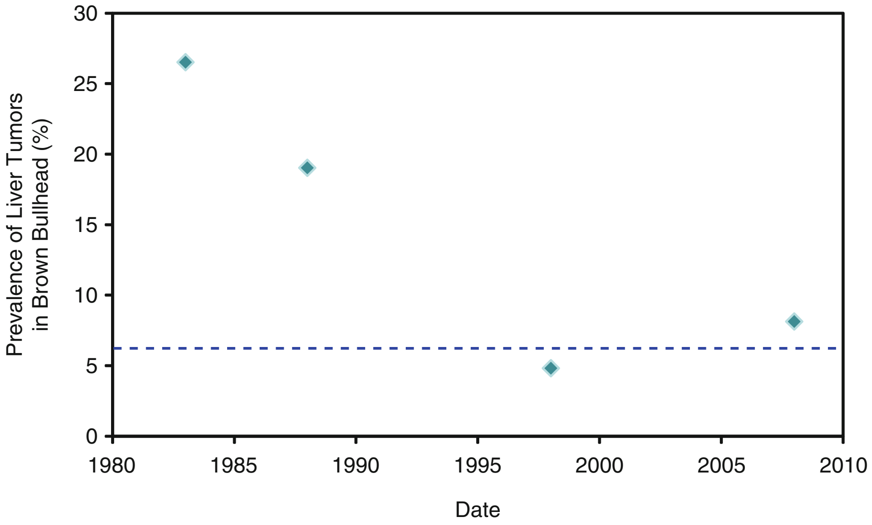


Figure 9.3. Long-term trend in hepatic neoplasms in the Buffalo River between 1983 and 2009. *Dashed line* is the currently proposed criterion for "delisting" this impairment in Lake Erie Areas of Concern (Baumann et al., 2000; Blazer et al., 2009; Lauren et al., 2010).

9.3.1 Temporal Trend Analysis

Monitoring is a critical component of MNR due to the need to establish the basis for recovery trends over time. By collecting comparable data repeatedly over time, historical trends in various measures of chemical exposures and biological responses can provide compelling evidence of the overall course of natural recovery. Indeed, relevant monitoring should be initiated early in the assessment process. Considering that assessment and management decisions at contaminated sediment sites can take years, there is often time to develop a strong temporal data set, as well as integrate historical data. Temporal trend analysis can consider metrics such as chemical concentrations in surface sediment or biological tissues, sediment toxicity in laboratory tests, benthic invertebrate or fish community composition and quality, incidence of health conditions such as fish tumors or avian deformities, or wildlife population abundance, depending on the objectives of the remedial project. Figure 9.3 presents an example of temporal trends in the Buffalo River, New York, showing a statistically significant decrease in fish liver lesions ($p < 0.05$) following 25 yr of natural recovery (Lauren et al., 2010). Such monitoring efforts can be paired with retrospective analyses to focus attention on relationships among multiple chemical and biological metrics. For instance, vertical contaminant concentration profiles in sediment cores can document historical changes in surface sediment chemical concentrations, which may be correlated with temporal trends in biological receptors.

Figure 9.4 shows an example of temporal trends derived from a vertical sediment core. The figure shows a long-term trend for total chromium concentrations from a sediment core collected in the lower Hackensack River. Lead-210 (^{210}Pb) and cesium-137 (^{137}Cs) data are used to age-date sediment deposits and to establish vertical temporal trends that may be linked to historical sedimentation rates and chemical deposits. Based on the peak ^{137}Cs level, the 200-cm interval was deposited *circa* 1963, suggesting a relatively high deposition rate of 5 cm/yr at the location where the sediment core was collected.

While temporal trend analysis is a valuable tool in evaluating the potential for natural recovery of contaminated sediments, it is important to understand that historical trends integrate effects of past source control and natural recovery processes. Thus, a marked decline

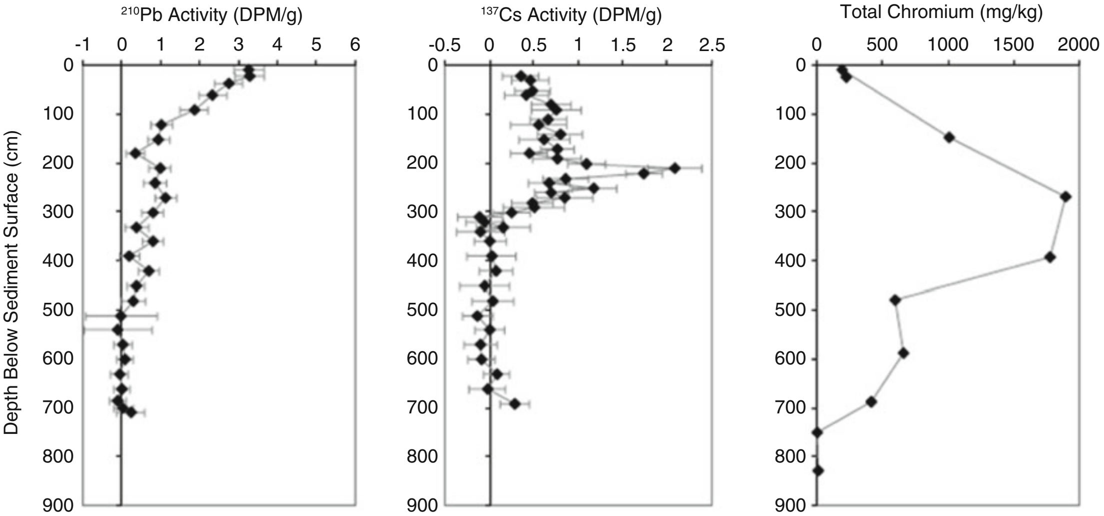


Figure 9.4. Long-term trend total chromium concentrations from sediment cores collected in the lower Hackensack River. ^{210}Pb and ^{137}Cs data are used to establish vertical temporal trends that may be linked to historical sedimentation rates and chromium deposits.

in chemical concentrations in fish following cessation of related effluent discharges is not necessarily predictive of continued recovery rates into the future. Conversely, following control of upland sources to an aquatic system, future natural recovery rates may be greater than those documented historically. To project the future course of natural recovery with sufficient confidence to support environmental management decisions, specific data and evidence must be developed in regard to source control and natural recovery processes.

9.3.2 Source Control

Source control is critical to the success of any sediment remedy, including MNR. Lack of understanding and management of sources can compromise the ability to monitor and quantify MNR processes, and can limit the effectiveness of the remedy where natural recovery rates are outpaced by ongoing releases. This is not to say that elimination of all sources is a prerequisite for a successful MNR remedy, but rather that the balance between any ongoing sources and natural recovery processes should be understood well enough to judge the adequacy of expected risk reductions over time. A useful CSM identifies historical contaminant sources and demonstrates source control or source minimization based on investigations of historical and ongoing releases and evidence establishing historical or ongoing termination of those releases (Magar et al., 2009). Examples of related investigation tools include:

- Compilation and documentation of existing information on historical contaminant releases, transport pathways, source control measures, and their effectiveness, including identification of background sources or sources from offsite contributors that may continue and thus slow recovery.
- Measurement of contaminants in entry points to sediment, such as from upstream locations, outfalls, and other point or non-point sources.
- Contaminant mass balance modeling, to determine whether known sources (e.g., storm water outfalls, groundwater, sediment contamination) account for observed concentrations in biota tissue.

- Chemical forensics techniques to associate the chemical fingerprint of sediment contaminants with that of suspected sources.
- As noted above, the effectiveness of past source control measures can also be inferred from temporal trends that indicate recovery, recognizing that historical recovery trends integrate the effects of source control with those of natural recovery processes.

At sediment sites receiving chemical inputs from multiple sources, a regional or catchment-scale management approach to source control is likely to be required to ensure potential chemical inputs are controlled to the extent practicable. Regardless of whether a site-specific or regional management approach is adopted, an assessment of ongoing contamination potential is a necessary precondition to defining realistic remedial goals, particularly if source control is incomplete or cannot be fully achieved. Although elevated background chemical concentrations or widespread chemical distributions may not preclude the implementation of an MNR remedy, these data should be applied as appropriate to adjust expectations of remedy success.

9.3.3 Chemical Transformation

When evaluating the feasibility of MNR as a remedy, relevant lines of evidence may address whether chemical transformation is occurring (or has occurred in the past); how transformation processes affect chemical toxicity, bioavailability, and mobility; and whether chemical transformation will contribute to risk reduction within an acceptable timeframe. Biodegradation processes in sediment and associated investigation tools are discussed in detail by Himmelheber and Hughes in Chapter 10; this section provides an overview of relevant assessment approaches.

The potential of chemical transformation to contribute significantly to natural recovery should be evaluated initially based on literature review and a preliminary understanding of site geochemical conditions. Once a transformation process is established, it must also be confirmed that its products are less toxic or bioavailable than the parent compounds – otherwise it is clearly not a recovery process. For example, an MNR scenario that results in the methylation of inorganic mercury would not be considered as demonstration of recovery because of the enhanced toxicity and biomagnification potential of methylmercury relative to inorganic mercury. If warranted, site-specific investigations can confirm the suitability of site-specific geochemical conditions for transformation processes of interest and measure the occurrence of parent compounds, intermediate byproducts, and end products, either *in situ* or in the laboratory, depending on project requirements.

Well-established scientific findings – such as the rapid chemical transformation of trinitrotoluene in sediment (Conder et al., 2004; Elovitz and Weber, 1999) – may require only a thorough literature review to demonstrate widespread acceptance of an effective natural recovery process. Depending on the level of uncertainty of such initial conclusions, however, site-specific empirical studies, such as porewater measurements or laboratory work, could be required to demonstrate that the general principle holds in the particular case.

Investigations may be needed to determine the extent to which chemical transformation processes are likely to reduce risks. Risk assessment techniques, such as modeling or measuring bioavailable concentrations in porewater or tissue, measuring sediment toxicity in laboratory tests, and/or assessing benthic invertebrate community quality, can be applied in this context. The toxicity and partitioning characteristics of transformation products often are available from the literature; however, controlled experiments may be appropriate to determine these characteristics for poorly studied chemicals.

Understanding the rate of a chemical transformation is important to determine its utility as part of an MNR remedy. Tools to measure transformation processes and kinetics begin with identifying processes and kinetics documented in the literature, measuring site-specific geochemistry to identify potential transformation pathways, and measuring transformation byproducts in field samples using chemical forensics or in laboratory controlled experiments. Transformation kinetics can be established in a laboratory setting, but may be relatively slow without enhancements such as substrate addition, changing redox conditions, or mixing. Kinetics also can be derived using field samples by collecting sediment cores and age-dating sediment horizons in parallel with detailed chemical analyses to identify parent chemical compounds and transformation byproducts (e.g., Magar et al., 2005b).

Interestingly, the implications of chemical transformation processes also are relevant to other remedial approaches. For example, PCBs in sediments of the Hudson River have undergone extensive dechlorination, resulting in a site-specific PCB mixture dominated by mono- and dichlorobiphenyls, which are considerably more mobile in the water column than higher-chlorinated congeners due to their relatively high solubility. This site's unique PCB composition, resulting from previous transformations, likely contributed to the higher than expected releases of PCBs into the Hudson River during recent dredging efforts (The Louis Berger Group, 2010; Anchor QEA, 2010).

9.3.4 Reduction in Contaminant Bioavailability/Mobility

Chemical sequestration in sediments can progressively reduce bioavailability and mobility over a period of years. At many sites, contaminants have been in contact with sediments for years or decades, and the outcome of sequestration processes is already evident. Therefore, development of the CSM should consider whether bioavailability has been considered appropriately in site risk assessments, and whether existing conditions that limit chemical bioavailability are permanent. An accurate understanding of baseline risks will establish the anchor point for predictions about risk reduction trajectories for MNR and other remedies under consideration. If chemical bioavailability is not well understood, further characterization may be warranted.

Bioavailability plays an important role in understanding baseline risks, and there is an increasing recognition that whole sediment chemical concentrations alone do not adequately predict chemical bioavailability and toxicity (USEPA, 2003a, b, c, 2005b). Biological responses to chemicals in sediments are different across sediments when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on a dissolved, porewater basis or on a carbon-normalized basis (e.g., gram(s) [g] chemical/g organic carbon). Methods to measure porewater directly are improving and may be used for the direct measurement of dissolved hydrocarbons (Hawthorne et al., 2006; McDonough et al., 2010), PCBs (Hawthorne et al., 2009), and metals (Harper et al., 1999; Serbst et al., 2003). U.S. Environmental Protection Agency (USEPA) provides guidance on the development of equilibrium partitioning sediment benchmarks (ESB) for determining the toxicological contributions of PAHs (USEPA, 2003a), pesticides (USEPA, 2003b, c), and metals (USEPA, 2005b) in sediments, and to determine if their concentrations and corresponding exposures in sediment would be toxic to benthic organisms. Lu et al. provide a detailed discussion of techniques for measuring bioavailable chemical concentrations (Chapter 7).

Questions about the reversibility of chemical sequestration are most often raised with regard to divalent metals. Once introduced to sediment, metals typically accumulate via adsorption or nonspecific binding to either inorganic or organic phases. Metals also form precipitates of varying stabilities under either oxidizing or reducing conditions. Precipitation in oxic environments frequently takes the form of oxide or oxyhydroxide phases. Precipitation under reducing conditions requires the presence of dissolved sulfide, generally present as the result of microbial respiration of available sulfate. These mechanisms can substantially limit the bioavailability and mobility of divalent metals, and thus substantially limit divalent metal toxicity (USEPA, 2005b; Axe and Trivedi, 2002).

The stability of sorbed and/or precipitated forms of divalent metals varies as a function of the specific metal and factors including organic matter input rates and system hydrodynamics that dictate ambient geochemical conditions (Kalnejais et al., 2007). Resuspension of anoxic sediments may cause oxidation and acidification (if sulfide were originally present), which may increase the mobility and bioavailability of previously sequestered divalent metals (Caetano et al., 2002; Calmano et al., 1993). However, Cantwell et al. (2008) found minimal release of dissolved metals upon resuspension of metal-contaminated, estuarine field sediments or spiked sediments containing higher sulfide concentrations. Site-specific investigations to address releases from suspended sediments could include (1) modeling the likelihood and duration of geochemical changes that could cause releases of sequestered contaminants (such as sediment erosion), (2) modeling the relative kinetics of sequestration and release processes, and (3) laboratory or field experiments to detect the occurrence and extent of actual releases under relevant geochemical conditions (e.g., Magar et al., 2008).

Long-term changes in sediment geochemistry (i.e., mineral diagenesis) can result in incorporation of metals into crystal lattices – a particularly stable form of sequestration. In some cases, metals sorbed to porous hydrous metal oxides can also be excluded during crystal formation, causing desorption (Ford, 2007). This process of desorptive exclusion may also occur in reducing environments during the slow conversion of rapidly precipitating iron-sulfide phases (FeS) to the more stable diagenetic form FeS_2 (pyrite) (Roberts et al., 1969). Because desorptive exclusion is typically very slow, it is not expected to be a significant release mechanism in terms of short-term environmental exposures.

9.3.5 Physical Isolation, Dispersion, and Reduced Contaminant Exposures

Physical isolation involves the deposition of increasingly clean sediment with time, resulting in the burial of sediment contaminants. Natural recovery via physical isolation entails multiple processes – including sedimentation and erosion, chemical diffusion, bioturbation and hydrodynamic mixing, and advection – that contribute to reduced contaminant concentrations in surface sediment, and thus reduce risk to biological receptors (USEPA, 2005a). By incorporating lines of evidence developed to characterize sedimentation and physical isolation processes, the CSM facilitates the evaluation of the nature and magnitude of exposures and risks where contaminants disperse and/or deposit.

Physical isolation of contaminated sediments via sediment burial occurs in net depositional environments, where the rate of sediment deposition exceeds the rate of sediment erosion. Natural deposition of clean material can result in contaminant concentrations that approach or achieve cleanup levels and reduce risks to human health and the environment (Magar and Wenning, 2006; Brenner et al., 2002, 2004; USEPA, 1998).

In contrast, dispersion occurs where the sediment erosion rate exceeds the sediment deposition rate, resulting in lower chemical concentrations due to contaminant transport. Dispersion mechanisms include physical sediment resuspension, movement of dissolved chemicals via surface water currents or groundwater advection, and simple chemical diffusion. This process must be gauged carefully with respect to MNR effectiveness because it may result in broader exposure – albeit at lower concentrations – rather than eliminating exposure pathways (USEPA, 2005a).

Isolation and dispersion processes are active at almost every site, and should be considered both for their direct effects on exposure, and for the manner in which they may interact with and influence other natural recovery processes. In particular, dispersion is usually part of a dynamic process of resuspension at the sediment bed surface. Dispersion mechanisms may transport contaminants from higher-energy areas to depositional areas, where they then undergo physical isolation or other recovery processes. At many sites, such processes account for substantial historical reductions in contaminant exposures.

Because sediment transport processes are so central to contaminant exposures – and so site-specific – understanding these processes is especially important for building and refining the CSM to inform well-founded remedial decisions. This section discusses a range of lines of evidence – including tools and key considerations for MNR – used to establish an understanding of the principal factors influencing isolation and dispersion, including deposition, mixing characteristics, and sediment bed stability and erosion potential.

9.3.5.1 Sediment Deposition

Net depositional environments result from the erosion of watershed soils and sediments, precipitation of solids from the water column, and accumulation of the remains of aquatic biota such as plankton, algae, and aquatic macrophytes. Sedimentation rates vary according to hydrodynamics, upstream conditions, and watershed characteristics. An understanding of site-specific sedimentation rates and the extent of physical burial and isolation of sediment contaminants may be achieved through site-specific investigations such as the following:

- **Vertical sediment contaminant profiles.** Sediment coring and analysis of contaminant concentrations at appropriate segment intervals can be used to determine whether persistent historical deposits exist, and whether the deposition of cleaner material is contributing to the burial of historical chemical deposits and the dilution of surface sediment chemical concentrations.
- **Geochronological isotope analyses.** Depositional patterns or rates of sediment deposition can be determined by measuring changes in levels of atmospherically deposited radioactive isotopes, such as ^{210}Pb or ^{137}Cs within a vertical sediment profile. ^{210}Pb geochronology relies upon natural decay processes to estimate sediment age based on the extent of ^{210}Pb decay with sediment depth and age. ^{137}Cs is an independent indicator of sediment age, which is based on anthropogenic inputs of ^{137}Cs into aquatic systems that began in 1950 and peaked around 1963, corresponding to atmospheric testing of nuclear weapons. The concentration and depth of ^{137}Cs in the sediment provide a means of determining the age of the sediment layer.
- **Sediment geophysical analyses.** Bathymetry, side-scan sonar, or sub-bottom profiling surveys can characterize riverbed topography and the thickness of surficial sediments. These surveys can be used to both establish baseline conditions and monitor changes over time, thus providing a further understanding of depositional areas and patterns. Bathymetric measurements may be collected over consecutive years to monitor bed elevation changes over time; however, measurement of bed elevation changes is limited by the precision of the instrument employed.
- **Bed pins.** A bed pin consists of a rod with a chain attached to one end. The rod is inserted into the sediment chain-end first to a depth equal to the length of the chain, so that the sediment compresses the chain in a vertical position against the rod, and the end of the chain is exactly at the sediment surface. A known length of rod extends above the sediment surface. The pin is inspected periodically. Under depositional conditions, the length of rod above the sediment surface will decrease over time. Under erosional conditions, the length of exposed rod will increase, and the chain will become exposed. If the sediment has been eroded and redeposited, then careful excavation of the bed pin will reveal the chain in a horizontal position beneath the sediment surface, at the depth of maximum erosion.
- **Review of historical dredging records** may offer further evidence to establish site-specific deposition rates. Such records may quantify the amount of sediment routinely removed from an area and facilitate the estimation of localized deposition rates.

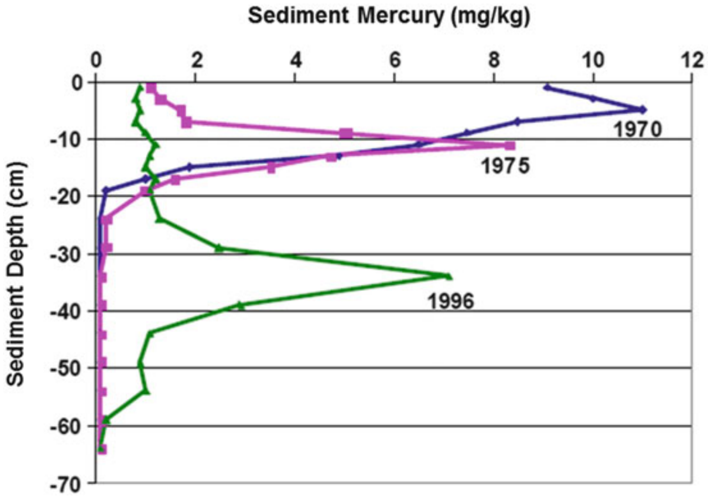


Figure 9.5. Historical changes in sediment core profiles, Bellingham Bay, Washington (data courtesy of Clay Patmont, Anchor QEA, LLC).

- **Sediment traps.** A sediment trap can be conceptualized as a test tube buried in the sediment, with the top of the test tube exactly at the sediment surface. Alternatively, a sediment trap can be deployed in the water column. In either case, the sediment trap captures suspended material as it settles. Sediment traps tend to overestimate the rate of sediment deposition, because the trap creates a microenvironment that promotes deposition. However, they can be very useful for sampling settling solids, to measure chemical and physical characteristics of the newly deposited sediment. Consideration should be given to whether the resulting samples represent locally resuspended sediment, material transported from upstream, or both, based on knowledge of site-specific conditions.

Results from field investigations of sediment deposition, in combination with historical data, can also be used to calibrate sediment transport models that characterize and predict ongoing sedimentation and contaminant burial rates.

Whatcom Waterway in Bellingham Bay, Washington, provides an example of surface sediment recovery through natural sedimentation. Sediment core profiles were used to establish vertical mercury concentration profiles, age-date sediments, and determine surface sedimentation rates. Mercury was introduced into Whatcom Waterway through historical wastewater discharge from local chloralkali and wood pulping plants. Monitoring data, collected under wastewater discharge permits, demonstrated that significant reduction in mercury loadings to the bay were achieved in the early 1970s. Subsurface sediment coring data with supporting radioisotope geochronology and chemical analyses of total mercury were collected at several time intervals following source control. Results demonstrated a reduction in surface sediment concentrations since 1970 and burial of elevated mercury concentrations over time (Figure 9.5) (Magar et al., 2009).

9.3.5.2 Surface Sediment Mixing

Surface sediment mixing processes, such as benthic mixing (bioturbation) and hydrodynamic mixing, can influence the rate of change in surface sediment chemical concentrations.

Surface sediment mixing may slow contaminant burial by mixing older, deeper contaminated sediments into the surface layer and slowing the rate of recovery. However, mixing also contributes to reduced risk by diluting contaminated surface sediments with freshly deposited cleaner material, resulting in lower surface-sediment contaminant concentrations. In addition, surface sediment mixing can lead to more rapid declines in exposure and risk for contaminants that rely on mixing to enhance degradation.

Thus, the depth of hydrodynamic and benthic surface sediment mixing should be considered when evaluating sedimentation rates and the rate of physical isolation. Bioturbation depths also factor into the depth to which biological exposures are addressed; in freshwater systems, for example, bioturbation depths are typically < 10 cm. The overall effect of mixing is governed by site-specific factors and processes that can be determined using the following tools:

- **Sediment Profile Imaging (SPI).** SPI camera surveys provide qualitative and quantitative information for assessing benthic and hydrodynamic mixing depths, including evidence of biological activity (burrows, voids, or actual animals), indications of aerobic and/or anaerobic conditions (redox transition zones), and indications of sediment deposition or disturbance (changes in physical sediment characteristics). The sediment penetration depth of SPI cameras is 15–20 cm in soft sediment.
- **Benthic surveys.** The depth of the bioturbation zone is dependent on site location and the type and density of benthic organisms present (USEPA, 2005a). Benthic surveys can identify the type and density of organisms present. A literature review can help establish the typical depth of biological activities for the identified organisms.
- **Luminophores.** Luminophores are colored sediment particle tracers that can be used to measure sediment mixing depths. A range of luminophore particle sizes are available so that site-specific sediment grain size distribution can be duplicated. Luminophores typically are introduced to the sediment surface, and following a specified time-period, sediment cores samples are collected, and luminophores are enumerated across the depth of the sediment core.
- **Beryllium-7 (^{7}Be) profiles in surface sediment.** ^{7}Be has a very short, 23-day half-life. Thus, its presence can be an indication of recently mixed surface sediment and, thus, of biological mixing at the sediment surface. However, investigation of sediment mixing based on ^{7}Be relies on fine sectioning of shallow sediment cores and rapid analysis. Because this method is relatively expensive and difficult to implement effectively, it is not commonly used. ^{7}Be is often accompanied by measurements of dissolved oxygen or redox potential transitions across surface sediment depths to establish the aerobic/anaerobic transition zone and the depth of surface sediment mixing. However, oxygen and redox potential measurements also present accuracy challenges in non-laboratory natural settings.

9.3.5.3 Sediment Stability

Sediment stability is determined using sediment properties (e.g., sediment grain size, bulk density, cohesiveness, organic content, gas content, burial depth, and age) and hydrodynamic conditions (e.g., current flow rates and wave energy during normal- and high-energy events) (Ziegler, 2002; McNeil et al., 1996). Sediment stability should be investigated to assess the stability of the sediment bed and buried chemical deposits. The goal is to determine whether normal or high-energy conditions could contribute to sediment erosion, and whether the magnitude and extent of erosion could contribute to adverse chemical exposures and unacceptable risks at the sediment bed surface. High-energy conditions generally include storms, flood events, wind-wave impacts, other natural events, and human disturbances, such as ship wake and propeller wash.

Whether sediment erosion and transport contribute to increased surface sediment exposures and risk depends on site physicochemical conditions and contaminant mobility. Sediment transport is most relevant to areas of relatively high hydrodynamic energy where contaminated sediment particles do not accumulate. Such areas may include rapidly flowing portions of rivers, ports, and harbors, or rivers where ship traffic persistently resuspends sediment particles and prevents sediment accumulation, or areas with episodic flows that also persistently suspend settled particles, limiting or preventing sediment accumulation.

Factors that can limit contaminant erosion potential include burial of contaminated sediments beneath cleaner sediments and bed armoring, a natural process by which sediment erosion potential decreases over time. Armoring can occur regardless of whether the bed consists predominantly of cohesive (i.e., silt/clay) sediment or non-cohesive (i.e., sand/gravel) sediment, or a mixture of these two types. The physicochemical, geochemical, and transport processes that contribute to bed armoring include the consolidation and cohesion of cohesive sediments with depth and over time, the background shear conditions under which sediment has been deposited (Lau and Droppo, 1999), deposition of relatively coarser sediments on the sediment bed, the preferential erosion or winnowing of finer sediments from the surficial sediment layer (Charlton, 2008; Jones and Lick, 2001), and mineral precipitation (Bayless and Schulz, 2003; Mariner et al., 1996). Armoring of the sediment may occur as the result of moderate-flow events, which tend to preferentially erode finer particles from the sediment surface. The result of this process is a coarsening of the surficial sediment layer relative to the grain size distribution of underlying sediment, which tends to progressively stabilize the sediment bed from erosion during subsequent higher-flow events. Biological processes may also contribute to bed armoring through the creation of cross-linkages between organic materials and sediment inorganic particles (Gerbersdorf et al., 2008). Chemical processes may contribute to bed armoring through precipitation of iron oxides released via acid mine drainage (Bayless and Schulz, 2003), or cementation reactions resulting from surface discharge of high-pH, high-silica groundwater (Mariner et al., 1996).

An important component of the evaluation of MNR processes is to determine whether contaminated subsurface sediments are below the depth at which sediments are considered stable. Erosion potential is one line of evidence for understanding sediment stability and depositional conditions, and it can be determined from analysis of sediment properties and hydrologic conditions. Sediment stability or the potential for sediment erosion can be assessed through site-specific evaluations and measurements, such as the following:

- **Characterize fluvial morphology.** The presence of sediment bed forms, point bars, and additional in-channel geomorphologic features can be examined to further understand depositional and erosional behaviors.
- **Measure sediment bed bathymetry over time.** A comparison of high-resolution, multi-beam sediment bathymetric data can demonstrate changes (or the absence of changes) in the sediment bed elevation over time. This information highlights sediment areas that are depositional, erosional, or stable. In addition, this information can be used to estimate rates of erosion or deposition.
- **Assess hydrodynamic conditions.** Monitoring of flow velocities and surface water elevations, both under normal and high-energy events (storms, winds, prop wash) can be used to assess the hydrodynamic forces that drive sediment transport. This information can also support the development of site-specific hydrodynamic and sediment transport models.
- **Measure sediment bed properties.** Sediment bed properties, such as grain size distribution and bulk density, provide clues about the sediment transport environment. For example, a net deposition of coarse sediments may indicate sediment bed armoring

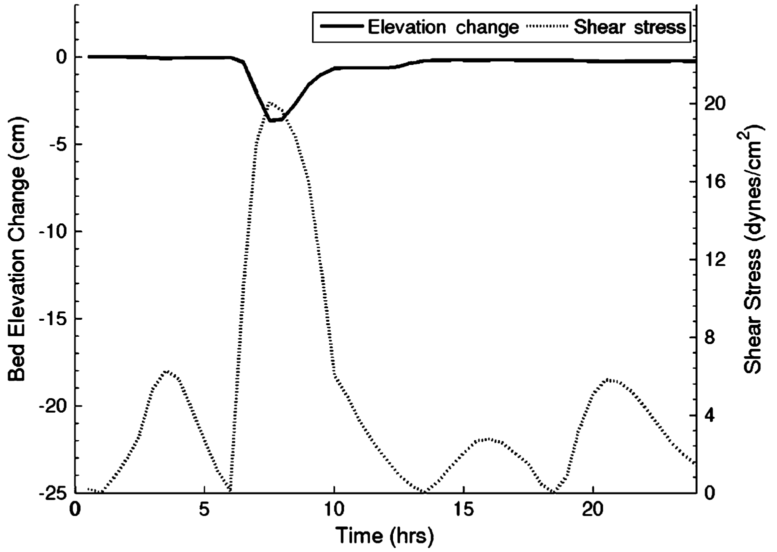


Figure 9.6. Bed elevation changes in lower Hackensack River sediments versus hydrodynamic shear stresses modeled for a 100-yr storm event. Bed elevation is predicted using a SEDZL-J, one-dimensional model. A very limited bed elevation change of <4 cm is predicted during the period of peak shear forces. Following this peak period, the bed elevation is predicted to rebound, approaching baseline conditions within a 24-hour period.

over time, but also may be an indication of relatively high-energy conditions. Conversely, fine-grained and organic-rich sediment particles are generally found in relatively quiescent, depositional environments. Their cohesive properties and ability to consolidate increase sediment shear strength with time. Sediment bed properties also contribute to an understanding of sediment shear strength. These data, along with an understanding of site-specific hydrodynamic conditions, are typically used in the development of a sediment transport model.

- **Measure sediment shear strength.** The erosional behavior of non-cohesive sediments (i.e., coarse sediment deposits) can typically be estimated using site-specific grain size and bulk density data. However, the erosional behavior of cohesive sediments (i.e., fine grained sediment deposits) cannot be predicted based on physical sediment properties and must be measured directly. Various *in situ* and *ex situ* flume technologies have been developed to directly measure sediment shear strength at the sediment surface, or with depth in a sediment core. The flume approach relies on the application of predetermined hydraulic shear forces over the sediment bed surface or over the surface of an *ex situ* box core. By graduating controlled surface flows, the operator can identify the velocity at which the sediment bed begins to erode. *In situ* flumes provide a measurement of surface sediment critical shear strength for which sediment erosion is initiated, and *ex situ* flumes provide a vertical profile of critical shear strength with sediment depth (Lick, 2009). Critical shear strength values can be used in a sediment transport model to predict erosion potential under a range of hydrodynamic conditions.
- **Model sediment transport.** Site-specific surface water hydrodynamic shear forces and sediment shear strength properties may be integrated into a sediment transport model, which can be used to predict sediment stability, sediment deposition, and to estimate erosion potential under various flow conditions, including high-energy events (e.g., Figure 9.6).

Because sediment suspension and deposition processes and rates are highly interconnected, lines of evidence that assess sediment stability – such as sediment physical characteristics and hydrodynamic conditions – also are used to evaluate sediment transport processes. Further, if contaminant transport is predicted, lines of evidence should be developed to understand where and at what concentrations they will deposit.

9.4 ENHANCED MNR

EMNR is a hybrid remedy that relies on the combined effects of engineered means of accelerating natural recovery – often thin-layer placement of cap material – and the development and implementation of a detailed monitoring plan that charts progress toward, and interim targets for, demonstrating natural recovery (USEPA, 2005a; Magar et al., 2009). If thin-layer placement is undertaken as the engineered portion of EMNR, cap thickness is typically between 15 and 30 cm and is driven by consideration of biological and physical mixing processes and chemical fate and transport dynamics, as well as site-specific goals for natural recovery acceleration and the rate and extent of reductions in chemical exposure sought. Overall, EMNR sites are typically characterized by moderately elevated sediment chemical concentrations and relatively quiescent near-bed conditions, but are limited in their capacity for rapid natural recovery because of low background sedimentation rates (Merritt et al., 2010).

EMNR typically is implemented in order to reduce the concentration of chemicals in the biologically active zone of sediment without causing widespread disturbance to existing habitat. Thus, the thin-layer placement component of EMNR is not intended to provide the same degree of separation between contaminated sediments and organisms as afforded by a thicker cap. An effective thin-layer placement rapidly reduces sediment exposures and facilitates recovery of the benthic community by providing a new surface sediment layer of lower chemical concentration than existed previously (NRC, 2003; USEPA, 2005a). Successful implementation of EMNR is measured in terms of the stability and function of the engineered component of the remedy, the accuracy of the CSM in defining a timeframe for ecological recovery, and the ability of the monitoring plan to assess whether risk reduction and ecological recovery are occurring at the rate and to the extent predicted.

9.4.1 Thin-Layer Placement and Stability

Field implementation and pilot studies have demonstrated a variety of successful thin-layer placement strategies under a range of site conditions, including hydraulic washing of capping material from a barge; aerial, surface, or underwater discharge of capping material from a swinging cable arm bucket; use of a split hull hopper barge; underwater discharge using Tremie tubes (i.e., a large-diameter, inflexible conduit designed for underwater release of material near the sediment bed) (Merritt et al., 2010); hydraulic spraying of sand slurry; and use of a spreader barge/diffusive plate (Bailey and Palermo, 2005). Further, results from field implementations suggest that conditions that may initially appear problematic from a geotechnical perspective do not preclude stable cap material placement. For example, at the Ketchikan Pulp Co. site in Alaska, thin-layer placement was initially considered impractical for areas with a very high density of sunken logs, water depth exceeding 30 meters (m), bottom slopes exceeding 40%, organic-rich sediment with inadequate bearing capacity ($<$ 30 kilograms per square meter [kg/m^2]) to support a thin sand cap, and/or locations subject to routine maintenance dredging operations (USEPA, 2005c). Although overall remedial design for the Ketchikan site specified that implementation of EMNR would be limited to water depths less than 30 m, observations and experience at this site suggested that placement of a thin (and consistent) layer of sand was possible in even greater water depths and under sediment conditions (e.g., organic enrichment, prone to gas generation, poor structural stability) initially thought to limit material placement (USEPA, 2005c).

Evaluating the placement and stability of 15–30-cm caps presents a challenge because existing tools are frequently limited in their ability to discern the intermixing of thin sand layers with underlying sediment, particularly when underlying sediment has similar characteristics to the material chosen for thin-layer placement. Although post-placement bathymetric surveys have been conducted at a range of EMNR sites, including the West Harbor Operable Unit (OU) of the Wyckoff/Eagle Harbor Superfund site in Washington (USEPA, 2007) and OU B Marine of the Bremerton Naval Complex in Washington (NAVFAC, 2006a, b), bathymetric monitoring appears to have offered minimal benefit to date for thin-layer-placement areas.

Ongoing improvements in the capabilities of multi-beam bathymetry suggest that resolution on the scale required for effective monitoring of thin cap stability is improving. Alternately, SPI, such as has been employed at the Palos Verdes shelf site in California (Fredette et al., 2002), can facilitate high-resolution inspection of near-surface sediment and can be employed as a technique for monitoring the evolution and consolidation of thin caps over time, although SPI camera surveys are typically limited to sediment depths of 15–20 cm. Visual (plan-view) inspection of the EMNR area, such as was undertaken at the Ketchikan Pulp Co. site, has also proven adequate for verifying material placement and would likely serve to at least confirm the absence of significant erosion within the EMNR footprint over time.

9.4.2 Impact on Benthic Communities

The extent to which the thin-layer placement component of EMNR either directly impacts the existing benthic community or creates changes to sediment chemical and physical properties that impact the benthos has not been fully determined, although several case studies are available as discussed below. Because the benthic community can play a fundamental role in EMNR performance by mechanically mixing the sediment, it is important to rigorously assess hypotheses regarding the low direct impact of thin-layer placement on the existing benthic community. Although thin-layer placement should reduce biotic exposure to sediment-associated chemicals, thereby ameliorating impacts of chemical pollution on benthic ecology, benthic community structure may also be directly impacted by remedy implementation or may ultimately be limited by local conditions unrelated to sediment contamination. Examples of such impacts include the effect of changing sediment bulk density during remedy implementation on benthic community composition (e.g., Kelaher et al., 2003) and the impact of estuary salinity gradients and water level variations on benthic community development (Nichols, 1979; Chapman and Wang, 2001). Thus, a better understanding of the recovery timeframe of the benthic community and benthic habitat quality following material placement is warranted.

At the Ketchikan Pulp Co. site, it appears that significant benthic recovery was achieved within a 5-yr period (Becker et al., 2009a, b). For this site, successful benthic recovery was identified in terms of reduced acute sediment toxicity, and an increase in the number, diversity, and species balance in the benthic community relative to the baseline (pre-placement) community (Becker et al., 2009b). The benthic community present within the EMNR area was identified as representing a transitional community (Becker et al., 2009b) consistent with recolonization patterns commonly observed during the recovery of organically impacted or disturbed sites (e.g., Rhoads and Germano, 1986; Diaz and Rosenberg, 1995).

As a second example, following placement of pilot-scale reactive material caps in the Anacostia River in Maryland, benthic community analysis suggested that recolonization was dominated by deposit-feeding organisms and that although faunal density remained lower than documented in the pre-placement survey, it had increased over the 30+ month monitoring period (Horne, 2007). The reductions in faunal density relative to the pre-placement density may be partially explained by the use of sand as the uppermost layer on the Anacostia River reactive caps (i.e., sand is not an ideal habitat for deposit-feeding organisms). Results from the Anacostia River site highlight the effect of surface sediment quality on benthic invertebrate community recovery, and suggest that for thin-layer placement (and by association, for implementation of EMNR), clean native sediment may be a better substrate than sand for encouraging benthic recolonization. This point is supported by data from the Grasse River site, in which the addition of topsoil to a sand cap improved the characteristics of the sand cap as benthic habitat. For this site, benthic monitoring data from on-cap and reference stations indicated little difference in benthic community metrics 1 yr following material placement (McShea, 2003; Bailey and Palermo, 2005).

A better understanding of the recovery timeframe of the benthic community also allows for more precise assessment of ecosystem services provided by site benthos (including food supply for higher trophic level organisms, and support of recreational, subsistence, and/or commercial harvesting activities), as well as the extent to which these services have been affected by chemical inputs, and to which they may be expected to recover through application of EMNR.

9.4.3 Source Control Considerations

As with MNR and any other sediment remedy, inadequate source control may limit the effectiveness of EMNR. Investigation approaches to determine the effectiveness of past source control measures and the extent of any ongoing sources are discussed further above. A difference between MNR and EMNR with respect to source control is that under an EMNR remedy, the effects of ongoing sources are readily perceived as recontamination of the thin-placement area, whereas effects on the natural recovery rate under MNR are less clearly evident.

For example, at the Wyckoff/Eagle Harbor site, a modest increase in mercury concentrations was measured within the EMNR footprint over time. This modest increase was potentially attributable to multiple processes, including lateral transport and deposition of mercury-enriched flocculent material from the water column, mixing of the cap material with underlying sediment, and/or potential erosion or failure of the thin cap (Merritt et al., 2010). The mean surface sediment mercury concentration was also observed to have increased over the same interval within the reference area (HEC, 2006), however, suggesting that sediment erosion and resuspension – potentially associated with vessel traffic – could be transporting mercury-enriched sediment within the general area.

Similarly, sediment core data collected following pilot-scale placement of a thin cap in the Grasse River (New York) indicated that a layer of low-density solids had settled on the new sediment surface post-capping and that PCB concentrations in the low-density solids (0.2 milligrams per kilogram [mg/kg]) were elevated relative to PCB concentrations in the cap material (< 0.05 mg/kg) (McShea, 2003; Bailey and Palermo, 2005). Although PCB concentrations in the surface sediment remained significantly lower than PCB concentrations in the underlying (native) sediment (mean concentration of 6.8 mg/kg), this relative PCB enrichment in surface sediment relative to capping material suggested that transport of PCB-impacted solids onto the cap was occurring.

9.5 MONITORING NATURAL RECOVERY

USEPA (2005a) identifies the following reasons for long-term monitoring: (1) to assess compliance with design and performance standards, (2) to assess short-term remedy performance and effectiveness in meeting sediment cleanup levels, and (3) to evaluate long-term remedy effectiveness in achieving remedial action objectives (RAOs) and in reducing human health and/or environmental risk. Post-remedy monitoring recognizes that uncertainty is inherent to any cleanup activity and must be managed through data collection and uncertainty mitigation (i.e., using monitoring data and contingency planning to counteract the impacts that may arise from unexpected conditions) (USDOE, 1997, 1999). Common sources of MNR uncertainty may include (SPAWAR and ENVIRON, 2010):

- The vertical and lateral extent of sediment contaminants
- Exposure pathways and kinetics of contaminant transport in aquatic environments
- Future hydrodynamic conditions and sedimentation rates
- Sediment stability and erosion resistance
- Future changes to site use and subsequent impacts on sedimentation, sediment stability, and chemical stability
- Background contaminants and ecological stressors, whether or not they are related to the primary contaminants of concern
- Adequacy of source control

If all uncertainties could be eliminated prior to remedy implementation, there would be no need for post-implementation monitoring (USDOE, 1999). In fact, cleanup decisions typically are made with incomplete data, and uncertainties always exist in remedy selection, design, and implementation. Long-term monitoring is used to determine the extent to which the CSM and remedy selection achieve long-term RAOs. Monitoring programs should ensure that long-term monitoring is clearly tied to RAOs and that clear exit criteria are established to facilitate timely and cost-effective site closure while protecting human health and the environment (SPAWAR and ENVIRON, 2010). An adaptive management approach is a necessary component of implementing an MNR remedy, allowing assessment of alternative approaches if RAOs are not met while facilitating efficiency where natural recovery is demonstrated to be successful (Magar et al., 2009).

9.5.1 Establishing Monitoring Goals

Monitoring provides empirical data to evaluate the extent to which sediment remedial actions achieve short- and long-term goals. Monitoring also can provide information on changing conditions that can impact the remedy, external influences on ecosystem recovery, background sources that can influence or mask recovery, and sedimentation processes that can accelerate recovery. Monitoring may focus on chemical concentrations in various physical (e.g., sediment or water) or biological (e.g., benthic animals, plants, fish, or other relevant receptors) media, physical processes such as hydrodynamics or sedimentation, ecosystem recovery and biological population dynamics, remedy stability, or combinations of these metrics (SPAWAR and ENVIRON, 2010).

According to the *Navy Guidance on Long-Term Monitoring Strategies for Contaminated Sediment Management* (SPAWAR and ENVIRON, 2010), the first step in developing an effective monitoring plan is to determine specific monitoring objectives by analyzing the remedial action and its intended outcomes. This activity results in the formulation of critical monitoring questions. Identifying and asking the right questions from the start focuses the experimental design and ensures the collection of useful information (USEPA, 2004). Critical monitoring questions are driven by the specific functions of the remedy. Sample questions are provided below (SPAWAR and ENVIRON, 2010):

- Are chemical concentrations in physical and biological media decreasing at an acceptable rate to achieve site-specific RAOs within a reasonable timeframe?
- Are sediments stable under normal or high-energy events, and are physical conditions favorable to maintain the physical stability of sediments?
- What is the extent of benthic ecological recovery and/or recovery of higher-trophic species of concern over time?
- Do ecological recovery trends match expectations based on measured physical/chemical trends?
- Do changes in site conditions show diminished risks associated with sediment contaminants and ecological receptors?
- Do changes in site conditions show diminished risks associated with sediment contaminants and human exposures? For example, is there reduced bioaccumulation in organisms? Are human health risks associated with consumption of fish reduced?
- For sites where RAOs already have been achieved, are sediment biological and geochemical conditions favorable to maintain current low-risk conditions?

Formulating questions related to site-specific physical/chemical/biological processes can help establish focused monitoring goals and measurable metrics to support those goals. The inclusion of multiple lines of evidence – such as sediment chemistry, benthic toxicity, benthic community recovery, and tissue chemistry – frequently requires a weight-of-evidence approach whose components should be identified explicitly before inception of post-implementation monitoring.

9.5.2 MNR Monitoring Case Studies

Long-term monitoring for changes in surface sediment chemical concentrations is statistically challenging. Measuring statistically significant changes going from low concentrations to lower concentrations often requires a substantial data set or long time periods. By comparison, biological metrics can provide a higher-level averaging approach that captures the net recovery with respect to important biological end points. Three U.S. case studies are described below, which illustrate the utility of such biological monitoring approaches.

9.5.2.1 Case Study 1: Lower Hackensack River, New Jersey

A key monitoring concern for this chromium-impacted site was the stability of total chromium as Cr(III) in sediments – Cr(III) is not associated with toxic effects. Figure 9.7 shows laboratory toxicity test results measuring polychaete survival in the presence of sediment samples collected from the lower Hackensack River, which was impacted by historical chromium releases. (Figure 9.4, discussed above, shows sediment coring results from the same river). Monitoring revealed no measurable biological impacts to polychaetes associated with total chromium at levels approaching 2,000 mg/kg, although the polychaete species tested are among the most sensitive of all saltwater aquatic species to Cr(VI) (Sorensen et al., 2007). These results were consistent with sediment porewater data collected from the site and the

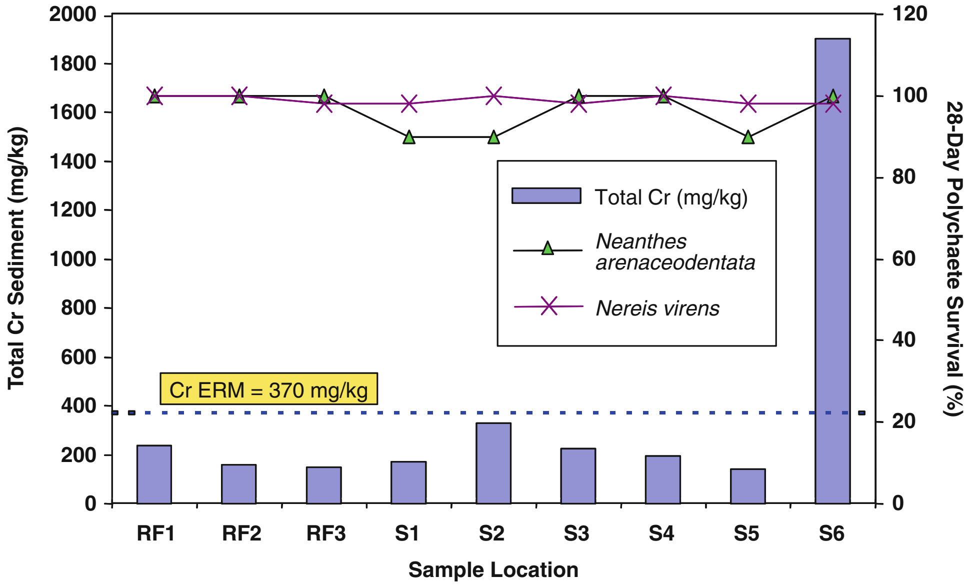


Figure 9.7. Polychaete survival in the presence of chromium in lower Hackensack River sediment. Results show no measurable response to total chromium concentrations approaching 2,000 mg/kg, well above the effects range median (ERM) of 370 mg/kg. These results were supported by non-detect Cr(VI) levels in over 100 porewater samples collected in the vicinity of the site (Sorensen et al., 2007; Martello et al., 2007).

understanding that the chromium in sediment was present as Cr(III), rather than Cr(VI). Porewater Cr(VI) concentrations were below the method detection limit[1] in over 100 samples collected in the vicinity of the site, regardless of the total chromium concentration (Magar et al., 2008). Laboratory resuspension and oxidation testing also demonstrated the geochemical stability of total chromium as Cr(III) in sediment, eliminating concern of chromium oxidation to Cr(VI) (Magar et al., 2008).

9.5.2.2 Case Study 2: Ward Cove, Ketchikan, Alaska

Chemicals of concern in Ward Cove sediment (Ketchikan, Alaska) include ammonia, sulfide, and 4-methylphenol. These contaminants are not considered bioaccumulative. Ecological risks to sediment-dwelling organisms from exposure to sediment are considered significant, but human health risks are considered minimal. Site-specific RAOs for sediment are to reduce toxicity of surface sediments and enhance recolonization of surface sediments to support a healthy marine benthic infaunal community with multiple taxonomic groups (USEPA, 2000).

Sediment sampling occurs every third year in July (e.g., 2004, 2007, and 2010) until RAOs are achieved, or as modified and agreed to by USEPA. Evaluations of sediment chemistry and toxicity and benthic community characteristics (sampling year 2004) indicate EMNR areas of Ward Cove improved substantially and were comparable to reference values. Some natural recovery areas improved, but most were not yet considered sufficiently recovered, supporting the predicted timeline for natural recovery (Exponent, 2005). Monitoring of sediment

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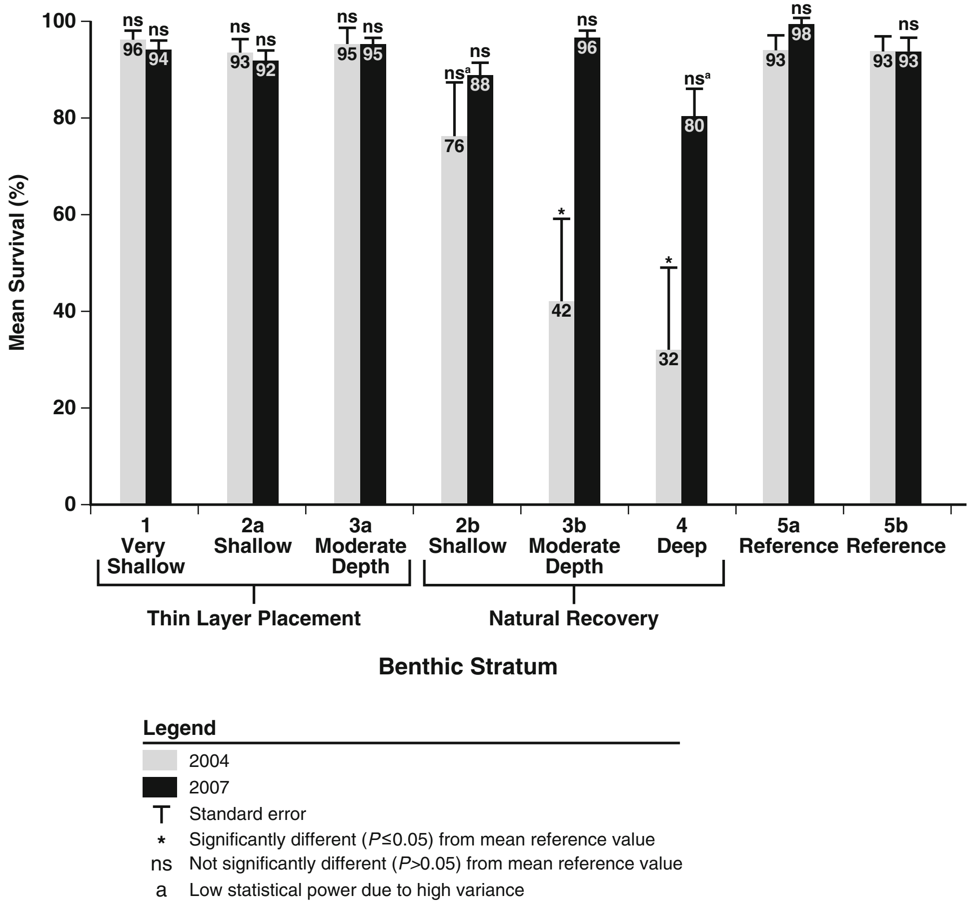
[1] The detection limit for Cr(VI) was 5–10 micrograms per liter (µg/L), well below the USEPA's ambient water quality criterion of 50 µg/L for Cr(VI) in brackish and saltwater systems.



Note: Value of mean amphipod survival is noted at top of each bar

Figure 9.8. Amphipod survival measured in Ward Cove, Alaska, sediment. The figure compares 2004 and 2007 results, showing significant biological recovery in MNR areas, approaching conditions in reference areas and thin-layer placement areas (reprinted with permission from Integral Consulting, 2009).

concentrations, benthic toxicity, and community health in 2007 indicate that MNR continues to reduce risk. Figure 9.8 suggests that the MNR areas are approaching the same level of recovery that background and thin-layer placement areas have achieved.

9.5.2.3 Case Study 3: James River, Virginia

Manufacture of an insecticide known as Kepone (chlordecone) began in Hopewell, Virginia, in 1966 and peaked in 1974 at an estimated 457,630 kg. Kepone was banned in 1975, after employees manufacturing it developed serious health problems linked to the chemical. An estimated 90,720 kg Kepone was released to the environment, and some researchers have estimated that up to 30,000 kg of Kepone could have deposited into sediments (Luellen et al., 2006).

The Virginia State Water Control Board began monitoring fish tissue, river water, and sediment concentrations in 1976. Water sampling was discontinued in 1981, due to sufficiently

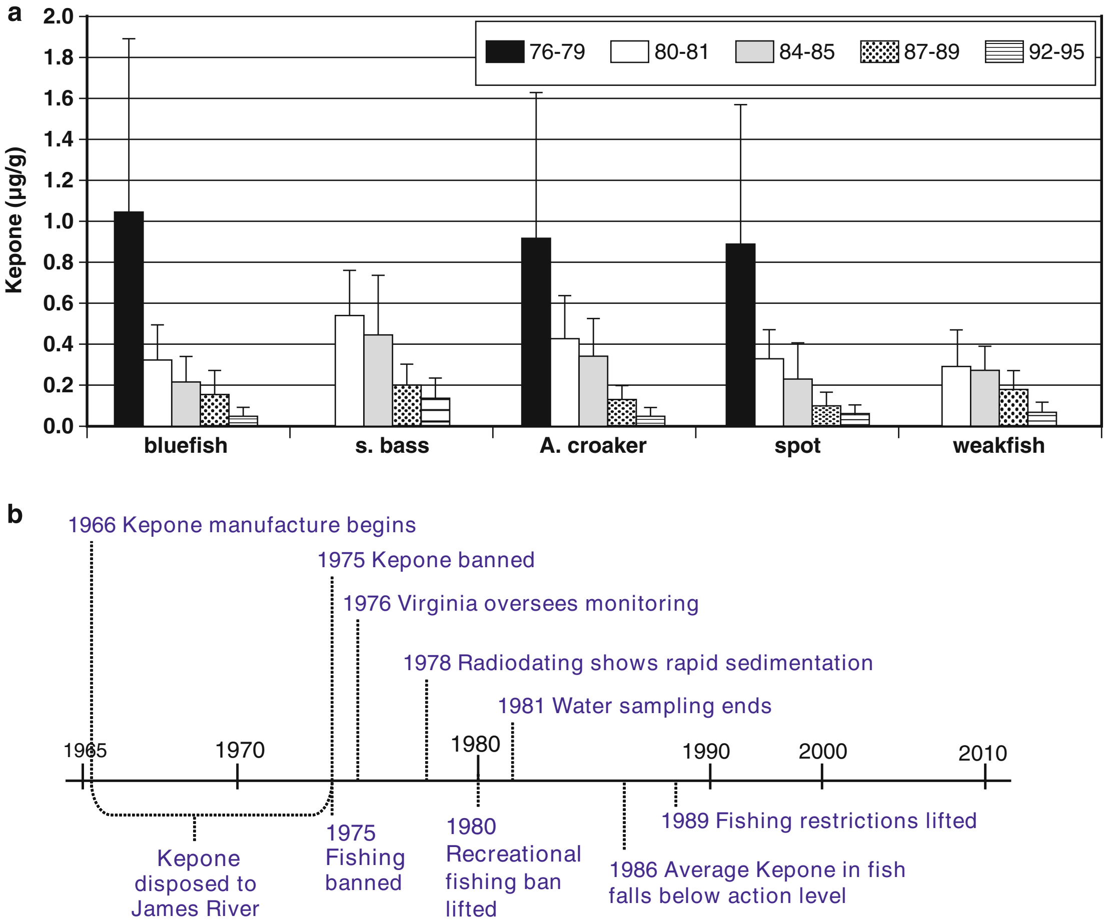


Figure 9.9. (a) Monitoring results for Kepone concentrations in fish over time, from the James River, Virginia (reprinted from Luellen et al., 2006, with permission from Elsevier). (b) Timeline shows changes to fish consumption criteria based on results of fish monitoring and the natural recovery of Kepone in the river.

low average Kepone concentration in the water column (Luellen et al., 2006). Figure 9.9 shows declining Kepone concentrations in fish tissue from a variety of fish species monitored in the river.

On the basis of the fish, water, and sediment sampling, MNR is generally considered to have been successful in reducing Kepone contamination in the James River, and specifically in fish collected from the James River (Magar et al., 2009). The timeline in Figure 9.9 shows that average Kepone concentration in fish fell below the action level by 1986, 11 yr after the contaminant source was controlled. Kepone has persisted in fish tissue samples at low levels that have remained consistent since the late 1980s. Since 1987, 94% of samples have continued to contain Kepone concentrations above detection limits (Luellen et al., 2006), but at relatively low concentrations. The ban on recreational fishing was lifted in 1980, when Kepone levels in fish began to fall below the established action level, and all fishing restrictions related to Kepone contamination were lifted in 1989. While a fish-consumption advisory is still in effect, it is less stringent than the advisory for PCBs in fish from the same area (Virginia Department of Health, 2008; Luellen et al., 2006).

9.6 CONCLUSION

Monitored natural recovery is a USEPA-recognized remedial alternative that – like other remedies – entails contaminant source control, site investigation, development of a CSM, and long-term monitoring. At some sites, MNR has proven to be the most effective option for timely reduction of environmental and human health risks from contaminated sediments (Table 9.1). In some cases where natural processes are not predicted to act quickly enough, EMNR may achieve risk reduction goals. At other sites, remedial alternatives such as capping or removal may be more suitable. However, because natural processes are always ongoing, building a site-specific understanding of natural processes is worthwhile even at sites where constructed remedies are contemplated (Magar and Wenning, 2006; USEPA, 2005a; NRC, 2001). In fact, natural processes play a significant role in recovery dynamics at all sediment remedial projects. Developing a thorough understanding of the role of these processes is critical to successful implementation of MNR.

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CHAPTER 10

IN SITU BIOTRANSFORMATION OF CONTAMINANTS IN SEDIMENTS

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10.1 INTRODUCTION

Challenges to sediment remediation include not only the sheer scope of contamination but also technical limitations and escalating costs associated with cleanup. The development of *in situ* sediment remediation technologies, mirroring the development of successful *in situ* groundwater remediation approaches, has recently been identified as a priority research need (SERDP and ESTCP, 2004) and could result in treatments that are more effective compared to traditional methods. Implementation of technically feasible and cost-efficient *in situ* remediation approaches, such as *in situ* biotransformation, provides numerous potential advantages which could contribute to successful contaminated sediment management. Most notably, *in situ* biotransformation can directly reduce contaminant concentrations and/or toxicity. When occurring naturally, *in situ* biotransformations could serve as a key component for management strategies based on monitored natural recovery (MNR) and could potentially be incorporated into capping and combined remedy designs. In other scenarios, engineering may be required to stimulate particular microbial populations and/or manipulate environmental conditions to optimize biotransformation (and biodegradation) activity.

Properly investigating, implementing, and monitoring *in situ* biotransformation can be complex, especially when attempting to apply remedial strategies at the pilot- and field-scale. It should be noted early that much of the research successes described herein have occurred in laboratory settings, with technical and engineering uncertainties associated with the application of bioremediation at larger, field-scale sediment sites. This is because (1) co-mingled sediment contamination may require competing biotransformation processes to achieve detoxification, (2) low bioavailability of many sediment contaminants can limit the rate and extent of biotransformation, (3) the large spatial footprint of many contaminated sediment sites can make treatment technically and economically impractical (note that this challenge impacts all sediment remedy designs) and (4) introduction of stimulatory amendments (e.g., oxygen) targeting specific biotransformation pathways are subject to rapid consumption, often by competing microbial processes.

The intent of this chapter is to help environmental researchers, practitioners, and regulators address these issues and advance the development of *in situ* sediment bioremediation by providing a better understanding of (1) the fundamentals of *in situ* biotransformations, including key biogeochemical processes present in aquatic sediments, (2) select contaminant biotransformation pathways and (3) how *in situ* biotransformations can be incorporated into sediment remedy options.

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10.2 BASICS OF *IN SITU* BIOTRANSFORMATION

In situ biotransformation of sediment contaminants provides an opportunity to reduce contaminant concentrations and/or toxicity to help achieve adequate risk reductions as a component of site management. Successful investigation and implementation of *in situ* biotransformation requires an understanding of how biotransformations occur, what conditions are required for optimal microbial activity, and what factors may curtail microbial activity and contaminant breakdown. This section introduces principles associated with contaminant biotransformation processes to frame discussions in subsequent sections.

In order to accurately discuss biological activity towards contaminants, a few terms should first be defined. *Biotransformation* is a general term that refers to any chemical transformation that occurs through a microbially- or plant-catalyzed pathway, or through an extracellular enzyme excreted by a microbe or other organism. For the discussions herein, biotransformation will refer to transformations associated with microorganisms. The dechlorination of trichlorobenzene (TCB) to dichlorobenzene (DCB) by *Dehalococcoides* strain CBDB1 is an example of biotransformation. Note that this example does not result in a non-toxic, environmentally-acceptable product since DCB is still a contaminant. *Biodecay* is a term that is generally not preferred in bioremediation practice and refers to the disappearance of a contaminant from a system, presumably via biotransformation, but may not ultimately lead to non-toxic, environmentally-acceptable metabolites. *Bioattenuation* refers to the loss of a contaminant from an environmental system due to biological activity, generally regarded to result in environmentally-acceptable products. Finally, *biodegradation* refers to microbially-mediated mineralization and complete detoxification of contaminants. Biodegradation pathways can include multiple biotransformation reactions occurring in series (e.g., aerobic oxidation of polycyclic aromatic hydrocarbons [PAHs] to carbon dioxide). A term synonymous with biodegradation is *mineralization*. Note that detoxification is not strictly tied to mineralization, as, for example, complete reductive dechlorination of trichloroethene (TCE) to ethene represents detoxification but not mineralization. Confusing the semantics of biological activity can have real-world implications. For instance, some biodegradation rates for TCB obtained under anaerobic conditions may not actually be *biodegradation* rates but rather *biotransformation* rates if only the disappearance of TCB is monitored. The biotransformations of TCB to DCB, monochlorobenzene (MCB), and benzene all need to be considered to quantify true biodegradation rates under anaerobic conditions. Incorrect utilization of biodegradation rates in models could lead to inadequate remedial designs (i.e., overestimation of biodegradation rates and extent). It is also important that numerous lines of evidence demonstrate biotransformation is responsible for contaminant disappearance as opposed to abiotic processes such as sorption, diffusion, or transformation; example data include the concomitant formation of daughter products, the growth of microbial populations (for growth-related processes), increased biomarker expression, the presence of enzymatic activities capable of metabolic or cometabolic biotransformation, and/or ancillary geochemical data.

10.2.1 Environmental Conditions Influencing Biotransformation

For *in situ* biotransformation to occur, the correct microorganisms and the correct environmental conditions need to be present in the sediment. Microbial populations responsible for contaminant biotransformations may exhibit diverse metabolic behaviors, but most processes require similar environmental conditions for optimal activity. Common parameters that influence biotransformation processes are provided here.

Redox Conditions/Electron Acceptors. Proper redox conditions (i.e., electron acceptors) need to be present in the local environment to promote microbial activity and associated contaminant biotransformation. For aerobic biodegradation processes, for instance, oxygen needs to be present to serve as the electron acceptor. Preferential utilization of terminal electron acceptors (TEAPs) by microbial communities leads to vertical separation of biogeochemical cycling processes, such that organic matter oxidation occurs in overlapping regions of dissimilatory microbial reduction of oxygen, nitrate (via denitrification and nitrate reduction), manganese, iron (freshwater), sulfate (marine), and carbon compounds. Spatial microniches of redox processes can also occur in sediments due to localized variances in site conditions. Knowledge of biotransformation pathways and processes in various redox regimes, including differences between freshwater and marine environments, allows investigators to take full advantage of *in situ* biotransformations. For example, low-molecular weight PAHs present in anaerobic portions of sediment can be biodegraded in localized zones where nitrate and sulfate are utilized as electron acceptors but exhibit more recalcitrant behavior under methanogenic conditions. Table 10.1 provides an overview of biogeochemical processes in sediments, methods utilized to identify each redox zone, and example contaminant biotransformations associated with each redox zone.

pH Value. Porewater pH needs to be maintained as close to neutral as possible to allow microbial populations to thrive. Some sites may require porewater pH to be corrected or buffered before microbial activity is observed. Also note that reductive dechlorination of chlorinated organics results in the production of hydrochloric acid, and care should be taken to account for drops in pH during dechlorination activity and the effect it could have on performance.

Nutrients. Nutrients and minerals such as nitrogen and phosphorus need to be present in porewater and available for biological uptake. For example, studies have shown how the addition of limiting nutrients such as B_{12} can improve dechlorination performance (He et al., 2007). Microcosm studies with site material can help identify if nutrient limitations are an issue.

Temperature. Temperatures outside favorable ranges can kill or inactivate bacteria responsible for biotransformations. Population shifts can also occur with swings in temperature, since different organisms thrive in different temperatures, potentially resulting in diminished contaminant biotransformation. For instance, methanogenic activity tends to increase with temperature and can compete with reductive biotransformation processes during warmer months. Therefore, seasonal changes in microbial activity should be considered for sediment sites in environments subject to temperature fluctuations.

Electron Donors. Sediment environments typically have suitable electron donors for microbial growth but organic matter generally becomes more recalcitrant with depth and time. The presence of labile organic matter that can be broken down to carbon and energy sources may therefore be required depending on the site. Himmelheber et al. (2007) showed that biotransformation activity within sediments can be directly correlated to electron donor availability.

Microbial Community Composition. Of primary importance, the microorganisms responsible for contaminant biotransformation need to be present in the matrix in order for reactions to occur. The likelihood of whether the correct microbes are present depends on the type of biotransformation desired and the redox conditions at the site. Additionally, a diverse microbial community needs to be present to break down organic matter and supply electron donors and fermentation products to microbes performing reductive contaminant biotransformation. As an example of how microbes can function better in groups than in pure culture, co-culturing of dechlorinating species with other organisms has been shown to improve overall dechlorination

Table 10.1. Selected TEAPs Common to Sediment Environments and Example Contaminants That Can Be Biotransformed Under the Associated Redox Condition

Sequenced TEAP	Reaction Stoichiometry	Energetic Yield $\Delta G^{\circ\prime}$ ($kJ\ mol^{-1}$)	Field Sampling Indicators for TEAP	Example Contaminant Biotransformations
Aerobic respiration	$\frac{1}{2}O_2 + H_2 \rightarrow H_2O$	−237.2	Presence of dissolved oxygen via microelectrodes or other quantitative means of sampling; detection of enzymes associated with biotransformation (oxygenases); observation of a color change; very strongly positive ORP values (ca. >800 mv)	*Oxidation*: PAHs, fuel hydrocarbons (BTEX), tetra- and lower chlorinated PCBs, chlorinated benzenes, DCE, VC
Nitrate reduction (Denitrification)	$\frac{2}{5}NO_3{}^- + H_2 + \frac{2}{5}H^+ \rightarrow \frac{1}{5}NO_2{}^- + \frac{6}{5}H_2O$	−240.1	Presence of $NO_3{}^-$ (and potential depletion with time); presence of $NO_2{}^-$ (and potential formation with time); detection of *narG*, *nirK*, *nirS*, *norB*, *nosZ* enzymes; nitrate detected via microelectrodes; strongly positive ORP values (ca. 740 mv); dissolved H_2 levels approximately <0.05 nM	*Oxidation*: PAHs, fuel hydrocarbons (BTEX)
Manganese reduction	$MnO_{2(s)} + 2H^+ + H_2 \rightarrow Mn^{2+} + 2H_2O$	−217.4	Presence of $Mn(IV)_{(s)}$ and formation of Mn^{2+}; detection of Mn(IV)-reducing populations; highly positive ORP values (ca. 540 mv)	*Oxidation*: fuel hydrocarbons (BTEX)
Ferric-iron reduction	$2FeOOH + H_2 + H^+ \rightarrow 2Fe^{2+} + 4H_2O$	−182.5	Presence of $Fe(III)_{(s)}$ and formation of Fe^{2+}; detection of iron-reducing populations; detection of *gltA* for *Geobacter*; slightly negative ORP values (ca. −50 mv); dissolved H_2 levels approximately 0.2–1.0 nM	*Oxidation*: fuel hydrocarbons (BTEX), naphthalene *Reduction*: dechlorination of PCE, TCE; mercury methylation

(*continued*)

Table 10.1 (continued)

Sequenced TEAP	Reaction Stoichiometry	Energetic Yield $\Delta G^{\circ\prime}$ (kJ mol^{-1})	Field Sampling Indicators for TEAP	Example Contaminant Biotransformations
Sulfate reduction	$\frac{1}{4}SO_4^{2-} + H_2 + \frac{1}{4}H^+ \rightarrow \frac{1}{4}HS^- + H_2O$	−48.0	Presence of SO_4^{2-} (and potential depletion with time); presence of dissolved sulfide; detection of *dsrA* gene; detection of known sulfate-reducing populations; strongly negative ORP values (ca. ≤ -220 mv); dissolved H_2 at levels approximately 1–1.6 nM; strong odor	*Oxidation*: PAHs and fuel hydrocarbons (BTEX)
				Reduction: PCBs and possible chloroethene dechlorination; mercury methylation
Methanogenesis	$\frac{1}{4}HCO_3^- + H_2 + \frac{1}{4}H^+ \rightarrow \frac{1}{4}CH_4 + \frac{3}{4}H_2O$	−43.9	Presence of methane; detection of *mcrA* gene; very strongly negative ORP values (ca. < -240 mv); dissolved H_2 levels approximately > 5 nM; strong odor	*Oxidation*: fuel hydrocarbons (BTEX)
	$^{*}CH_3{}^{\#}COO^- + H_2O \rightarrow {}^{*}CH_4 + H^{\#}CO_3^-$	−31.0		*Reduction*: dechlorination of PCBs, chlorobenzenes, chloroethenes (PCE, TCE, DCEs, VC), and other chlorinated organics

Note: BTEX – benzene, toluene, ethylbenzene, and total xylenes; DCE – dichloroethene; mv – millivolt(s); nM – nanometer(s); ORP – oxidation reduction potential; PAH – polycyclic aromatic hydrocarbon; PCB – polychlorinated biphenyl; PCE – perchloroethene; TCE – trichloroethene; VC – vinyl chloride performance (May et al., 2008; He et al., 2007). In sediment environments, microbial diversity should not be a concern unless extreme conditions exist (e.g., low pH).

Concentration and Bioavailability of the Contaminants. The concentration of the contaminants in porewater needs to be high enough to support growth for metabolic processes while also not too high such that it becomes toxic to the organisms. For example, Cho et al. (2003) report a PCB concentration threshold of 40 parts per million (ppm) in St. Laurence River sediment, below which dechlorination did not occur. Kjellerup et al. (2008) attributed varying dechlorination activities in three different sediments, in part, to concentration differences among each sediment sample.

History of the Contaminated Environment. In general, microbial activity towards contaminants is highest in areas where contamination has historically been present. Microbes in such areas can adapt mechanisms to respond to the contamination (e.g., a demethylation pathway; Schaefer et al., 2004) or the long-term exposure can allow populations to grow to sufficient numbers to impact contaminant concentrations through biotransformation (Coates et al., 1996). Also, environmental contamination can create biologically selective conditions that allow some populations to flourish; thus, biotransformation activity can be advantageous if the conditions promote its selection.

10.2.2 Intrinsic Biotransformation

Intrinsic biotransformation is the natural occurrence of biotransformation processes by indigenous microorganisms. Microbes capable of contaminant biotransformation are already present in the sediment and environmental conditions are suitable such that the organisms are active and catalyzing biotransformations. For instance, intrinsic biotransformations are responsible for both the methylation and demethylation of mercury since these processes occur without exogenous stimulation. Intrinsic biotransformation can theoretically lead to significant toxicity reductions and serve as an important component of a sediment remedy. For instance, natural attenuation/recovery-based remedies may strongly rely on intrinsic biotransformations along with other attenuation processes (diffusion, sorption). Note that spatial heterogeneity in microbial distribution and local environmental conditions can result in non-uniform reductions in contaminant concentrations. For example, PAHs may be intrinsically biotransformed within the aerobic region of a sediment, but in the underlying anaerobic (i.e., methanogenic) portion of the sediment, PAHs could be recalcitrant. By the same token, some contaminants can be susceptible to intrinsic biodegradation (e.g., benzene) while others are not (e.g., MCB).

10.2.3 Biostimulation

Enhanced in situ bioremediation/biotransformation (EISB) involves the addition of stimulants (e.g., electron donors, pH buffers, nutrients, etc.) to enhance biotransformation processes. *Biostimulation* is the addition of amendments to enhance contaminant biotransformation by native microbial communities. During biostimulation, the microbes required to perform contaminant biotransformations are already present in the site sediment but environmental conditions prevent (or impair) biotransformation activity. An example of biostimulation would be the addition of gypsum (calcium sulfate) to sediments to stimulate sulfate-reducing bacteria (SRB) with the intent of promoting the anaerobic biodegradation of PAHs (Rothermich et al., 2002). Researchers have explored the potential for biostimulation of chlorinated organics, such as PCBs, by providing alternative growth substrates to boost target microbial populations (see examples discussed by Krumins et al. (2009) and Bedard (2008)). Biostimulation has not traditionally been implemented in sediment remediation designs since the distribution of sediment contaminants can be extensive and delivery of stimulants presents an engineering challenge. Biostimulation may be most appropriate for hotspot recovery and opportunities exist for innovative research, development, and implementation in the area of biostimulation for sediment remediation applications (SERDP and ESTCP, 2004).

10.2.4 Bioaugmentation

Bioaugmentation is a form of EISB that involves the injection of microbial populations capable of specific biotransformations into sediment porewater to achieve desired degradation reactions and/or rates. Bioaugmentation is becoming an established practice at groundwater sites where the existing bacterial population is either incapable of complete contaminant detoxification or where the required bacteria are low in number and the addition of a concentrated bacterial culture will accelerate detoxification processes. In most groundwater cases, bioaugmentation is accompanied by biostimulation to ensure that conditions are appropriate for injected microorganisms to remain active in the subsurface following injection. Microbial cultures utilized for bioaugmentation can be very specialized and are typically maintained in mixed, aqueous cultures for community synergism and ease of injection. However, simpler forms of bioaugmentation are possible. One example is supplementing a sand-based *in situ* sediment cap with sediment from a location where intrinsic biodegradation is documented. Since the sediment component of the cap would contain microorganisms and nutrients required for biotransformation, the result would be a bioaugmented cap.

Successful bench-scale demonstrations of bioaugmentation for sediment remediation under both aerobic (Rockne and Strand, 1998) and anaerobic (Ahn et al., 2008; May et al., 2008) conditions have been reported. Bioaugmentation was utilized at the pilot-scale at a tidal wetland seep where groundwater contaminated with numerous halogenated organics was discharging to overlying surface water (Majcher et al., 2007). A microbial community cultured from the site and enriched on halogenated substrates was able to completely dechlorinate the organics found in the sediment porewater (Lorah et al., 2008). To treat the organic discharge, a peat-based organic layer was installed at the sediment surface and bioaugmented with the enriched microbial culture via direct surface application (Majcher et al., 2009; see capping section of this chapter for more discussion). Despite these examples, bioaugmentation has not traditionally been implemented in sediment remediation designs since the distribution of sediment contaminants can be extensive and the (anaerobic) delivery of stimulants and microorganisms presents an engineering challenge. Thus, opportunities exist for innovative research, development, and implementation in the area of bioaugmentation for sediment remediation, especially with the identification and enrichment of microbial cultures capable of biotransforming recalcitrant compounds such as MCB (Fung et al., 2009) and PCBs (May et al., 2008).

10.2.5 Metabolic Versus Co-metabolic Processes

Bioremediation approaches that rely on metabolic processes, in which the organisms benefit and derive energy for growth from contaminant transformation, are generally preferred over fortuitous, co-metabolic processes. Metabolic processes are easier to stimulate and/or implement, sustain, and control under field conditions. In co-metabolic processes, contaminant biotransformations occur as a side-reaction and the microorganisms do not necessarily benefit. For example, PAHs can be degraded in aerobic regions through the action of methane monooxygenase (MMO), an enzyme expressed by methanotrophs utilizing methane as a substrate. MMO attacks the C-H bonds primarily of methane, but halogenated hydrocarbons and aromatics (i.e., PAHs) are also susceptible to attack. Thus, when MMO is expressed, both methane and select contaminants can be degraded. Note that if methane is depleted in this example, contaminant biodegradation would also stop.

10.3 SELECTED CONTAMINANT BIOTRANSFORMATION PATHWAYS

Numerous contaminant biotransformations are possible within sediments and understanding respective pathways allows researchers and investigators to better anticipate which processes may occur at a particular site. Knowledge of biotransformation pathways, the intermediates formed, and the microorganisms responsible can also allow for direct performance monitoring. At sediment sites where multiple contaminants are present, parallel or even synergistic biotransformation pathways may exist; alternatively, opposing pathways may be required for biotransformation of all contaminants (e.g., multiple contaminants requiring different redox conditions). Additionally, some contaminants may be preferably degraded prior to others, potentially leading to sequential bioremediation strategies.

This section provides a brief overview of selected contaminant biotransformation pathways and directs the reader to more extensive reviews of individual processes where applicable. The pathways noted below were selected due to the detection frequency of the contaminant at sediment sites and the potential for biotransformation; note that several other biotransformation pathways exist that are not covered here. Microorganisms responsible for contaminant biotransformations are described and tools for tracking specific pathways are also presented.

10.3.1 PCBs

Polychlorinated biphenyls (PCBs) are halogenated organic compounds consisting of a biphenyl structure – two hexagonal, aromatic carbon rings – connected by a single carbon-carbon bond. Hydrogen and chlorine atoms populate the twin aromatic rings. Individual PCBs can have between 1 and 10 chlorine atoms substituting for hydrogen atoms on the biphenyl rings, resulting in 209 possible chemical structures designated as PCB congeners. PCBs were most commonly utilized as mixtures of 60–90 congeners marketed in North America under the name Aroclor followed by a four-digit number. The first two digits generally refer to the number of carbon atoms in the biphenyl skeleton (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture. Environmental release of these Aroclor mixtures has therefore resulted in sites contaminated with multiple PCB congeners.

PCB congeners exhibit a range of values for aqueous solubility and sediment-porewater partitioning coefficient (K_{oc}) depending on molecular structure; K_{oc} values for PCBs increase with the degree of chlorination, resulting in greater sorption of higher chlorinated PCBs and lesser chlorinated PCBs being more soluble. Variance in these physical-chemical properties among congeners creates temporal changes in total and congener-specific concentrations at field sites. The result is congener mixtures in the environment can be substantially different from the original mixtures released, thus making identification and quantification of PCB biotransformation quite complicated (Quensen and Tiedje, 1997).

PCB congeners can be categorized according to both the number and stereochemistry of the chlorine atoms on the biphenyl molecule. Subdividing PCBs based on the number of chlorines leads to groupings known as homologues (e.g., the trichlorobiphenyl homologues). Examining PCBs stereochemistry, chlorine atoms located adjacent to the carbon-carbon bond bridging the aromatic rings are in the *ortho* position; chlorine atoms located next to the *ortho* position (i.e., two carbons away from the C-C bond) are in the *meta* position; and chlorine atoms located next to the *meta* position (i.e., three carbons away from the C-C bond) are in the *para* position. Chlorine positions on the chlorinated biphenyl (CB) are numbered 2 through 6 sequentially on one aromatic ring (position 1 is the carbon-carbon bond) and 2′–6′ on the second ring. Finally, chlorine atoms located on adjacent carbons are termed *flanked*; chlorine atoms without adjacent chlorines located next to it are *unflanked*.

These distinctions regarding chlorine positioning on the biphenyl molecule are important in many respects. For instance, higher chlorinated PCBs tend to be more sorptive and less bioavailable than lower chlorinated PCBs. Also, anaerobic reductive dechlorination tends to prefer doubly flanked chlorines rather than unflanked chlorines. Perhaps most importantly, toxicity is dependent on chlorine position and can drive risk at many sites; coplanar PCBs, with non-*ortho* substitutions, tend to have dioxin-like properties and are generally the most toxic congeners.

In terms of biotransformation, it is generally true that higher chlorinated PCBs can be dechlorinated under anaerobic conditions to lower chlorinated congeners, which are more susceptible to aerobic biodegradation. Complete PCB biodegradation is theoretically possible by coupling these anaerobic and aerobic processes. Preventing the coupling of sequenced biotransformation pathways at many sites are mass transfer limitations (i.e., sorption) that limit PCB bioavailability and prevent transport of PCB molecules from anaerobic to aerobic zones. To that end, complete biodegradation of PCBs in field sites remains a challenge.

10.3.1.1 Anaerobic Biotransformation Processes

PCBs can be reductively dechlorinated by specialized microbial populations under highly anaerobic conditions (i.e., sulfate-reduction, methanogenesis). Reductive dechlorination is the replacement of chlorine atoms on the biphenyl backbone with hydrogen atoms, resulting in the transformation of higher-chlorinated to lower-chlorinated PCB congeners. Reductive dechlorination has been observed in laboratory and field studies from many different sites (see Bedard, 2003 for an example list), suggesting intrinsic dechlorination can result in alteration of congener mixtures. Microbial reductive PCB dechlorination can provide a natural means of reducing PCB toxicity in aquatic sediments since lower-chlorinated PCB congeners are more soluble (i.e., more bioavailable and less persistent), more easily metabolized, and more biodegradable than higher chlorinated PCBs. Dechlorination also reduces the concentration of dioxin-like congeners which display higher toxicity. These congeners have two *para* chlorines, at least two *meta* chlorines, and no more than one *ortho* chlorine. Dechlorination of non-*ortho* substituted, coplanar congeners thus targets the more toxic congeners and, importantly, does not create more toxic daughter products.

PCB dechlorination from higher chlorinated congeners to biphenyl can proceed through 840 possible pathways (Hughes et al., 2010). Eight different microbial PCB dechlorination patterns have been described, as shown in Table 10.2, with each pattern referring to a particular set of reactions that contain the same susceptible chlorines and chlorine substrate range. Each process is denoted by a letter and described in great detail with diagrams elsewhere (Bedard et al., 2005; Bedard and Quensen, 1995). Combination of the dechlorination patterns *in situ* is common and extends the overall degree of dechlorination. For instance, heptachlorobiphenyls (major components of Aroclor 1260) can theoretically be dechlorinated to 2-2-CB via sequential dechlorination by Processes N and LP (Bedard et al., 2005). Hughes et al. (2010) describe an alternative statistical approach, classification trees, to assess dechlorination patterns that explicitly considers all 840 pathways. The results suggest that the generalized, qualitative dechlorination activities used to group subsets of the 840 dechlorination pathways into processes (Table 10.2) are not specific enough to accurately reflect complete dechlorination patterns.

Table 10.2. PCB Dechlorination Patterns as Described by Bedard et al. (2005) and Bedard and Quensen (1995)

Pattern	Dechlorination Activity
P	Removal of flanked *para* chlorines
H	Removal of flanked *para* chlorines and the doubly flanked *meta* chlorine of 234-CB groups
H’	Removal of flanked *para* chlorines, doubly flanked *meta* chlorine of 234-CB groups, and *meta* chlorine from 23-CB
N	Removal of flanked *meta* chlorines
M	Removal of flanked and unflanked *meta* chlorines
Q	Removal of flanked and unflanked *para* chlorines, doubly flanked *meta* chlorine of 234-CB groups, and *meta* chlorine from 23-CB
T	Pattern T Removal of doubly flanked *meta* chlorines, but has only been observed at elevated temperatures (50–60 °C)
LP	Removal of flanked and unflanked *para* chlorines from 24- and 246-chlorophenyl rings

PCB dechlorination occurs under highly reducing conditions, with some PCB dechlorination processes apparently mediated by SRB, while others are not influenced by sulfate addition (Bedard et al., 2005). Some researchers have observed dechlorination under methanogenic conditions (Ye et al., 1995). Additionally, changes in environmental conditions or concentrations of PCB congeners themselves can shift dechlorination patterns (Cho et al., 2003). These collective observations support the hypothesis that different strains of microorganisms catalyze dechlorination pathways and operate in a mixed consortium. Fagervold et al. (2007) arrived at this same conclusion when examining dechlorination patterns and dechlorinating organisms from Baltimore Harbor sediment.

The recent identification of several PCB-dechlorinating organisms has allowed significant progress in understanding the physiology and capabilities of microbes involved in PCB biotransformation. A number of researchers have linked PCB dechlorination to the activity of microbial strains belonging to the genera *Dehalococcoides* (*Dhc*) (Adrian et al., 2009; Bedard et al., 2007; Fennell et al., 2004) or closely related organisms belonging to a “*Dehalococcoides*-like group” (May et al., 2008; Fagervold et al., 2007; Cutter et al., 2001). *Dehalococcoides* are strict anaerobes found in highly reducing environments that can only utilize halogenated organic molecules as electron acceptors. *Dhc* strains exhibiting activity towards PCBs have been isolated: strains *Dhc ethenogenes* 195 (Fennell et al., 2004) and CBDB1 (Adrian et al., 2009) have each demonstrated the ability to dechlorinate PCB congeners. Importantly, Adrian et al. (2009) demonstrated that *Dhc* strain CBDB1 can dechlorinate 43 different PCB congeners in pure culture, only the second organism isolated exhibiting metabolic activity (see discussion below on *Dehalobium chlorocoercia* DF-1). The pattern of dechlorination of Aroclors by CBDB1 matched Process H, representing the first time that a complex naturally occurring PCB dechlorination pattern has been reproduced in the laboratory using a single bacterial strain. PCB dechlorination carried out by CBDB1 substantially reduced the Aroclor 1248 and 1260 congener concentrations and reduced the concentration of dioxin-like PCBs, thus representing reductions in risk and toxicity. Bedard et al. (2007) provided another quantitative line of evidence implicating *Dhc* by reporting growth of *Dhc* concurrent with PCB dechlorination while no *Dhc* growth occurred in parallel cultures without PCBs.

Reductive dehalogenase genes carried by *Dhc* (and other organisms) encode the enzymes that catalyze the reductive dehalogenation. Only six of the approximately 100 (McMurdie et al., 2009) putative reductive dehalogenase genes in *Dhc* strains have been characterized, most of which are active towards chlorinated ethenes (Müller et al., 2004; Krajmalnik-Brown et al., 2004; Suayama et al., 2002; Magnuson et al., 2000). Adrian et al. (2007) identified dehalogenase gene *cbrA,* which is responsible for chlorobenzene dechlorination, but activity on PCBs has not yet been reported. Consequently, many *Dhc* strains have unknown metabolic, dehalogenating capabilities. For example, strain CBDB1 can grow on PCBs but only has two (*pceA*; Morris et al., 2007 and *cbrA*; Adrian et al., 2007) of its 32 (Kube et al., 2005) putative dehalogenase genes characterized while *Dhc* strains 195, FL2, BAV1, and VS contain at least 18 (Seshadri et al., 2005), 14 (Hölscher et al., 2004), 11 (Löffler et al., 2013), and 36 (McMurdie et al., 2009) non-identical dehalogenase genes, respectively. The unknown potential of these putative dehalogenases offers promise for unlocking currently unknown PCB dechlorination capabilities. Monitoring *in situ* levels of PCB-dechlorinating *Dhc* strains, and potentially dehalogenase genes, by molecular methods can serve as biomarkers for PCB dechlorinating populations (see Bedard et al. (2007), Watts et al. (2005) as examples).

Potential also lies in recently identified *Dhc*-like strains in the phylum *Chloroflexi*. An organism capable of *ortho* dechlorination of 2356-CB, *o*-17, has been described and observed during periods of PCB dechlorination but absent during PCB inhibition (Cutter et al., 2001). Phylogenetic analysis of the 16S rRNA gene of *o*-17 place it in a deep branch of the *Chloroflexi* with *Dhc* strains 195 and CBDB1 as *o*-17's closest cultured relatives; however, *o*-17 has yet to be isolated in pure culture. Bacterium *Dehalobium chlorocoercia* DF-1 is another *Dhc*-like strain in the *Chloroflexi* phylum, which was isolated from Charleston Harbor sediment (May et al., 2008), representing the first microorganism in pure culture demonstrated to grow by dehalorespiration with PCBs. Watts et al. (2005) developed specific primers targeting the *o*-17 and DF-1 strains and identified the *o*-17/DF-1 bacteria as the main dechlorinating organisms in sediment microcosms exhibiting active dechlorination of PCBs. Yan et al. (2006) observed PCB dechlorination in three geographically unique sediment samples, with the same *Dhc*-like organism present in each culture. The presence of this *Dhc*-like organism, and its demonstrated PCB dechlorination abilities, in three different samples suggests it may be relatively well disbursed among PCB-contaminated sites, leading to some degree of intrinsic dechlorination if the organisms are active.

Intrinsic PCB dechlorination activity has been observed in a number of locations. Bedard (2003) and Abramowicz (1995) tabulated over 20 locations each where microbial PCB dechlorination activity was observed along with the presence of microorganisms capable of PCB dechlorination. However, numerous other case studies document a lack of dechlorination or inhibited dechlorination, even when dechlorinating microorganisms are present (see Bedard (2008) as an example). Lack of biotransformation can be attributed in part to bioavailability issues. PCBs are very sorptive compounds (i.e., high K_{oc} values) which keep porewater concentrations low. The lack of bioavailable, dissolved PCBs can limit the growth of *Dhc* and other PCB dechlorinating populations (Cho et al., 2003; Sokol et al., 1998; Quensen et al., 1988), suggesting that PCB concentrations may actually be too low at some sites to initiate dechlorination activity. Note that this phenomenon is not a steadfast rule, and dechlorination potential at each site should be examined before assuming PCB concentrations are too low. The addition of alternative halogenated substrates to PCB-contaminated sediments has been shown to increase PCB dechlorination rates by artificially boosting ("priming") dechlorinating populations (Krumins et al., 2009; Bedard et al., 1998). Biostimulation of dehalogenating populations is a potential bioremediation strategy if economical, environmentally-acceptable priming compounds can be identified. An alternative biostimulation strategy was investigated at the bench-scale by Rysavy et al. (2005) who provided Fe(0) to microcosms to produce cathodic hydrogen to serve as electron donor to PCB-dechlorinating populations. The addition of Fe(0) reduced the lag time for removal of doubly flanked *para* chlorines by approximately 100 days, a result that was replicated following the addition of hydrogen directly to the headspace. These results suggest that small doses of Fe(0), to avoid build-up of inhibitory metabolites, could potentially be used to stimulate PCB degraders *in situ*. Note that adequate numbers of indigenous PCB dechlorinators must be present for biostimulation to succeed (Winchell and Novak, 2008) and that bioaugmentation coupled with biostimulation may be more beneficial to overcome slow growth kinetics and competing microbial demand for electron donor.

10.3.1.2 Aerobic Biotransformation Processes

Aerobic biotransformation of PCBs can ultimately lead to detoxification of the persistent organic compounds. In general, lesser chlorinated congeners are more easily oxidized compared to higher chlorinated congeners under aerobic conditions. Also, PCB congeners with chlorines only on one aromatic ring are more easily oxidized compared with those with chlorines on both rings. Microbial oxidation of mono- through trichlorobiphenyl congeners is catalyzed by many different aerobic biphenyl-degrading bacteria found in soils and sediments, suggesting that intrinsic PCB oxidation is a common biotransformation potentially leading to reductions in contaminant concentrations. Microbial isolates possess unique substrate ranges with regard to the type and extent of PCB congeners metabolized. Some strains have a narrow spectrum and others, notably *Burkholderia xenovorans* LB400, are able to transform a broad range of congeners (Seeger et al., 1999). Reviews of aerobic PCB biotransformation containing further information and detail can be found in the literature (Pieper and Seeger, 2008; Pieper, 2005; Seeger et al., 1997).

Aerobic bacteria use dioxygenases to hydroxylate PCBs and initiate a four-step biphenyl upper (bph) pathway to ultimately break open one of the biphenyl rings and generate chlorobenzoic acid and a five-carbon fragment, as depicted in Figure 10.1. This fragment is metabolized to acetyl Coenzyme A and enters the tricarboxylic acid cycle (TCA) cycle, providing an example of how microorganisms break down xenobiotic chemicals into common intermediates for incorporation into metabolic cycles. Biphenyl 2,3-dioxygenases (BphA) catalyze the first step of the process and dictate the range of PCB congeners that can be transformed (Figure 10.1). BphAs have considerable differences in their congener selectivity, as well as their preference of the attacked ring. The preferred order of dioxygenase attack, from most favorable to least, has been observed to be: unsubstituted biphenyl, 2-CB, 25-CB, 24-CB

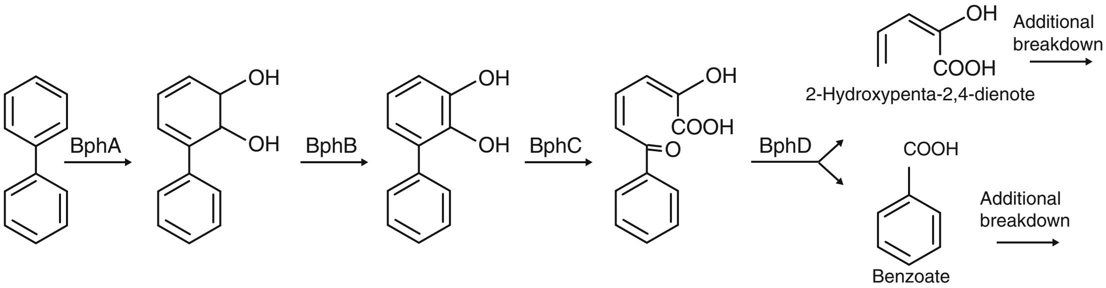

Figure 10.1. Upper pathway of aerobic biphenyl biodegradation and associated enzymes (adapted from Seeger et al., 1997 and Pieper and Seeger, 2008).

and 3-CB, 4-CB, and finally 23-CB (Pieper and Seeger, 2008). The second step in the metabolic pathway is catalyzed by *cis*-2,3-dihydro-2,3-dihydroxybiphenyl dehydrogenases (BphB) and produces (chlorinated) 2,3-dihydroxybiphenyl. BphB are involved in various aromatic degradation pathways and have a broad substrate range. The third step of aerobic PCB oxidation in the bph pathway, ring-cleavage of aromatic intermediates having hydroxyl groups on adjacent carbon atoms, is catalyzed by 2,3-dihydroxybiphenyl1,2-dioxygenases (BphC). These enzymes specialize in transforming (chlorinated) 2,3-dihydroxybiphenyl to a dienote intermediate. The final step in the bph pathway is catalyzed by 2-hydroxy-6-phenyl-6-oxohexa-2,4-dieneoate (HOPDA) hydrolase (BphD), which hydrolyzes chlorinated HOPDA to yield chlorinated 2-hydroxypenta-2,4-dienoate and chlorobenzoates (Seeger et al., 1997). Monitoring of chlorobenzoates can serve as a marker for aerobic PCB oxidation (Harkness et al., 1993). Additional Bphs carry out the remainder of the biodegradation process producing metabolites that enter metabolic cycles.

Strain LB400 and *Rhodococcus* sp. strain RHA1 are two model microorganisms that can metabolize a broad range of PCBs. Genomes of both organisms have recently been sequenced (Chain et al., 2006; McLeod et al., 2006) to provide previously unknown information regarding the overall physiology and capacity of these organisms to biodegrade PCBs, potentially with applicability for bioremediation purposes. For instance, the genome sequences indicate unusually high metabolic versatilities as LB400 and RHA1 funnel a broad range of aromatic compounds through peripheral aromatic pathways (20 and 26, respectively) into central aromatic pathways (11 and 8, respectively). Work by Rodrigues et al. (2001) highlights the value of understanding the molecular mechanisms of microbial biotransformations through genomic studies. Rodrigues et al. (2001) utilized a previously augmented strain of RHA1 and created an engineered strain of LB400 by incorporating chlorobenzoate dechlorinating genes into the organisms. The addition of *ortho* (*ohb*) and *para* (*fcb*) chlorobenzoate dechlorinating genes allowed the microbes to grow on 4-chlorobenzoate and consequently mineralize 2-chlorobiphenyl with growth quantitatively tracked through novel primers targeting the organisms. The group then simulated an anaerobic-aerobic biodegradation pathway by coupling the reductive dechlorination with aerobic mineralization resulting in significant destruction of PCB mixtures (>50%) coupled with growth (Rodrigues et al., 2001).

Aerobic metabolism of PCBs is limited not only by PCB toxicity and the lack of microbial activity towards higher chlorinated congeners, but also by the availability of oxygen for incorporation into substrates by dioxygenases. Oxygen penetration into sediments can be limited to a few centimeters while PCB contamination extends much deeper. Harkness et al. (1993) was able to overcome this limitation in a pioneering field study through the addition of inorganic nutrients, biphenyl, and oxygen to stimulate *in situ* aerobic biodegradation of PCBs in the Hudson River. Loss of lesser-chlorinated PCBs and the production of chlorobenzoates confirmed microbial activity of the indigenous population. However, distributing adequate levels of oxygen into sediments, both spatially and temporally, is an engineering challenge that restricts this biostimulation approach.

10.3.2 PAHs

Polycyclic aromatic hydrocarbons (PAHs) are another class of contaminants commonly encountered in sediments. PAHs result from incomplete combustion of organic material, and are often associated with industrial activity and urban runoff. PAH molecules consist of multiple fused aromatic rings, with individual rings on PAH molecules consisting of either five or six carbons. Similar to PCBs, PAHs consist of a large number of compounds and environmental contamination is generally in the form of mixtures. Of primary environmental concern are compounds ranging from relatively mobile naphthalene ($C_{10}H_8$; two rings) to coronene ($C_{24}H_{12}$; six rings).

PAHs are categorized both by the number of aromatic rings on the structure (two rings, three rings, four rings, etc.) and by molecular weight. Low molecular weight (LMW) PAHs are generally regarded to be composed of four rings or less; while high molecular weight (HMW) PAHs are composed of greater than four rings. PAH K_{oc} values tend to increase with the number of rings, and sorption to hard carbon components of organic matter is especially strong, making LMW PAHs more soluble. Toxicity also generally increases with the number of rings, and the combination of greater solubility and lower toxicity make LMW PAHs more amendable to microbial biotransformation compared with HMW PAHs. Field sites contaminated with aged PAHs thus tend to be enriched in HMW PAHS. Alternatively, because LMW compounds are more bioavailable compared to HMW PAHs, they contribute most to the acute toxicity of PAH contamination, underscoring the importance of biotransformations in risk abatement.

PAH biodegradation has been observed under both anaerobic and aerobic conditions, suggesting biotransformations can play a major role in remedies for PAH contaminated sediments. Much research has investigated PAH biotransformation under various redox conditions resulting in improved understanding of the capacity of microorganisms to mediate *in situ* contaminant destruction. However, the persistence of PAH contamination indicates that factors are present that limit extensive biodegradation. Low bioavailability has been reasoned to be a primary cause of PAH persistence, leading to the development of models that account for the influence of different types of organic matter (i.e., hard carbon) and PAH desorption resistance on PAH biotransformation (e.g., Beckles et al., 2007). In addition to physical partitioning and low aqueous PAHs concentrations, other biologically-related factors seem to inhibit intrinsic biodegradation (e.g., threshold concentrations, enzyme expression), summarized well by Tang and Carothers (2007).

10.3.2.1 Anaerobic Biotransformation Processes

PAHs have traditionally been regarded as recalcitrant to biodegradation under anaerobic conditions; however, research indicates that select LMW PAHs can be mineralized under nitrate-reducing and sulfate-reducing conditions through metabolic and cometabolic pathways. Due to the recent discovery of these pathways, and difficulties cultivating denitrifying or sulfate-reducing PAH-degrading pure cultures and enrichments, anaerobic PAH biotransformation pathways still need to be resolved and detailed information is limited. Consequently, mechanistic discussions of anaerobic PAH biotransformations will largely be avoided here, but thorough discussions are provided elsewhere (Foght, 2008; Meckenstock et al., 2004).

PAH biodegradation under nitrate-reducing conditions was first reported by Mihelcic and Luthy (1988) and subsequently reported by other groups. Bregnard et al. (1996) used ^{14}C-napthalene under nitrate-reducing conditions to confirm anaerobic mineralization of weathered PAHs under nitrate-reducing conditions. Rockne et al. (2000) and Rockne and Strand (1998, 2001) similarly found that naphthalene and phenanthrene could be degraded by a denitrifying enrichment culture derived from creosote-contaminated marine sediment. Different mineralization capacities were observed for different PAHs. Rockne et al. (2000) reported 17% naphthalene mineralization compared to 96% phenanthrene; however, the amount of naphthalene incorporated into biomass was higher (Rockne and Strand, 2001). Three nitrate-reducing, naphthalene-degrading strains were isolated from these studies (Rockne et al., 2000) and two were characterized. NAP-3-1 (phylogenetically related to *Pseudomonas stutzeri*) coupled partial naphthalene mineralization to complete denitrification whereas strain NAP-4-1 (related to *Vibrio pelagius*) reduced nitrate to nitrite.

These collective studies indicate that PAH mineralization under nitrate-reducing conditions can occur. Note, however, that the nitrate-reducing zone in sediments tends to be compressed and spatially limited. This means that intrinsic PAH oxidation under nitrate-reducing conditions, although a reported pathway, may not be a significant process at field sites. Biostimulation of nitrate-reduction is also challenging due to toxicity and water quality concerns regarding the addition of nitrate and the possible production of ammonium. With these concerns in mind, Tang et al. (2005) examined the feasibility of incorporating a slow-release nitrate source (nitrocellulose) into marine sediments in an attempt to stimulate nitrate-reducing PAH degraders. The authors report nitrocellulose addition increased phenanthrene biodegradation rates compared to intrinsic rates and resulted in greater than 40% mineralization, suggesting the potential for innovative approaches of stimulating *in situ* anaerobic PAH biodegradation. Tang et al. (2005) also examined the addition of sulfate (in the form of gypsum) to marine sediment to stimulate PAH biodegradation mediated by sulfate-reducing populations, a process that also shows potential.

Coates et al. (1996) reported the mineralization of ^{14}C-naphthalene and phenanthrene within contaminated harbor sediments dominated by sulfate-reducing conditions. Bedessem et al. (1997) observed mineralization of ^{14}C-naphthalene incubated with nine different enrichment cultures under sulfate-reducing conditions, although the lag times and degradation rates varied widely among enrichments. These early studies, along with others (Meckenstock et al., 2000; Zhang and Young, 1997) have helped establish the role sulfate-reducing microbes play in PAH biodegradation. Rothermich et al. (2002) constructed microcosms from sulfate-reducing site material with long incubation periods (1 year) to observe considerable depletion of multiple 2–3 ring PAHs and even HMW PAHs (e.g., chrysene, pyrene, and benzo[*a*]pyrene [BaP]), demonstrating for the first time that unsubstituted HMW PAHs could be attacked under sulfate-reducing conditions. The mode of the attack is unknown, however, since diagnostic intermediates were not assessed and because the larger PAHs were not radiolabeled for measurement of $^{14}CO_2$ production. Additional PAHs reportedly vulnerable to biodegradation under sulfate-reducing conditions, in addition to naphthalene and phenanthrene, include fluorene and fluoranthene (Coates et al., 1996), anthracene, acenaphthene, and pyrene (Chang et al., 2002). Note that in many of these studies, however, the production of intermediates was not followed nor were cell growth rates monitored. Young and Phelps (2005) describe the elucidation of a carboxylation-initiated pathway for naphthalene degradation, which produces 2-naphthoic acid (2-NA) as an intermediate that can be tracked as a biomarker. Given this documentation of PAH biodegradation under sulfate-reducing conditions, sulfate addition to stimulate biodegradation has been examined in microcosms (Rothermich et al., 2002) and in columns (Tang et al., 2005) by adding gypsum.

Anaerobic naphthalene oxidation under iron-reducing conditions has been reported (Anderson and Lovley, 1999; Ramsay et al., 2003), indicating another potential attenuation pathway for PAHs. However, anaerobic PAH biodegradation coupled with ferric iron-reduction has not been widely observed and remains relatively uncommon. Evidence of PAH biodegradation under methanogenic conditions is limited but recent theoretical (Dolfing et al., 2009) and field studies (Wook et al., 2005) suggest it may be possible. These studies offer an opportunity to study novel biodegradation mechanisms, but mineralization of PAHs under methanogenic conditions at field sites should remain unexpected.

Monitoring anaerobic PAH biodegradation has mostly been done with samples collected and brought back to the laboratory. This is because the products of mineralization (CO_2, water) cannot easily be discerned from background levels. Laboratory data are therefore needed to corroborate potential *in situ* anaerobic PAH biodegradation, and the utilization of ^{14}C-labeled substrates (e.g., naphthalene, phenanthrene) is needed to conclude mineralization. The presence of 2-NA as an intermediate during naphthalene biodegradation under sulfate reducing conditions provides an additional *in situ* parameter for assessing biodegradation (Young and Phelps, 2005). Finally, note that most studies investigating anaerobic PAH oxidation have focused on naphthalene and phenanthrene. Biodegradation of these compounds is becoming better understood; however, biodegradation of alternative PAH, especially HMW PAHs, is challenging and documented cases exhibiting such activity in the field remain limited.

10.3.2.2 Aerobic Biotransformation Processes

Biodegradation of PAHs under aerobic conditions in sediments has been documented as a robust and relatively well-understood pathway for many congeners. Aerobic biotransformations can directly lead to rapid mineralization for both LMW and HMW PAHs, making it an important process for the remediation of contaminated soils and sediments. Researchers have recognized this importance and aerobic PAH biodegradation has been the subject of intense study over the last two decades. However, transference of laboratory successes to field-scale remedial designs relying on aerobic PAH biodegradation is lacking. Information here will be limited to brief descriptions of specific PAH biodegradation pathways, tools to help assess aerobic PAH biodegradation, and what limitations may prevent intrinsic biodegradation. References to additional sources of information are provided where appropriate.

Many microorganisms have been isolated that utilize naphthalene as its carbon and energy source (see reviews by Seo et al., 2009 and Samanta, 2002). Aerobic naphthalene biodegradation pathways are initiated by the activity of an evolutionarily conserved naphthalene dioxygenase (NDO) system. The two primary NDO-mediated degradation pathways are distinguished by conversion of naphthalene, via salicylate, to either catechol (e.g., *nah* genes) or gentisate (e.g., *nag* genes) to enter into the TCA-cycle. A schematic of the pathway is provided in Seo et al. (2009). Many organisms have also been isolated that utilize phenanthrene as the sole carbon and energy source (see Seo et al., 2009; Samanta et al., 2002 for reviews). The structure of phenanthrene allows it to form an epoxide (bay- and K-regions), and leads it to be used as a model substrate for studies on bay- and K-region containing carcinogenic PAHs such as BaP, benzo[*a*]anthracene, and chrysene. Bacterial degradation of phenanthrene is initiated by 3,4-dioxygenation to yield *cis*-3,4-dihydroxy-3,4-dihydrophenanthrene, which undergoes enzymatic dehydrogenation to 3,4-dihydroxyphenanthrene before further breakdown. Seo et al. (2009) provides an overview of the scheme. Phenanthrene dioxygenases have been identified and tracked in the field, including *phn* genes in *Burkholderia* (Laurie and Lloyd-Jones, 2000) and *phd* genes in *Nocardioides* sp. strain KP7 (Saito et al., 2000). Several bacteria use fluorene as their sole source of carbon and energy, employing one of three major catabolic pathways. The first pathway initiates with a 1,2-dioxygenation of fluorene and forms a dihydrodiol (fluorene-1,2-diol) characteristic of aerobic PAH biotransformation, which is further transformed (Casellas et al., 1997; Monna et al., 1993). The second pathway begins at an initial 3,4-dioxygenation of fluorene leading to eventual salicylate formation (Casellas et al., 1997; Grifoll et al., 1995). The third pathway starts from C-9 monooxygenation in *Brevibacterium* sp. DPO1361 and *Pseudomonas* sp. F274 (Trenz et al., 1994; Wattiau et al., 2001). Refer to Seo et al. (2009) for illustrations of the three pathways.

A key advantage of aerobic PAH biotransformation is that it also targets HMW PAHs, including fluoranthene, pyrene, chrysene, and benz[*a*]anthracene. For instance, *Stenotrophomonas maltophilia* strain VUN 10,003 was evaluated in a basal liquid medium for fluoranthene degradation and co-metabolism of other PAHs, including pyrene, benz[*a*]anthracene and coronene (Juhasz et al., 2000). Several bacteria have been isolated from varying hydrocarbon contaminated soils and use fluoranthene, pyrene, and chrysene as sole carbon and energy sources. Kanaly and Harayama (2010) provide extensive information regarding the biodegradation of pyrene, fluoranthene, and other HMW PAHs including pathways and the microbes implicated.

A few studies have documented the bacterial degradation of BaP, a five-ring molecule that is one of the more toxic PAH congeners and serves as a benchmark against which the toxicity of other PAH congeners are measured. Although BaP has been detected in a variety of environmental samples, so far no microorganism has been reported that can use BaP as a sole source of carbon and energy. Biodegradation is therefore a result of cooperation among different organisms. Modest degradation of BaP in a PAH mixture has been reported with *Mycobacterium* sp. (Kelley and Cernigilia, 1995). *M. vanbaalenii* PYR-1 was shown to metabolize BaP in laboratory cultures with defined medium and the addition of phenanthrene in dimethylformamide to induce enzyme expression (Moody et al., 2004). Initial enzymatic attack of BaP appears to occur at the 45-, 78-, and 910-positions based on the intermediates formed (Seo et al., 2009; Kanaly and Harayama, 2010).

Advancements in molecular biology and culture-independent techniques has allowed for the detection and quantification of target microorganisms in field samples. For instance, a soil-derived consortium capable of rapidly mineralizing BaP was analyzed using denaturing gradient gel electrophoresis (DGGE) profiling of polymerase chain reaction (PCR)-amplified 16S rDNA gene fragments to reveal sequence types that were closely related to known HMW PAH-degrading bacteria (Kanaly et al., 2000). Many PAH-degrading bacteria and/or phylotypes have been detected using similar 16S rRNA-based approaches, with special attention focused on the detection and quantification of common genes encoding subunits of dioxygenases, which initiate the PAH biodegradation pathway in Gram positive organisms (*nar*Aa, *phd*A/*pdo*A2, *nidA*/*pdoA1*, *nid*A3/*fad*A1) and Gram negative organisms (*nah*Ac, *nah*A3, *nag*Ac, *ndo*B, *ndo*C2, *pah*Ac, *pah*A3, *phn*Ac, *phn*A1, *bph*Ac, *bph*A1, *dnt*Ac and *arh*A1). Monitoring of these genes can provide valuable information regarding genotypic potential for PAH mineralization and also serve as a line of evidence to support observations of potential biodegradation (Widada et al., 2002).

The number of identified dioxygenases active towards PAH molecules, especially naphthalene and phenanthrene, reflect the robust nature of aerobic biodegradation of these compounds. However, non-detection of a biomarker at a site does not necessarily equate to a lack of activity, since other known (and unknown) dioxygenases may be present. Cébron et al. (2008) tried to overcome this problem by designing primer sets targeting genes encoding the alpha subunit of the PAH-ring hydroxylating dioxygenases (PAH-RHD$_\alpha$) of both Gram positive and Gram negative organisms and found correlation between the amounts of PAH-RHD$_\alpha$ gene copies and PAH contamination in field samples. DeBruyn et al. (2009) provide another example as pyrene dioxygenases genes (*nidA*) were quantified in Lake Erie sediments to better understand microbial communities and genotypic potential for biodegradation. The authors reported the highest abundances of *nidA* at the most contaminated PAH site; however, naphthalene dioxygenases investigated (*nahAc* and *nagAc*) were not correlated to PAH concentrations, and other naphthalene dioxygenases may have been present.

A case study where aerobic PAH biodegradation contributed to PAH attenuation in the field is the Eagle Harbor Superfund site located in Seattle, Washington. Brenner et al. (2002) performed a thorough characterization of the creosote-contaminated sediments, tracking 50 different PAH congeners. Radiogeochemical analysis (^{210}Pb and ^{137}Cs) provided sediment age dating and allowed the investigators to distinguish among different sources of PAH contamination: creosote, urban runoff, and background. Tracking of the PAH congeners over time indicated a loss of LMW PAHs attributed to weathering processes and an increase in the percentage of HMW PAHs (i.e., HMW PAHs were more recalcitrant towards weathering processes). Although biodegradation was not explicitly found to be the cause of LMW depletion at the site, it likely caused some of the loss of PAHs along with other weathering processes. Another example of aerobic PAH biodegradation incorporated into a sediment remedy was a small-scale study where downflow of surface water through a sand-based sediment cap induced aerobic conditions within the cap and allowed for aerobic oxidative biodegradation processes (Hyun et al., 2006).

The hydrodynamics of this latter example allowed for oxygen penetration into the matrix, however minimal oxygen penetration into most aquatic sediments greatly restricts the amount of PAH biodegradation. Stimulation of PAH biodegradation by introducing oxygen to sediments is challenging due to natural oxygen demand (biological and chemical), rapid depletion, and limited spatial impact. This leads to uncertainty regarding the extent and rate to which aerobic biodegradation can achieve acceptable risk levels at sites. Because of rate variations among sites, site-specific studies are suggested to resolve uncertainties concerning degradation rates and whether these rates will contribute to recovery within an acceptable timeframe.

10.3.3 Mercury

Elevated mercury (Hg) concentrations, most notably in the form of methylmercury (MeHg), drive risk at many contaminated sediment sites. Complex *in situ* biogeochemical cycling, as illustrated in Figure 10.2, makes assessment and characterization of Hg risks complex. This cycling includes processes such as methylation and demethylation that can be mediated by bacterial populations. Thus, although Hg (like other elements) cannot degraded through microbial activity, it is included in this discussion due to its prevalence at contaminated sediment sites and because its toxicity and environmental fate are directly related to microbial transformations. Mercury is deposited into sediment environments through local releases and atmospheric deposition and exists in aquatic systems as elemental (Hg[0]), inorganic (Hg[I] and Hg[II]), and organic (e.g., MeHg) forms. Elemental mercury is volatile and exhibits low

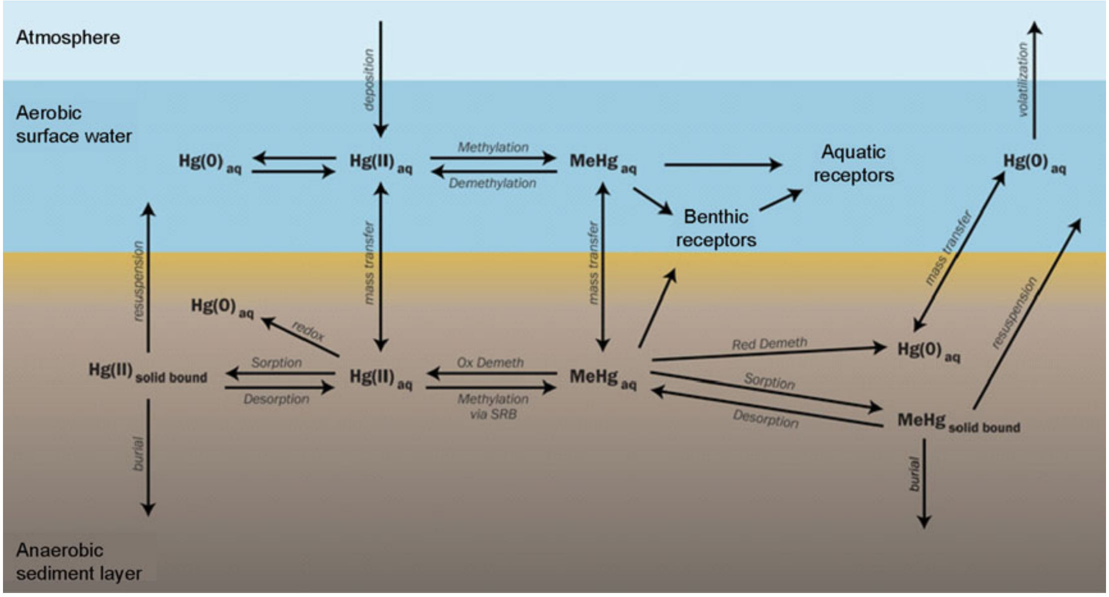

Figure 10.2. Conceptual illustration of dominant biogeochemical cycling mechanisms of mercury in aquatic sediments. Methylation and demethylation pathways, along with the redox reduction of $Hg(II)_{aq}$ to $Hg(0)_{aq}$, is mediated by microbial biotransformations in the sediment. Ox Demeth – oxidative demethylation; Red Demeth – reductive demethylation; SRB – sulfate reducing bacteria.

aqueous solubility. Inorganic mercury is the most prevalent form of mercury in aquatic systems and is generally the type deposited to the environment. Hg^{2+} is the most common form of inorganic mercury and consists of both Hg^{2+} ions and Hg^{2+} complexes. Organic Hg can either be covalently-bonded (MeHg) or complexed (with humic substances). Transformations of mercury species include the methylation of Hg(II) to MeHg and its subsequent degradation, either via reduction to form methane and Hg(0) or via oxidation to produce Hg(II) and CO_2. Reduction-oxidation reactions of Hg(II) and Hg(0) also occur and affect MeHg formation indirectly by controlling levels of Hg(II).

Although all forms of mercury are toxic, MeHg is the most toxic and bioaccumulates through the food chain to present exposure risks to humans and other higher-trophic organisms. Here we provide a brief overview of methylation and demethylation processes; much greater detail on the biogeochemistry and methylation/demethylation of Hg can be found elsewhere (Merritt and Amirbahman, 2009; Fitzgerald et al., 2007; Barkay and Wagner-Döbler, 2005; Ullrich et al., 2001).

10.3.3.1 Methylation of Mercury

It has been known since the mid-1980s that the methylation of Hg(II) to MeHg in anaerobic sediments can be mediated by SRB (Compeau and Bartha, 1985). The role of SRB was demonstrated through the addition of a methanogenic inhibitor (2-bromoethanesulfonic acid), which stimulated methylation (by eliminating competing processes) and through the addition of molybdate, an inhibitor for sulfate-reduction, which quenched methylation. Gilmour et al. (1992) added sulfate and inorganic mercury to anaerobic lake sediment slurries to stimulate methylation. They postulated that acid precipitation could provide the needed sulfate for methylation in their largely freshwater system. King et al. (2000) examined the coupling of sulfate-reduction and methylation in marine sediments and in pure cultures of SRB. Their results indicated that methylation was linked to respiration in *Desulfobacterium* and *Desulfovibrio* strains, but that some sulfate-reducers methylate mercury more rapidly than others and electron donor speciation influences methylation rates.

Several strains of methylating sulfate-reducers have since been isolated; however, it should be noted that not all sulfate-reducing species are capable of methylation. Most sulfate-reducers found to methylate Hg belong to the δ-subclass of the *Proteobacteria* and two general groups of sulfate-reducing populations can be categorized based upon their methods of organic matter oxidation. Complete oxidizers convert acetate to carbon dioxide while incomplete oxidizers convert LMW fatty acids (e.g. lactate, propionate, and butyrate) and alcohols to acetate. Complete oxidizers methylate mercury through an enzymatic transfer of a methyl group to Hg(II) via methylcobalamin (methylated vitamin B_{12}) in the acetyl-Coenzyme A (acetyl-CoA) pathway (Choi and Bartha, 1993; Choi et al., 1994a, b). This is supported by Ekstrom and Morel (2008) who demonstrated that Hg methylation in complete oxidizers was limited by the availability of cobalt (Co), which comprises the active center in methylcobalamin. Incomplete oxidizers were not limited by Co availability, reflecting how incomplete-oxidizing strains do not utilize the acetyl-CoA pathway either for metabolism or mercury methylation (Ekstrom et al., 2003). Additionally, methylation rates can be significantly increased when cysteine is present in solution, promoting the formation of a mercury-cysteine complex, which enhances both the cellular uptake of Hg and the enzymatic formation of MeHg (Schaefer and Morel, 2009).

Although methylation is linked to sulfate reduction, accumulation of sulfides can lead to the inhibition of mercury methylation. Methylation rates consequently peak at a sulfate concentration above which excessive sulfide is produced. In freshwater sediments, methylation has been observed to be optimal when sulfate concentrations ranged between 2 and 100 micromolar (μM) (Gilmour et al., 1992); above these levels the methylation rate was inversely related to sulfate reduction rate and sulfide concentration (Gilmour et al., 1998). This relationship is rooted in soluble, uncharged forms of mercuric sulfide ($HgS^0 + Hg(HS)_2{}^0$), which are the likely substrate of methylation and are formed at low sulfide concentrations (Benoit et al., 1999). Notably, methylation by a pure culture of *Desulfobulbus propionicus* (1pr3) declined when sulfide concentrations exceeded those shown to favor the formation of neutral dissolved species (Benoit et al., 2001a). It has also been reported that solid mercuric sulfide (cinnabar) can indirectly serve as a substrate for microbial transformations, possibly as a result of sulfide-induced dissolution rather than direct utilization of the solid cinnabar (Benoit et al., 2001b).

In addition to sulfide concentrations, it has been found that organic matter content also strongly contributes to methylation. A high concentration of labile organic matter in sediments produces tight redox stratification and brings more reducing biogeochemical process (e.g., sulfate reduction) closer to the sediment surface and overlying water. The presence of sulfate-reduction in close proximity to overlying water in estuarine and brackish settings, where sulfate can be exchanged between porewater and surface water, promotes MeHg production without the accumulation of high concentrations of sulfides (Lambertsson and Nilsson, 2006). These results agree with other studies indicating that mercury methylation rates are greatest near the sediment-water interface (SWI) and tend to diminish with depth (see Merritt and Amirbahman (2009) for discussion). Lambertsson and Nilsson (2006) also observed that MeHg levels did not correlate to total mercury concentrations, a conclusion shared by others at different sites (see Schaefer et al., 2004 as an example). Mitchell et al. (2008) found that methylation was stimulated considerably in a peat sediment following the concurrent addition of both sulfate and labile organic carbon, much more than either agent independently, indicating organic carbon availability can limit bacterial metabolism (e.g., sulfate reduction) and thus methylation in sediments. Recent laboratory research indicates that dissolved organic matter (DOM) can promote methylation through the stabilization of nanoparticulate metacinnabar particles, which appear to be a substrate for methylation (Zhang et al., 2012). Conditions which promote the formation of nanoparticulate metacinnabar, and thus promote methylation rates, include DOM with high aromaticity (Gerbig et al., 2011) and higher DOM to Hg ratios (Graham et al., 2012), tend to increase methylation rates. The kinetically controlled process of nanoparticulate cinnabar formation suggests that equilibrium-based models of methylation may underestimate MeHg production in some ecosystems (Slowey, 2010), especially where high levels of both organic matter and sulfide coexist (e.g., wetlands). Alternatively, DOM can act to limit methylation in low sulfide settings by binding with Hg(II) to prevent inorganic mercury uptake due to molecular size restrictions (see Ravichandran, 2004 for a review) or by limiting the formation of neutral, soluble mercuric sulfide complexes (Miller et al., 2007).

Iron-reducing bacterial populations, in addition to sulfate-reducers, are also implicated in mercury methylation in freshwater settings. Warner et al. (2003) documented methylation in sediments where iron reduction was the dominant terminal electron acceptor, although rates of methylation were lower than those observed in sulfate-reducing sediments. Fleming et al. (2006) isolated an iron-reducing *Geobacter* species, strain CLFeRB, that could methylate mercury at comparable rates to the known sulfate-reducing, methylating *D. propionicus* strain 1pr3. Meanwhile, Kerin et al. (2006) reported multiple iron-reducing strains (*Desulfuromonas palmitatis* SDBY-1, *Geobacter hydrogenophilus*, *Geobacter metallireducens* GS-15, and *Geobacter sulfurreducens*) able to methylate mercury. It was noted that these *Geobacter* and *Desulfuromonas* strains are closely related to known Hg-methylating SRB within the *δ-Proteobacteria.* The ability of iron-reducing bacteria to methylate Hg has significant implications for iron-rich freshwater settings and for engineering controls on methylation via sulfate reducers.

Although the controls on mercury methylation are becoming better characterized, understanding the dynamics of mercury methylation at a site can be challenging since methylation can be a function of many site properties that themselves can be spatially and temporally variable, such as temperature, ambient Hg concentration, organic substrate concentration and type, sampling location, and seasonal changes in vegetation.

Strategies for suppressing methylation in bed and wetland sediments has focused on reducing the bioavailability of neutral mercuric sulfide complexes and Hg(II). Mehrotra and Sedlak (2005) observed decreases in Hg methylation rates in estuarine wetland sediment slurries from San Francisco Bay after the addition of ferrous iron (Fe[II]) and suggested this effect was caused by decreases in dissolved Hg and sulfide due to complexation with iron. Their work built on previous laboratory studies (Mehrotra et al., 2003) with pure cultures of *Desulfobulbus propionicus* (1pr3) showing that iron addition reduced net mercury methylation by decreasing free sulfide and dissolved mercury concentrations. Liu et al. (2009) have also proposed chemical amendments to limit bioavailability of uncharged sulfide complexes. They suggest solid iron-sulfides, perhaps as a component of an *in situ* cap, can reduce methylation by promoting the formation of charged Hg(II)-polysulfides. The effectiveness of iron addition to inhibit methylation still needs to be investigated further, especially in areas where tidal input of sulfate occurs. Molybdate is also a known inhibitor for sulfate-reduction; however, large injections of molybdate to field sites are impractical and not sustainable. Others have proposed eliminating vegetation from wetlands, via aboveground and below-ground mechanical severing, to reduce photosynthetic production of acetate *in situ* and thus eliminate a source of preferred, labile organic carbon for methylators (Windham-Myers et al., 2009). Devegetation and subsequent shading associated with this approach to prevent regrowth can become impractical in large wetland areas and may only be applicable to spatially limited hotspots of methylation. Sequestering agents (activated carbon, organo-modified clays) designed to decrease bioavailable soluble Hg are becoming commercially available but still require field validation.

Another proposed approach to mitigate methylation is to engineer shifts in biogeochemical processes such that sulfate reduction is not located near mercury contaminated zones. *In situ* capping can result in shifts in biogeochemical processes with oxygen reduction moving from the former sediment-water interface to the newly-created cap-water interface. Anaerobic TEAPs move vertically into the cap layer along with microbial populations to develop stratified biogeochemical processes (Johnson et al., 2010; Himmelheber et al., 2008, 2009). This shift could potentially move active sulfate-reducing zones from the sediment, where bioavailable Hg is located, into the clean cap layer to result in reduced methylation rates. Liu et al. (2007) likely observed this effect during laboratory experiments, even with a very thin (10 millimeter [mm]) sand cap, reporting undetectable total mercury flux through a cap (compared to ~ 10^{-2}–10^{-3} ng m^{-2} s^{-1} from uncapped sediment) and decreased ratio of MeHg to total Hg. However, Himmelheber et al. (2009) monitored the spatial distribution of *dsrA* genes and observed sulfate-reducers present within a sand cap, implying that methylation may occur in the cap and shallow sediment if soluble mercuric sulfide species are also transported to the area. Experimental and modeling results suggest that this may in fact occur, especially in a sediment with high organic matter content. Biogeochemical shifts resulting from *in situ* capping may enhance methylation in (formerly) surficial sediment, whereas a less dramatic effect would be observed following the capping of a sediment with low organic matter content (Johnson et al., 2010). An accelerated methylation rate following capping would likely be temporally limited, since capping materials typically possesses little organic matter within the matrix and eliminates deposition of labile organic matter to underlying sediment, thus limiting organic carbon supply for microbial activity (Himmelheber et al., 2007). Finally, control of MeHg accumulation is also influenced on MeHg degradation, such as microbially-mediated demethylation processes, and development of mitigation strategies that employ demethylation can aid in reducing MeHg concentrations.

10.3.3.2 Demethylation of Mercury

Demethylation processes result in the mineralization of MeHg and thus represent an important pathway for reducing mercury toxicity in the environment. Demethylation can proceed through either abiotic or biological mechanisms. Two biological mechanisms of demethylation are (1) oxidative demethylation (OD) to produce CO_2, small amounts of CH_4, and Hg(II), which can subsequently be re-methylated, and (2) reductive demethylation to produce CH_4 and Hg(0) (Figure 10.3). Two factors that influence the reductive and oxidative pathways in the environment are redox conditions and levels of mercury contamination. Compilation of literature data (Barkay and Wagner-Döbler, 2005) indicates that reductive demethylation is favored at high mercury concentrations and oxic conditions, whereas OD dominates at low mercury concentrations and anoxic conditions (Schaefer et al., 2004). Generally, MeHg is degraded oxidatively unless total Hg concentrations exceed thousands of nanograms per gram of sediment in anaerobic conditions, or hundreds of nanograms per gram in oxic conditions. When these thresholds are exceeded, reductive demethylation tends to occur. Thus, MeHg is degraded reductively in highly contaminated settings and oxidatively in less contaminated settings.

OD has been observed in freshwater, estuarine, and alkaline hypersaline sediments (Marvin-DiPasquale et al., 2000). OD is thought to represent a co-metabolism of MeHg analogous to the metabolism of other small organic substrates (e.g., C_1 compounds) by heterotrophic bacteria. Sulfate-reducing, methanogenic, and aerobic bacteria have all been implicated in the OD pathway. For example, Marvin-DiPasquale and Oremland (1998) added sulfate and nitrate to sediments and increased the ratio of $^{14}CO_2$ to $^{14}CH_4$, suggesting that sulfate reducers and denitrifiers transformed MeHg oxidatively. Also, the addition of the methanogenic inhibitor 2-bromoethanesulfonate significantly reduced demethylation rates but had no effect on the dominant demethylation pathway. This latter observation may have been a result of disturbances to the community structure and syntrophic activities among different organisms.

Reductive demethylation centers on a detoxification mechanism performed by microorganisms carrying the mercury resistance (*mer*) operon. A thorough review of the *mer* system is provided by Barkay et al. (2003) and Barkay and Wagner-Döbler (2005). Reductive demethylation via the *mer* operon involves the sequential action of two enzymes: organomercurial lyase (*merB*), which cleaves the C-Hg bond of MeHg to CH_4 and Hg(II), and mercuric reductase (*merA*), which reduces Hg(II) to volatile Hg(0). It has also been observed that the reduction of Hg(II) to Hg(0) may occur via *mer*-independent pathways, coupled to dissimilatory iron-reduction by *Geobacter* for instance (Wiatrowski et al., 2006). MeHg degradation and resulting production of volatile products therefore results in the elimination of Hg from the microorganism's local environment. The expression of *merA* and *merB* is controlled by the Hg(II)-responsive regulatory protein, *merR*, which can be induced by Hg(II) and organomercury complexes. As the bioavailable concentration of Hg(II) or organomercurials increases, the mercury compound binds to *merR* and induces expression of *merA* and *merB* (Brown et al., 2003). *merD* is the down regulator of the *mer* system and serves to repress expression once Hg(II) concentrations have decreased (Barkay and Wagner-Döbler, 2005).

The induction of *mer* transcription by Hg is proportional to the amount of Hg present (i.e., the more Hg present, the higher the level of expression), resulting in the rate of reductive demethylation being dependent on the concentration of Hg. This helps to explain why reductive demethylation, rather than OD, occurs at higher Hg concentrations. It also helps to explain why locations with high levels of total Hg can exhibit relatively low percentages of MeHg to total Hg and be inversely related to total Hg (Heyes et al., 2006; Shaefer et al., 2004). At sites with low total Hg, *mer* activity may not be induced and MeHg can accumulate until balanced by OD. This relationship should be considered during site investigations (i.e., monitor both total Hg and MeHg) and can come into play during risk assessments and remedy selection, since high levels of total Hg may not necessarily indicate equivalently high levels of MeHg.

A multitude of mercury resistant bacteria containing *mer* operons have been described encompassing diverse metabolic and physiological characteristics. It has been observed that mercury stress to microbial communities initially decreases microbial diversity at contaminated sites; however, as time elapses and microbes adapt, diversity is regained and a number of mercury-resistant organisms become active members of the community. Because of this diversity, targeting the *merA* and *merB* genes and transcripts via quantitative methods (e.g., quantitative PCR) is an efficient way to monitor demethylation, in concert with MeHg, total Hg, and Hg(0) analysis. Stable isotope analysis of ^{202}Hg/^{198}Hg is another method to discern dominant Hg transformation pathways (Kritee et al., 2007, 2008; Heyes et al., 2006). For instance, microbial degradation of MeHg by *E. coli* carrying a *mer* system caused the pool of MeHg to become progressively heavier (enriched with ^{202}Hg; depleted in ^{198}Hg) over time before low MeHg concentrations and elevated biomass limited substrate availability (Kritee et al., 2009). The mass-dependent fractionation from microbial transformations allows distinction from mass-independent fractionation by dissolved organic carbon mediated photodegradation of MeHg. Rates of methylation and demethylation have also been determined by stable isotope analysis (see overview by Heyes et al., 2006). However, stable isotope analyses of Hg isotopes at field sites is not possible at this time from a practical standpoint.

Application of mercury resistant bacteria carrying the *mer* operon to reduce MeHg concentrations in the environment is a potential treatment approach requiring development. An example application was documented by Wagner-Döbler (2003) where a packed bed bioreactor containing a bacterial biofilm of mercury-resistant strains was constructed to produce Hg(0) from Hg-containing industrial wastewater. This application succeeded, in part, due to the relatively constant source of Hg provided to the organisms to sustain the demethylation activity. Similar examples exist where mercury-resistant bacteria were employed to treat mercury in industrial waste streams (see examples provided by Barkay and Wagner-Döbler, 2005). With regards to sediment treatment, it is difficult to artificially biostimulate *in situ* MeHg biodegradation activities since the *mer* operon is “turned on” when mercury resistant bacteria are exposed to high levels of Hg. As an alternative, bioaugmentation of mercury resistant bacteria, to introduce or boost bacterial populations with the *mer* operon in Hg-contaminated settings, may be a more conceivable approach. Bioaugmentation was investigated at the laboratory-scale by Saouter et al. (1995a, b) to enhance Hg(II) reduction in a contaminated pond; results showed increased production of Hg(0) in overlying water, suggesting demethylation was occurring. Bioaugmentation as a field-scale remedy option for subaqueous sediments remains unproven, however, and engineering challenges first need to be addressed. Another proposed approach is the use of genetic engineering to insert the *mer* operon into microorganisms and plants for remediation efforts. Different types of engineered plants have been constructed using bacterial *merA* and *merB* for soil and possibly marsh phytoremediation (see Omichinski, 2007 for a brief overview). A disadvantage of phytoremediation in this case is that Hg(0) is produced and subsequently emitted from the plant into the atmosphere, which can lead to continued atmospheric deposition of Hg.

10.3.4 Chlorinated Ethenes in Groundwater Seeps

Discharge of contaminated groundwater plumes into aquatic sediments serves as another source of contamination and can often introduce mobile pollutants into sediment environments. Groundwater seepage into surface waters is common and contaminants present in such seeps threaten water quality and present dangers to the benthic community as well higher level receptors. The chlorinated solvents tetrachloroethene (PCE) and TCE are common groundwater contaminants with plumes that can extend considerable distances from their source to potentially discharge into surface water bodies. PCE, TCE, and their anaerobic biotransformation daughter products dichloroethenes (DCEs) and vinyl chloride (VC) are composed of a carbon to carbon double bond (ethene) with chlorine atoms substituting for hydrogen. PCE, TCE, DCEs, and VC hold four, three, two, and one chlorine atom(s), respectively, on the ethene structure.

As chloroethene-contaminated groundwater plumes migrate through sediment beds, sediments can serve as a natural biobarrier for chlorinated ethenes due to elevated amounts of organic matter and microbial biomass found in sediments compared to typical groundwater aquifers. Complete dechlorination of PCE and TCE to ethene, through the daughter products of DCEs and VC, occurs under highly reducing (i.e., methanogenic) conditions and can lead to detoxification in sediments. Alternatively, DCEs and VC are vulnerable to metabolic and co-metabolic oxidation in the aerobic sediment layer, whereas the higher-chlorinated ethenes are recalcitrant under such conditions (see discussions below). Therefore, detoxification of chlorinated ethenes in sediments can be accomplished either via (1) complete dechlorination to ethene in the anaerobic zone, or (2) sequencing of reductive dechlorination under anaerobic conditions with oxidative mineralization of daughter products under aerobic conditions.

10.3.4.1 Anaerobic Biotransformation Processes

Chlorinated ethenes can be biotransformed under anaerobic conditions to environmentally-acceptable, non-toxic end products through reductive dechlorination. Analogous to PCB dechlorination, reductive dechlorination of chlorinated ethenes involves the replacement of a chlorine atom with a hydrogen atom on the ethene backbone resulting in the formation of a hydrochloric acid (HCl) and a lower-chlorinated ethene. PCE is sequentially dechlorinated to TCE, DCEs, VC, and finally ethene. During this process, dissolved-phase chlorinated ethenes serve as electron acceptors for dehalogenating organisms (e.g., *Dhc*), while the source of electrons is hydrogen supplied from the oxidation of organic substrates via microbial fermentation. *cis*-1,2-DCE (*c*DCE) is the dominant DCE isomer produced during biological reductive dechlorination of TCE; however, other isomers (*trans*-1,2-DCE; 1,1-DCE) can also be produced in smaller quantities and in rare instances are dominant products (Kittelmann and Friedrich, 2008; Griffin et al., 2004). It should be noted that chlorinated ethenes can also be produced from abiotic and biological transformation of chlorinated ethanes (Hunkeler et al., 2005), which can be co-mingled with chloroethene contamination.

Several microbial species can dechlorinate PCE and TCE to *c*DCE but complete dechlorination past *c*DCE and VC to ethene, thus representing detoxification, has been linked exclusively to *Dhc* strains. Summaries of metabolic (and co-metabolic) *Dhc* capabilities towards chlorinated ethenes are provided by Futagami et al. (2008) and Löffler and Edwards (2006). Multiple strains of *Dhc* have been isolated that dechlorinate chlorinated ethenes: *Dhc* strains 195 (Maymó-Gatell et al., 1997), FL2 (He et al., 2005), and CBDB1 (Adrian et al., 2000) can metabolically dechlorinate higher-chlorinated ethenes (PCE, TCE, DCEs), whereas *Dhc* strains GT (Sung et al., 2006), BAV1 (He et al., 2003), VS (Cupples et al., 2004), and KB1/VC (Duhamel et al., 2004) can metabolically dechlorinate through VC to ethene, along with other higher chlorinated ethenes.

These latter strains are important for remediation applications since they result in detoxification. Quantitative monitoring of *Dhc* populations can be performed using molecular techniques employing the *Dhc* 16S rRNA gene (Cupples, 2008), with guidance on sampling techniques for such analyses available (Ritalahti et al., 2010). Enumeration of *in situ Dhc* levels utilizing quantitative PCR is becoming common practice in groundwater settings; however, strains GT, FL2, CBDB1, and BAV1 share at least 99.9% similarity of their 16S rRNA gene sequences but have different metabolic capabilities toward chlorinated ethenes (Sung et al., 2006).

Monitoring of genes encoding reductive dehalogenase (RDase) enzymes, which catalyze the reduction of chlorinated ethenes by *Dhc* spp., is an alternative approach that offers greater information on the potential for complete detoxification. Known, annotated RDase genes involved in chloroethene reduction are: *pceA*, encoding the reduction of PCE to TCE (Magnuson et al., 1998; Fung et al., 2007); *tceA*, encoding the reduction of TCE to VC (Magnuson et al., 2000); *vcrA*, encoding the reduction of VC to ethene (Müller et al., 2004); mbrA, encoding the production of *trans*-DCE during the dechlorination of TCE (Chow et al., 2010), and; *bvcA*, encoding the reduction of DCE to ethene (Krajmalnik-Brown et al., 2004). Correlation between reductive dehalogenase concentrations and dechlorination activity have been determined in laboratory (Amos et al., 2008; Lee et al., 2006) and field studies (van der Zaan et al., 2010; Lee et al., 2008; Scheutz et al., 2008). As a rule of thumb, *Dhc* levels below 10^3 gene copies per liter indicate suboptimal levels to sustain dechlorination rates, *Dhc* levels between 10^4 and 10^6 gene copies per liter may sustain appreciable dechlorination rates, and *Dhc* levels 10^7 and above should result in high rates of dechlorination (Petrovskis et al., 2013).

Dhc are widespread in nature (although not ubiquitous) and intrinsic dechlorination of chlorinated ethenes has been reported in sediment porewater from numerous sites (see examples of Abe et al., 2009; Kuhn et al., 2009; Himmelheber et al., 2007). *Dhc* possessing the VC-RDase genes that mediate the final dechlorination step are less prevalent. This results in stalling or incomplete reductive dechlorination at field sites, which can be overcome via bioaugmentation for groundwater sites. Additional reasons for dechlorination stall or incomplete dechlorination include unfavorable site geochemical conditions, such as the presence of alternative electron acceptors (e.g., oxygen, nitrate, sulfate), lack of bioavailable electron donor, improper pH, and elevated salinity. Despite the salinity concern, two recent studies suggest *Dhc*, or closely related organisms, can remain active in marine environments (Futagami et al., 2009; Kittelmann and Friedrich, 2008). Reductive dehalogenase genes were detected by Futagami et al. (2009) within marine subsurface sediments off the coasts of Asia, South America, and North America. Phylogenetic analysis revealed that all of the detected putative RDase sequences were related to those of *Dhc*, and sediment slurries demonstrated dehalogenation of brominated and chlorinated compounds; but dechlorination past DCE was not observed (Futagami et al., 2009). Kittelmann and Friedrich (2008) identified novel *Chloroflexi* populations related to *Dhc* as those responsible for PCE-to-DCEs biotransformation observed in marine tidal flats from the coast of Saxony, Germany. These two studies highlight the potential for reductive dehalogenation of contaminants, including chlorinated ethenes, but potentially chlorinated benzenes and PCBs as well, by *Dhc* strains in marine environments.

Because chlorinated ethenes are susceptible to numerous attenuation processes within zones of groundwater and surface water interaction (e.g., sorption, dilution, biotransformation), discerning the contribution of biotransformation towards attenuation at field sites can be challenging and requires multiple, converging lines of evidence. Field sampling and analysis activities could include:

- Monitoring changes in porewater and sediment chloroethene concentrations over space and time.
- Dhc and RDase levels to understand the genotypic potential for *in situ* anaerobic biotransformations and to help confirm that reductive dechlorination is biologically-mediated.
- Assessing site geochemistry determine if site conditions promote or inhibit reductive dechlorination.
- Compound-specific stable isotopic analysis can be performed to confirm contaminant biotransformation processes and to assess the extent of contaminant biotransformation (USEPA, 2008).
- Microcosm studies with site materials to simulate settings under controlled conditions to evaluate the potential (and limitations) of *in situ* biotransformations and quantify site-specific rates.
- Aerobic oxidation enzymes to help distinguish oxidative attenuation pathways from reductive pathways. Quantification of the Coenzyme M transferase (EaCoMT) gene, involved in the degradation of chlorinated ethenes via epoxidation (see subsequent section), can be performed in conjunction with monitoring oxygen penetration into sediments.

10.3.4.2 Aerobic Biotransformation Processes

The vulnerability of chlorinated ethenes to undergo aerobic oxidation increases as the number of chlorine substituents decrease, such that PCE and TCE are not susceptible to aerobic oxidation but VC and DCE can be oxidized. Rapid microbial mineralization of VC has been observed in laboratory cultures and aquifer samples under aerobic conditions (Coleman et al., 2002a). The microorganisms catalyzing the oxidation in the Coleman et al. (2002a) study were phylogenetically diverse and capable of growth on ethene in addition to VC. Metabolic VC oxidation proceeds through an initial monoxygenase attack and the production of a VC epoxide. The epoxyalkane EaCoMT and MMO enzymes encoded by a single operon (*etnEABCD*) catalyze aerobic VC biodegradation (Coleman and Spain, 2003). Abe et al. (2009) observed aerobic VC oxidation in streambed sediment microcosm studies spatially coupled with the detection of EaCoMT gene, indicating that aerobic biodegradation was a possible attenuation pathway for VC at the site. It has also recently been demonstrated that aerobic, microbial VC oxidation can be sustained at low oxygen concentrations typical of microaerophilic environments (Gossett, 2010), which can be found in sediments via microniches and/or enhanced solute transport from bioturbation. In addition to metabolic pathways, VC can also be oxidized to CO_2 through co-metabolic processes in the presence of monoxygenase inducers, such as methane, ethane, ethene, and propane, among others. DCEs can also be utilized as a growth substrate by microorganisms such as strain JS666 (Coleman et al., 2002b), the only bacterial isolated to date which can use cDCE as a sole carbon and energy source. Work by Jennings et al. (2009) has led to the identification of genes within JS666 upregulated upon exposure to cDCE and a potentially novel pathway of biodegradation initiated by a carbon-chloride cleavage. Further laboratory work is needed to confirm the possible cDCE degradation pathway, including genes involved and intermediates formed, and also demonstrate JS666's potential utilization as a bioaugmentation culture.

Aerobic oxidation has been identified as a major attenuation pathway for lower-chlorinated organics at groundwater plume edges and in near-surface sediments. Redox conditions close to the SWI may be aerobic depending on the oxygen conditions in the overlying water, leading to aerobic biotransformation of chlorinated ethenes. The lower chlorinated ethenes can be metabolically oxidized at the sediment surface, or potentially also consumed via co-metabolic oxidization by methanotrophic bacteria capable of producing monoxygenase. Lendvay et al.

(1998) demonstrated this coupled transformation pathway in a field study examining chlorinated ethenes discharging into an oxygenated lake. Reductive dechlorination in the methanogenic porewaters produced a mixture of dissolved DCE and VC, which entered the shallow, oxic zone of the sediment where co-metabolic oxidation of VC occurred via methanotrophic microorganisms while *c*DCE remained stable. Sequenced anaerobic-aerobic redox conditions within sediments can therefore lead to mineralization, especially in wetland environments where aerobic conditions may be extended due to expulsion of oxygen by plant roots.

10.4 INCORPORATING *IN SITU* BIOTRANSFORMATION INTO SEDIMENT REMEDIATION

In situ biotransformations have typically not been employed as a stand-alone treatment option for contaminated sediments. As noted earlier, this is because (1) co-mingled sediment contamination, a commonly encountered issue, may require competing processes to achieve detoxification (e.g., chlorobenzene dechlorination requiring accessible electron donor, anaerobic benzene oxidation requiring low levels of accessible electron donor), (2) low bioavailability of many sediment contaminants (PCBs, PAHs) can limit the rate and extent of biotransformations, (3) the large spatial distribution of some contaminated sediment sites, along with the subaqueous nature of the contamination, can make treatment technically and economically impractical (note that this challenge impacts all sediment remedy designs) and (4) introduction of stimulatory amendments (e.g., oxygen) targeting specific biotransformation pathways are subject to rapid consumption, often by competing microbial processes. As research and implementation advances continue in the field of bioremediation, solutions to these challenges will likely be developed. Currently, *in situ* biotransformations hold the most value as a complementary process for traditional remedy options.

10.4.1 Monitored Natural Recovery

Intrinsic bioremediation can be seamlessly incorporated into MNR-based remedies since they rely on existing site-specific attenuation processes and biodegradation can naturally reduce contaminant concentrations. Biotransformations to less toxic contaminants (e.g., biotransformation of dioxin-like PCBs) may also result in suitable risk reduction depending on source control and exposure pathways. Such applications of biodegradation in an MNR-based remedy may be best pursued in deeper sediments (i.e., below the biologically-active zone [BAZ]) where benthic receptors are not expected to be present, since biotransformation processes may require extended periods of time. Site-specific rates of biotransformation processes should be quantified to determine if biological activity can significantly contribute to risk reduction, in conjunction with abiotic transformations, dilution, sorption, and other MNR processes. In some locations, sediment deposition may result in quicker risk reductions in near-surface sediments, and *in situ* biotransformations at deeper depths can complement physical isolation processes. Biotransformations can also support the permanence of risk reduction at sites where the stability of freshly deposited sediment is uncertain (Magar et al., 2009). An example of biotransformations incorporated into MNR-remedy is the Lake Hartwell PCB site (Magar et al., 2005a, b). PCB dechlorination was monitored at the site, coupled to sediment age dating, to determine that active PCB dechlorination of higher-chlorinated congeners was occurring to produce lower-chlorinated congeners at a measureable rate. The dechlorination activity along with sediment deposition allowed for an MNR-based remedy to be appropriate and protective. Site-specific biotransformation rates to predict and model the long-term effect of biotransformations on contaminant concentrations are required, followed by continued monitoring and evaluation of biotransformation activity as evidenced by concentration reductions of contaminant and/or by biomarkers to indicate specific processes.

10.4.2 Dredging

Contaminated sediment removal through dredging and excavation typically targets hotspot removal and can result in long-term risk reductions. The contaminated material removed can be treated through *ex situ* biotransformation processes. Since *ex situ* treatment is not the focus of this chapter, this topic will not be discussed further; but *in situ* biotransformations can also be incorporated into dredging-based remedies through two means: (1) treatment of contaminant residuals post-dredging and (2) treatment of lower contaminated regions outside the spatial extent of hot spot dredging.

Concerns exist regarding contaminant residuals following sediment dredging (Bridges et al., 2008). A layer of relatively high contamination can remain on the sediment surface following dredging due to incomplete removal of the contamination, mixing of deeper, more contaminated sediment with cleaner surficial sediment, and the suspension of contaminated sediment particles into the water column with subsequent resettling onto the sediment surface. Residual issues are typically manifested during and following dredging operations, resulting in short-term risks. *In situ* biotransformations could help mitigate these risks through intrinsic or engineered methods, especially if the residual contamination has accumulated on the sediment surface where aerobic conditions are more likely to be present. Aerobic biodegradation could potentially reduce concentrations of contaminants associated with the resettling of solid-phase particles (PCBs, PAHs), however this application needs to be investigated. Site-specific rates of biotransformation, along with residual concentrations and benthic exposure, should be considered when assessing risk and if *in situ* biotransformations can achieve adequate risk reductions in an acceptable timeframe.

In addition, dredging may be restricted in some locations of a site due to infrastructure or other physical impediments causing lack of access. In these locations, natural recovery incorporating *in situ* biotransformation may be a suitable alternative if the concentrations are not exceedingly high and risk levels are acceptable. Similar applications may be appropriate in areas outside of contamination hotspots, since the cost of dredging (and capping) can make whole-site treatment impractical at large sediment sites. Combining remediation approaches, such that dredging eliminates immediate risk at hotspots while biotransformations as part of an MNR-strategy gradually reduce risk at lower-concentration areas, both laterally and vertically, can result in cost-savings while also providing treatment to the site.

10.4.3 *In Situ* Capping

In situ capping involves the placement of clean material at the sediment surface to physically and chemically isolate the contamination in the sediment from benthic receptors at the new cap-water interface. Biotransformation has been included in cap design models (Lampert and Reible, 2009) developed to predict cap effectiveness. When incorporating biotransformation into these models, it is important to note that biotransformations can result in the formation of metabolites, which may exhibit different physical-chemical properties and/or slow rates of complete detoxification (e.g., dichlorobenzene dechlorination to MCB for both cases), thus requiring multiple model scenarios.

Shifts in biogeochemistry (Himmelheber et al., 2008) and microbial communities (Himmelheber et al., 2009) from underlying sediments into the cap matrix indicate the cap

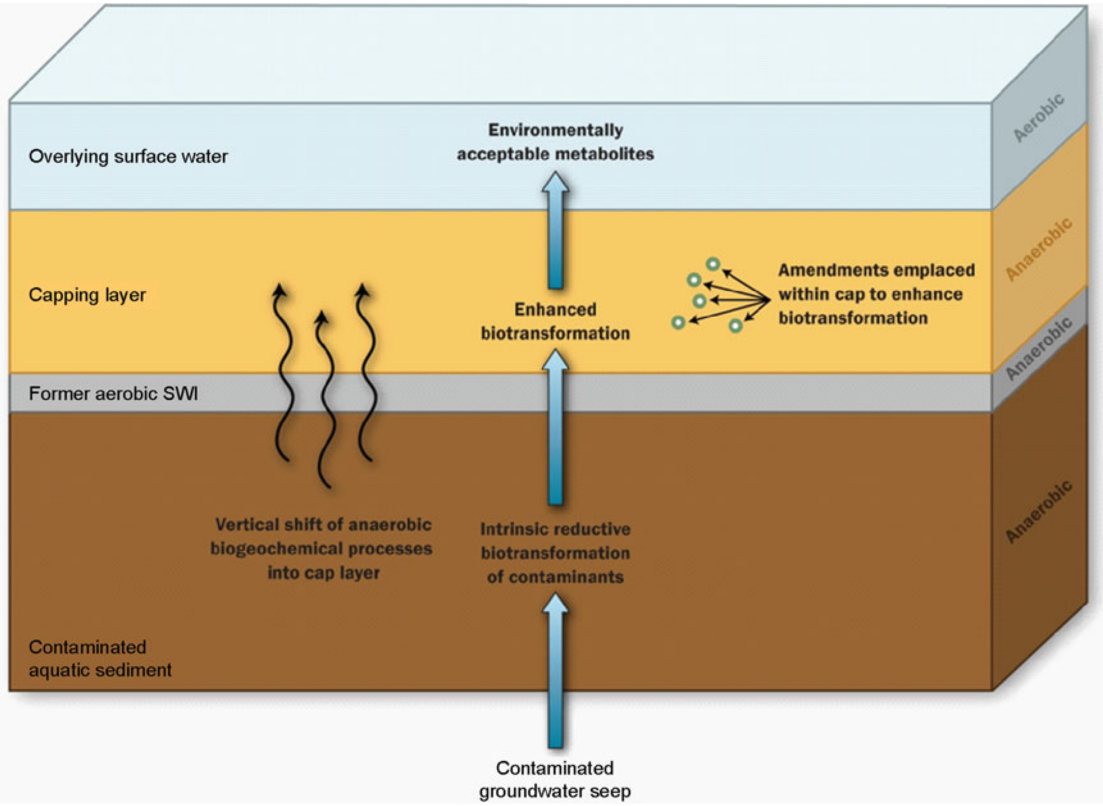

Figure 10.3. Conceptual model of an enhanced biotransformation remedial approach applied in conjunction with *in situ* capping. Intrinsic biotransformation of contaminants within the sediment bed commonly results in only partial detoxification. Upon cap placement anaerobic biogeochemical processes, including microbial populations, migrate from the sediment into the overlying cap to create a biologically-active cap layer (Himmelheber et al., 2009). Amendments placed within the cap matrix could enhance biotransformations to promote the production of non-toxic end products that discharge and/or diffuse to the cap-water interface where benthic receptors reside. Majcher et al. (2009) utilized a similar approach to treat chlorinated organics discharging into sediments within a groundwater seep.

layer can be a biologically-active region where anaerobic processes and reductive biotransformations occur. Therefore, as contaminants migrate through the cap, biotransformations can provide a method of treatment to prevent (or significantly delay) contaminant breakthrough to the BAZ at the cap-water interface. Active biological treatment within the cap could alleviate the primary concern of capping, eventual contaminant breakthrough, and also allow potential cap placement at locations with groundwater seeps where advective transport compromises traditional cap performance due to enhanced solute mobility. A limitation of biologically-active caps could be a shortage of electron donor within the cap material, since traditional caps have been constructed with sand possessing minimal amounts of organic matter. However, *in situ* capping also provides an opportunity to introduce metabolic amendments during placement to stimulate biotransformations within the cap matrix. Figure 10.3 provides a conceptual model of how biotransformations could be engineered within an *in situ* cap layer. Partially biodegraded products from intrinsic dechlorination occurring in the sediment bed could be complemented by reductive biotransformations in the anaerobic cap layer. Amendments supplied within the cap matrix (e.g., electron donor, nutrients, pH buffer) could enhance biodegradation performance to result in environmentally-acceptable metabolites entering the BAZ and overlying water. This conceptual model could be exploited to augment sand-based caps with organic carbon (i.e., electron donor) to promote and sustain microbial activity in the cap. A more aggressive approach has been proposed by Sun et al. (2010) who investigated the use of electrodes within a bench-scale cap to supply both hydrogen (electron donor) and oxygen (electron acceptor). The idea is intriguing since the electrodes could supply a stable source of electron donor within the cap to support reductive biotransformations and also provide oxygen to artificially create a sequenced anaerobic to aerobic treatment approach, which would be advantageous for the treatment of PCBs and chlorinated solvents. Other metabolic amendments proposed for inclusion in caps include those designed to stimulate nitrate and sulfate reducing biotransformations (Tang et al., 2005).

Principles of a biologically-reactive capping approach, very similar to what is shown in Figure 10.3, were demonstrated in the field by Majcher et al. (2009) and serve as a good example of a cap-based remedy that purposefully incorporated biotransformations within the cap matrix. The pilot-scale implementation of a biologically-reactive mat (biomat) at a groundwater seep was designed to treat a mixture of chlorinated aliphatics discharging into tidal wetlands. The biomat was bioaugmented with a robust mixed culture derived from the site that could completely dechlorinate a suite of chlorinated ethenes, ethanes, and methanes in the site groundwater. Bioaugmentation was performed at low tide during biomat construction via direct surface application due to the culture's demonstrated tolerance of transient oxygen exposure. The cap material, composed of an organic matrix of peat, chitin, and compost, supplied organic substrates and reducing equivalents to the bioaugmented microbes. Methanogenic conditions conducive to anaerobic biodegradation and efficient dechlorination activity were established and sustained. Mass removal of chloromethanes and total chlorinated ethenes and ethanes during the monitoring period was 98% and 94%, respectively, within the 1.5-ft-thick zone between the base of the mat and the middle of the organic zone, with concurrent generation of ethene and ethane (Majcher et al., 2009). Monitoring over 1 year, through various weather conditions, showed continued dechlorination and demonstrated the apparent longevity of the approach. Although the bioreactive mat was constructed on the banks of an intertidal wetland (i.e., not completely subaqueous and subject to cycles of inundation and exposure) and the design is not immediately suitable for submergence (e.g., buoyancy restrictions, delivery of bioaugmentation culture), the success of the approach indicates the concept of bioreactive capping as an *in situ* technique is viable.

10.5 CONCLUSIONS AND OPPORTUNITIES FOR FURTHER DEVELOPMENT

In situ biotransformations resulting in measureable reductions in contaminant concentration and toxicity could be a vital component of a sediment remedy. Understanding the possibilities and limitations of biotransformation (and biodegradation) processes allows for proper investigations and potential contribution to risk reduction at contaminated sediment sites. A number of contaminants are vulnerable to biotransformation processes within sediment environments, but recognizing site redox conditions and the biotransformation pathways characteristic of those conditions is a key step. The anaerobic nature of sediments, along with the amount of organic material present, causes reductive biotransformations to be the dominant pathways. To summarize:

- Contaminant biotransformations catalyzed by microbial populations require the presence of specific redox conditions and suitable environmental conditions.
- Aerobic processes, spatially restricted to the SWI due to limited oxygen penetration in most circumstances, are underlain by a gradient of anaerobic biogeochemical processes and generally lesser degrees of microbial activity, diversity, and biotransformation potential. Traditional geochemical analysis, complemented by newer tools such as molecular biomarkers and microelectrodes, can be employed to identify dominant TEAPs and biotransformation processes.
- Different strategies of *in situ* biotransformation (intrinsic biotransformation, biostimulation, and bioaugmentation) can each be incorporated into remedy designs; however, intrinsic biotransformation has been the most commonly employed approach for sediment remediation. Opportunities exist to further develop biostimulation and bioaugmentation approaches at lab- and field-scale activities.
- PCBs can be dechlorinated under anaerobic conditions by organisms within the phylum *Chlorflexi*, including *Dhc* and organisms closely related, resulting in decreased overall toxicity. Aerobic biodegradation of lower-chlorinated PCBs via the bph pathway can result in complete toxicity elimination.
- PAHs can be oxidized under aerobic, nitrate-reducing, and sulfate-reducing conditions, with LMW PAHs more readily oxidized under all three redox regimes compared with HMW PAHs. Detailed mechanisms of anaerobic oxidation are becoming better understood but are not yet complete. Aerobic PAH biodegradation via dioxygenase activity is relatively well characterized and more robust than anaerobic processes, with some evidence of HMW PAH mineralization.
- *In situ* biotransformations of PCBs and PAHs are limited, in part, by bioavailability restrictions due to sorption to sedimentary organic matter.
- Mercury methylation is an important biotransformation mediated largely by sulfate-reducing populations in estuarine environments with contributions from iron-reducing bacteria in freshwater environments. Methylation is tied to organic matter concentrations, sorption, and dissolved neutral sulfide species among other factors.
- Demethylation is an important pathway that can regulate MeHg accumulation in sediments. OD is typical at sites with relatively low levels of total mercury. Mercury demethylation via reductive processes, catalyzed by the *mer* operon, represents a detoxification response by microorganisms and is initiated at high concentrations of mercury.
- Chlorinated ethenes can be detoxified under anaerobic conditions in sediments via reductive dechlorination by *Dhc*, and through the coupling of anaerobic reductive dechlorination with aerobic oxidation by metabolic and co-metabolic pathways.
- Biotransformation pathways could be incorporated into existing sediment remediation strategies to help achieve risk reduction. MNR inherently relies upon *in situ* biotransformations, when present, to gradually decrease contaminant concentrations and toxicity. Dredging operations may benefit from a polishing step to treat contaminant residuals left at the sediment surface (or at depth) following removal, warranting additional investigation. Capping layers appear to naturally promote biological activity, which can be stimulated through the introduction of amendments (or organisms) during cap placement. Further research and development of bioreactive capping appears reasonable.
- Site-specific biotransformation rates should be utilized when possible to accurately predict and model the impact of biotransformation.

Although numerous biotransformation processes are documented within sediments, many organic contaminants exhibit recalcitrant behavior due to bioavailability restrictions and slow reaction rates. In some cases, coupled anaerobic-aerobic pathways are needed to achieve complete biodegradation (e.g., PCBs); however, toxicity reductions can still occur through single pathways. Generally, oxidative processes under aerobic conditions result in more rapid, complete biotransformations compared with reductive processes, but are limited by lack of oxygen penetration into waterway and wetland sediments.

These issues collectively illustrate that although there have been many successes and advances in understanding biotransformation of sediment contaminants under laboratory settings, there are still many uncertainties regarding field-scale application of the technology and the impact it can have towards lowering contaminant levels and overall risk. These uncertainties present opportunities for continued development of bioremediation technology in both laboratory and field settings. Understanding biotransformation pathways, including the intermediate products formed and microorganisms involved, can help identify how biodegradation processes can be enhanced and what limitations need to be overcome. For instance, continued efforts to find microbial species implicated with PCB dechlorination, along with the currently unknown dehalogenase(s) responsible, can provide knowledge regarding environmental conditions that promote dechlorination performance. Also currently unknown are the detailed mechanisms of anaerobic PAH biodegradation, which could provide additional means of monitoring and identification of rate-limiting steps. Better understanding of factors controlling mercury methylation is another subject area warranting attention. Transferring academic and laboratory successes to the field remains a significant challenge and requires continued attention through research and development. Key challenges preventing large-scale field deployment, among others, include limited bioavailability of hydrophobic organics, lack of sustainable means to stimulate intrinsic and engineered processes, and cost concerns regarding the treatment of large volumes of contaminated sediments. Given these issues, if *in situ* biotransformation technology can grow and ultimately meet these challenges, significant cost savings and technical advantages can be realized. Given this promise for future applications, *in situ* biotransformations currently serve as a key component for established remedial options of MNR, dredging, and capping.

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CHAPTER 11

IN SITU TREATMENT FOR CONTROL OF HYDROPHOBIC ORGANIC CONTAMINANTS USING SORBENT AMENDMENT: THEORETICAL ASSESSMENTS

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11.1 INTRODUCTION

Sediments accumulate hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dichlorodiphenyltrichloroethane (DDT). Sediments thus act as reservoirs, exposing HOCs to benthic biota, releasing HOCs into porewater, and contributing HOCs to the aquatic food web. It has been observed that certain sediment particle types, known as black carbon (BC), have stronger sorption capacity than inorganic particles with coatings or inclusions of natural organic matter (Ghosh et al., 2003). Char, charcoal, soot, and their derivatives are such types with strong sorption capacity. Once the HOCs are sorbed into the BCs, they become much less available than HOCs sorbed on other mineral-based particles (Ghosh et al., 2000, 2003). These findings motivated studies of a novel *in situ* sediment treatment strategy using carbonaceous strong sorbents such as activated carbon (AC) to sequester HOCs. Activated carbon has been selected for most studies due to its high affinity for HOCs. By incorporating AC into HOC-contaminated sediment, HOCs would be redistributed, sorbed onto AC particles, and become less available to porewater and biota. The proof of concept of this treatment approach was demonstrated in a series of laboratory studies (McLeod et al., 2004; Zimmerman et al., 2004, 2005; Millward et al., 2005; Tomaszewski et al., 2007). For instance, introducing 3.4 dry weight percent (wt%) of AC into well-mixed sediment-water slurries in the laboratory yielded about 90% reductions of PCBs, PAHs, and DDTs in water phases and benthic organisms (McLeod et al., 2004, 2007, 2008; Zimmerman et al., 2004; Millward et al., 2005). In the United States, two field trials on application of AC to sediments to sequester HOCs can be found: one at Hunters Point, San Francisco Bay, California (completed) (Cho et al., 2007, 2009), and one in the Grasse River, New York (on-going) (Alcoa Inc., 2008). The recently completed Hunters Point field study demonstrated the successful incorporation of AC by two commercially available equipments into a nominal 30 centimeter (cm) depth at dose of 2–3 dry wt% at a mudflat in San Francisco Bay, California. This resulted in 50–66% reduction in HOC concentrations in porewater, passive samplers, and transplanted benthic test organisms (Cho et al., 2007, 2009). Other than AC dosage, the difference in performance between laboratory and field trials may have

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been a result of HOC mass transfer in the field occurring without continuous and complete mixing of AC and sediment. In this case, contaminant diffusion between sediment and AC particles may be a limiting process for HOC mass transfer.

The field study also demonstrated that (1) AC stabilization capability was retained in the field at least up to 18 months and (2) neither PCB resuspension from the test plots nor adverse impacts to indigenous amphipods and the benthic community were observed during the entire assessment period (Cho et al., 2009). Cost analysis showed that scaling-up the AC treatment method would result in a potential total cost savings that may be 70–75% less than for dredging and disposal (Luthy et al., 2009). Overall, this field study indicated that if ongoing contaminant sources are eliminated and freshly deposited sediments are clean, *in situ* AC amendment to contaminated sediments can provide a suitable, cost-effective method for reducing contaminant exposure to the water column and biota.

Initial field results are promising, but important engineering and implementation questions remain. The final Feasibility Study for sediment cleanup at Hunters Point noted that the effectiveness and implementability of AC as an *in situ* treatment shows potential but the technology rating is moderate to low because of limited experience and questions about the long-term effectiveness (Brajas & Associates Inc. and Tetra Tech EM Inc., 2008). The study pointed out the need for more information regarding the long-term effectiveness and implementation practices for the AC amendment technique. In sum, there is regulatory interest for the application of AC amendments, but acceptance requires further development. To enhance the implementability and effectiveness of AC amendment, further studies should investigate (1) optimal AC dosing, deployment, and mechanical mixing strategies; (2) appropriate physicochemical and biological indicators for monitoring; (3) field conditions that affect the performance of AC amendment, such as bioturbation and particle deposition; and furthermore, (4) a general model framework to predict the effectiveness of the *in situ* sorbent amendment technique under various field conditions. The development of the model framework is especially essential because modeling will help to plan a remedial action at the early stage and predict long-term effectiveness during post-treatment monitoring periods. Therefore, this chapter will mainly focus on the up-to-date model framework for the *in situ* sorbent amendment technique.

This chapter describes two modeling approaches for the in-place treatment of hydrophobic organic contaminants in sediment through the action of a strong sorbent applied as an *in situ* amendment to sequester persistent hydrophobic organic compounds. The mechanistic processes that determine the effectiveness of the sorbent amendment are presented in the following models that describe organism uptake and biodynamics, and the contaminant mass transfer for both well-mixed and minimally-mixed systems. The discussion focuses on the action of AC amendment to reduce porewater concentrations and organisms' assimilation efficiencies for ingested sediment, and the relevant processes that influence the time to achieve a desired outcome.

11.2 BENTHIC ORGANISM UPTAKE OF PERSISTENT ORGANIC CONTAMINANTS: BIODYNAMIC MODELING

A deposit-feeding or filter-feeding organism's bioaccumulation of persistent organic contaminants can be explained by (1) contaminant uptake, (2) contaminant elimination and (3) contaminant dilution by organism growth. Although contaminant metabolism might be considered, it can be ignored for certain persistent organic contaminants and benthic organisms. In the aquatic environment, benthic organisms can accumulate contaminants through contact with water and/or sediment. Therefore, the temporal change of the contaminant concentration in an organism's tissue, dC_{org}/dt (micrograms per gram [µg/g] dry weight [dw] per day), can be described by:

$$\frac{dC_{\mathrm{org}}}{dt} = \underbrace{IR \cdot AE_s \cdot C_s}_{\text{uptake from sediment}} + \underbrace{k_w \cdot C_{\mathrm{w}}}_{\text{uptake from water}} - \underbrace{k_{e+g} \cdot C_{org}}_{\text{loss and growth}} \qquad \text{(Eq. 11.1)}$$

The contaminant uptake from sediment is a function of the organism's particle ingestion rate, IR (g/g dw per day), the contaminant's sediment concentration, C_s (µg/g dw), and the organism's contaminant assimilation efficiency from ingested solids, AE_s (µg HOC assimilated/µg HOC ingested). The value of the IR can be determined by a combination of pulse-chase feeding and stable isotope techniques as described in detail elsewhere (McLeod et al., 2008; Janssen et al., 2010; Croteau and Luoma, 2005; Croteau et al., 2004, 2007; Luoma et al., 1992). Briefly, food (e.g., diatoms or algae) that resembles 100% organic matter (OM) is enriched with specific tracers and fed to organisms for a certain time. Then, the food clearance rate is determined by the mass balance of the tracer(s) in the remaining food, the organism, and feces. This rate is normalized by the fraction of OM in the sediment of interest, assuming the food IR is equivalent to the organic matter IR. Also, for certain organisms (oligochaetes), IR can be measured directly by the collection of feces assuming that the defication rate equals the IR because only a very small fraction of the sediment is actually assimilated (Leppanen and Kukkonen, 1998). Similarly, the assimilation of contaminants from ingested solids, AEs, can be measured directly by targeted feeding studies when either radiolabeled compounds are tracked during feeding or feces collection is possible to analyze for non-assimilated contaminants (McLeod et al., 2004; Kukkonen and Landrum, 1995). Often such direct measurement is not practical, because labeling only allows one to monitor a subset of contaminants (e.g., few PCB congeners out of 209 existing) or feces collection is not possible. However, the biodynamic model makes it possible to provide the estimate of AE_s by an inverse solution using Equation 11.1 (Janssen et al., 2010). The value of AE_s is a central parameter in assessing the effectiveness of sorbent amendment because it represents the contaminant's bioavailability. Typically, AE_s is considered as a constant parameter that is species-specific and sediment-specific, but Janssen et al. (2010) reported that AE_s can change with time for an organism with changing gut residence times during rapid growth periods.

The contaminant uptake from water is described by an aqueous uptake rate constant k_w (liter(s) per gram [L/g] dw per day) and the aqueous contaminant concentration C_w (µg/L) (Janssen et al., 2010; Sun and Ghosh, 2007; Sun et al., 2009). The value of k_w can be determined from a relationship of contaminant tissue concentrations at different exposure times (on the order of hours) with constant aqueous concentration or at different aqueous concentrations at constant exposure time assuming that elimination and growth dilution are not relevant during the short exposure to water without any food source. For filter feeders, the uptake from the aqueous phase is mostly via filtration of overlying water, so the magnitude of k_w can be estimated by:

$$k_w = FR \cdot AE_w \qquad \text{(Eq. 11.2)}$$

where FR is the water filtration rate (L/g dw per day), and AE_w (µg HOC assimilated/µg HOC filtered, or -) is the absorption efficiency from water. In the absence of specific measurements, FR and AE_w may be estimated from literature for functionally similar benthic organisms and chemically and physically similar contaminants.

The loss of contaminant and growth dilution are described by a combined rate constant k_{e+g} (g/g dw per day) comprising:

$$k_{e+g} = k_e + k_g \tag{Eq. 11.3}$$

where k_e is the exponential elimination rate constant (g/g dw per day) and k_g is the exponential growth rate constant (g/g dw per day). The value of k_{e+g} can be determined from depuration studies wherein previously exposed organisms loaded with the contaminant are transferred to a contaminant-free exposure test. By monitoring growth, k_g can be obtained, which allows estimating the value for k_e with Equation 11.3.

Some parameters, such as feeding and growth behavior, can change with environmental conditions (e.g., food availability) and hence influence bioaccumulation. The model can be adjusted for these changed parameter and the contaminant uptake and evaluation of effectiveness of the sorbent amendment (reduced bioavailability, AE_s) can be estimated.

Unlike traditional equilibrium-based approaches, this biodynamic model allows for disequilibrium and offers insights into mechanisms governing contaminant uptake via filter feeding or deposit feeding, as well as loss via elimination and growth. Hence, this model can be used to investigate the relative importance of uptake routes for contaminant bioaccumulation in benthic organisms. McLeod et al. (2008) demonstrated with the biodynamic model that PCB body burden greatly depends on an organism's preferential uptake route (Figure 11.1). In the case of exposure to sediment as a main repository of a hydrophobic organic contaminant, the model predicts that a facultative deposit-feeder would accumulate much more contaminant mass per body weight than a filter-feeder. The correlation between modeled and observed data were well correlated with a slope of 1.06 ($r^2 = 0.87$) for *Macoma balthica* and *Corbicula fluminea* (McLeod et al., 2008).

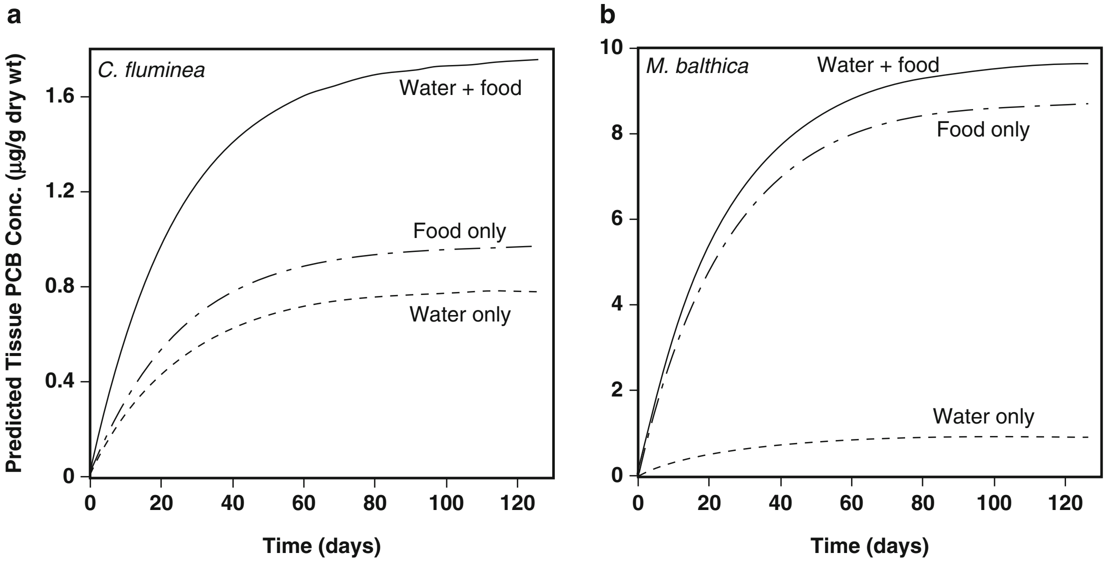

Figure 11.1. Relative contribution of PCB uptake via food and water for the freshwater clam *Corbicula fluminea* in Grasse River sediment (a) and the marine clam *Macoma balthica* in Hunters Point sediment (b), as predicted by the biodynamic model (McLeod et al., 2008) that considers assimilation by filter feeding and facultative deposit feeding uptake routes.

11.3 MECHANISMS OF *IN SITU* STABILIZATION AND REDUCTION OF BIOAVAILABILITY

The concept of AC amendment for *in situ* stabilization of HOCs builds on prior studies that describe the role of black carbon, e.g., soot, chars, and soot-like materials such as coal, to affect the transport, uptake, and biomagnification of HOCs in sediments (Ghosh et al., 2000, 2003; Bucheli and Gustafsson, 2001; Talley et al., 2002). Particle-scale analyses of sediment from the general study area at a field site in San Francisco Bay, California, showed that the majority of HOCs were associated with coal-derived materials and chars, for which the HOCs were not as readily released to water (Ghosh et al., 2000, 2003). These carbonaceous particles strongly affect the partitioning of HOCs due to their surface area and adsorption affinity. Furthermore, several studies showed that strong sorption onto such particles is responsible for slower HOC release rates and reduction in HOC bioavailability (Talley et al., 2002; Kraaij et al., 2001).

These observations led to the idea of using strong carbonaceous sorbent to shift contaminant sorption from a readily-available state to a strongly-sorbed state significantly enhancing a process that was occurring naturally, albeit slowly. Zimmerman et al. (2004) tested coke and AC as such sorbents, and found that AC showed significantly greater performance to reduce PCB contaminant availability to the aqueous phase than coke. The much greater specific surface area and a pore structure of AC appear to account for the greater effectiveness. Strong sorption would reduce the absorption (i.e., the bio-uptake) of HOCs as confirmed by McLeod et al. (2004) who showed significantly lower absorption efficiency of radiolabeled benzo(a)pyrene and a PCB congener from AC compared to other carbonaceous particle types. As shown in Figure 11.2, absorption efficiency is highest from wood and diatoms and lowest from AC.

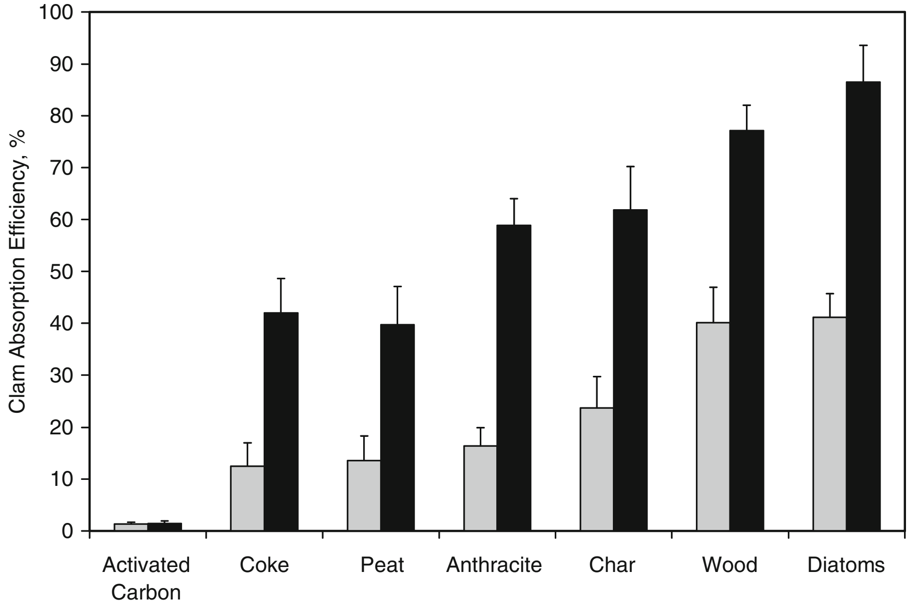

Figure 11.2. Absorption efficiency results for various particle types for the marine clam *Macoma balthica. Light columns* represent the polycyclic aromatic hydrocarbon benzo(a)pyrene; *dark columns* represent PCB-52. *Error bars* show 95% confidence intervals. For the particles tested, absorption efficiency for either compound is lowest from activated carbon and greatest from wood and diatoms (McLeod et al., 2004).

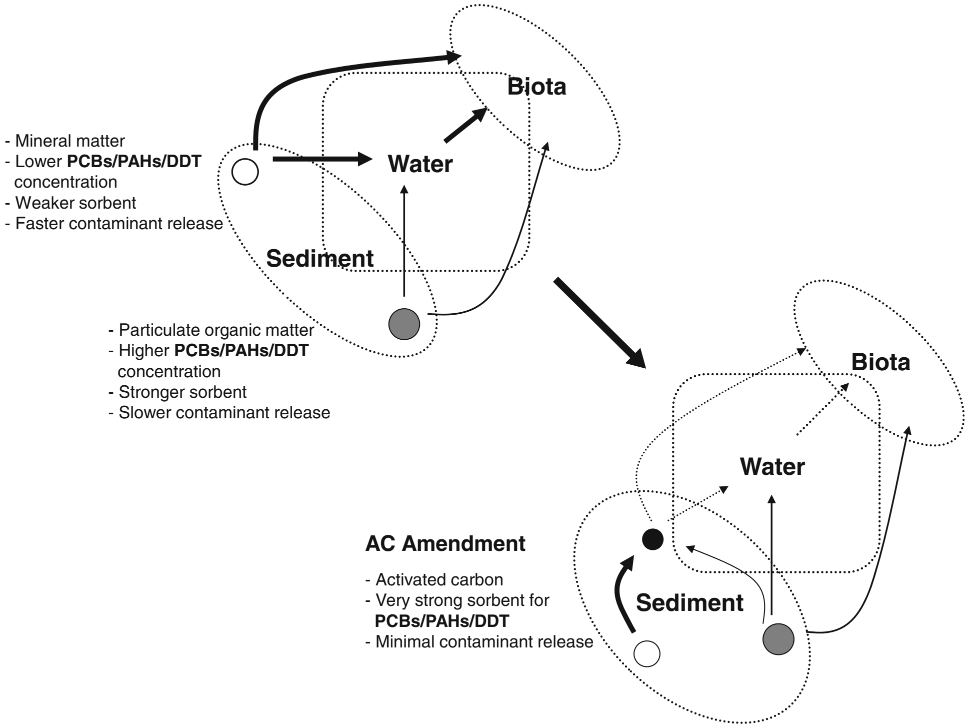

Figure 11.3. Schematic of the mechanisms involved with AC amendment applied to sediment in reducing exposure and environmental risk by lowering HOC release to water and bio-uptake by benthic biota, whether by dermal uptake, filter feeding, or deposit feeding (Cho, 2009).

A conceptual schematic of the *in situ* stabilization of HOCs by AC amendment is shown in Figure 11.3. Incorporation of AC into sediment promotes the repartitioning of contaminants from the more readily-available sorbed fraction onto AC particles. In consequence, the strongly sorbed contaminants become much less available to biota either via water contact or by particle ingestion.

From a biodynamic model's point of view, AC amendment reduces contaminant concentration in an organism by reducing (1) aqueous contaminant concentration, C_w, and (2) contaminant assimilation efficiency from ingested sediment particles, AE_s. The modified value of AE_s for AC-amended sediment can be expressed as:

$$AE_s = F_{\text{sed}} \cdot AE_s^{sed} + (1 - F_{\text{sed}}) \cdot AE_s^{AC} \qquad \text{(Eq. 11.4)}$$

with F_{sed} being the fraction of PCBs that remains on the sediment after sorbent amendment, $AE_s{}^{sed}$ being the assimilation efficiency from untreated sediment, and $AE_s{}^{AC}$ being the assimilation efficiency from AC. F_{sed} can be estimated from the ratio of porewater concentrations in sediment with and without AC-amendment, as:

$$F_{\text{sed}} = \frac{C_{\text{w}}^{\text{AC}}}{C_{\text{w}}^{\text{no AC}}} \qquad \text{(Eq. 11.5)}$$

with $C_w{}^{no\ AC}$ and $C_w{}^{AC}$ (µg/L) being the porewater concentrations before and after AC-amendment, respectively, assuming a linear partitioning at low aqueous concentration (a few nanograms per liter) (Werner et al., 2006). Two general scenarios can be considered to evaluate the value for F_{sed}. Well-mixed conditions with enough time for sequestration of contaminants to the AC yield lowest values of F_{sed} as often used *ex situ* to demonstrate the absolute efficiency of the sorbent treatment. For those quasi steady-state conditions, the aqueous concentrations are best represented by measuring water that has been contacted with the untreated and AC-amended sediment (e.g., *ex situ* in well-mixed slurry). Non-steady-state conditions require *in situ* measurement of the aqueous concentrations, and passive porewater samplers can serve as a time-integrated surrogate measures.

11.4 MODELING THE MASS TRANSFER OF HYDROPHOBIC ORGANIC CONTAMINANT IN AC-AMENDED SEDIMENTS

As described in the previous section, the *in situ* sequestration of hydrophobic organic contaminants by AC is expected to achieve a marked reduction in the uptake of HOCs to biota by consequence of change in the thermodynamic partitioning equilibrium to a more strongly sorbed state. However, slow mass transfer kinetics can hinder the mass movement and the establishment of the new thermodynamic equilibrium. Conceptually, the mass transfer resistances exist in (1) contaminant release processes from sediment particles to sediment porewater, (2) contaminant migration to the vicinity of the neighboring particle, (3) migration to the vicinity of the next particle, and (4) sorption of contaminant within the AC (Werner et al., 2006; Hale and Werner, 2010; Cho, 2009).

To account for the kinetics of this mass transfer process, Werner et al. (2006) developed a numerical model that simulates the release of HOCs from sediment, sorption by added AC, and the resulting change in pollutant-particle type associations and concentration in the aqueous phase (Hale and Werner, 2010).

11.4.1 Model Concept for a Well-Mixed System

The conceptual model is depicted in Figure 11.4. Each domain (fast release sediment particle, slow release sediment particle, and activated carbon) is represented by a geometric mean grain radius, solid density, and porosity. In its simplest form, the basic assumption is that

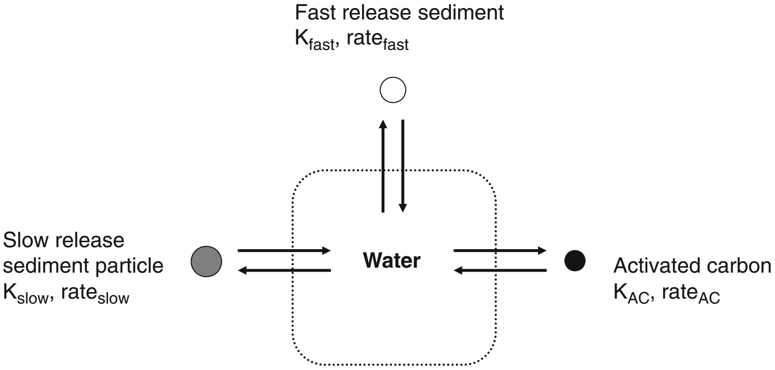

Figure 11.4. The conceptual model for a well-mixed system of sediment and AC particles. The four domains of the model comprise: fast release sediment particles, slow release sediment particles, AC particles, and an external aqueous phase. Each particle type is represented by a mean particle size (geometric mean); the surface of each particle type is in linear partitioning equilibrium with the external aqueous phase through respective partition coefficients (K_{fast}, K_{slow}, and K_{AC}); and the movement of compounds in and out of particles is described by apparent diffusive rate ($rate_{fast}$, $rate_{slow}$, and $rate_{AC}$).

the surface of each particle type is in linear partitioning equilibrium with the external aqueous contaminant concentration. The movement of contaminants in or out of the different solid-phase domains is described by intraparticle diffusion with a concentration-independent rate constant. The various fluxes determine the overall change in the bulk aqueous contaminant concentration S_{aq} (g/cm^3):

$$\begin{aligned}\frac{dS_{aq}}{dt} = &-\frac{V_{sed}}{V_{aq}}\cdot\frac{d}{dt}\left[3\int_0^1 q^2 S_{sed\_fast}(q,t)dq + 3\int_0^1 q^2 S_{sed\_slow}(q,t)dq\right]\\ &-\frac{V_{AC}}{V_{aq}}\cdot\frac{d}{dt}\left[3\int_0^1 q^2 S_{AC}(q,t)dq\right]\end{aligned} \qquad \text{(Eq. 11.6)}$$

where V_j (cm^3) and S_j (g/cm^3) denotes the total volume of each phase component and the volumetric pollutant concentration in that phase respectively, and q (-) the radial distance from the particle center divided by the particle radius. S_{sed_fast} (g/cm^3) is the amount of contaminant associated with $rate_{fast}$ per total volume of sediment and S_{sed_slow} (g/cm^3) is the amount of contaminant associated with $rate_{slow}$ per total volume of sediment. The implementation of the intraparticle diffusion part of this model is based on the explicit numerical scheme described by Wu and Gschwend (1988). The system of differential equations is solved with an explicit Euler scheme. A time step constraint avoids instability in the most sensitive component of the system. The detailed implementation, initial conditions, boundary conditions are described elsewhere (Werner et al., 2006).

11.4.2 Model Calibration for a Well-Mixed System

The mass transfer model for a well-mixed system requires a total 15 input parameters, as listed in Table 11.1. The parameter $rate_{fast}$, $rate_{slow}$, f_{fast}, and f_{slow} ($1-f_{fast}$) can be obtained by contaminant desorption experiments with bulk sediment and fitting a three parameter diffusive model equation (Werner et al., 2006; Hale and Werner, 2010):

$$\begin{aligned}\frac{m(t)}{m_{tot}} = 1 &- f_{fast}\left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-rate_{fast}n^2\pi^2 t)\right]\\ &-(1-f_{fast})\left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-rate_{slow}n^2\pi^2 t)\right]\end{aligned} \qquad \text{(Eq. 11.7)}$$

where $m(t)/m_{tot}$ is the contaminant mass fraction desorbed. The sorption coefficients K_{fast} (cm^3/g total sediment) and K_{slow} (cm^3/g) are calculated from the bulk sediment-water partitioning coefficient K_d (cm^3/g) by a linear contribution weighted by mass fraction f_{fast} (-) and f_{slow} (-), respectively (Hale and Werner, 2010). The AC-water partitioning coefficient K_{AC} and the bulk sediment-water partitioning coefficient K_d (cm^3/g) can be determined experimentally. The K_{AC} can be further corrected by an AC fouling coefficient. Necessary corrections may be determined by experiments and inverse modeling to considering possible fouling of AC by naturally existing natural organic matter, for which the correction factor would be highly site-specific (Hale et al., 2009).

The numerical model estimates the diffusion kinetic rate of contaminant uptake by AC, $rate_{AC} = D_{AC}/r^2_{AC}$ (s), according to Equation 11.8 (Werner et al., 2006):

$$rate_{AC} = \frac{D_{AC}}{r_{AC}^2} = \left(\frac{p_{AC}^2}{(1-p_{AC})d_{AC}K_{AC}+p_{AC}}\right)\cdot\frac{D_{aq}}{r_{AC}^2} \qquad \text{(Eq. 11.8)}$$

Table 11.1. Input Parameters for HOC Mass Transfer Model. Here, the third column denotes data possible. Sources: C (experimental variable), M (measurement), E (estimation), L (literature or manufacturer information). Also, site-specific parameters are marked as "site-specific"

Parameter	Parameter Annotation	Source
AC particle radius	r_{ac} (cm)	C, M, L
AC solid-phase density	d_{ac} (g/cm^3)	M, L
AC porosity	p_{ac} (-)	M, L
AC-water partitioning coefficient	K_{AC} (cm^3/g)	M, L
AC dose	dose (g/g)	C, M
Contaminant uptake rate by AC	$rate_{AC}$ (/s)	E
Fast release rate from sediment	$rate_{fast}$ (/s)	M, site-specific
Mass fraction of sediment with $rate_{fast}$	f_{fast} (-)	M, site-specific
Partitioning coefficient for sediment with $rate_{fast}$	K_{fast} (cm^3/g)	M, site-specific
Slow release rate from sediment	$rate_{slow}$ (/s)	M, site-specific
Partitioning coefficient for sediment with $rate_{slow}$	K_{slow} (cm^3/g)	M, site-specific
Sediment porewater tortuosity	τ (-)	M, site-specific
Water-phase diffusion coefficient	D_{aq} (cm^2/s)	L
Bulk dry sediment density	d_s (g/cm^3)	M, site-specific
Bulk sediment-water partitioning coefficient	K_d (cm^3/g)	M, site-specific

where r_{AC} (cm) is the AC particle radius, p_{AC} (-) the porosity of the AC particle, d_{AC} (g/cm^3) the solid density of the AC particle and K_{AC} (cm^3/g) the linear AC-water partitioning coefficient at the relevant aqueous concentration range. The AC radius is taken as half of the value of the geometric mean of the upper and lower grain size limits.

Generally, the mass transfer model tends to overestimate experimental data with respect to the time required to reach sorption equilibrium in batch studies (Zimmerman et al., 2005; Hale and Werner, 2010). This discrepancy could be due to accelerated diffusion of pollutants towards the AC particle core along preferential pathways in macropores (Ahn et al., 2005), or due to some AC particles fragmenting during equilibration. Also, the use of only one representative AC particle size may deviate model predictions from observations. Nevertheless, the model estimations agree within a reasonable factor of those measured (Zimmerman et al., 2005; Hale and Werner, 2010).

11.4.3 *In Situ* Treatment Model for a Briefly Mixed or Un-mixed System

The model for a completely mixed system is appropriate for a laboratory experimental setup that ensures complete mixing among AC, sediment, and porewater. Unlike the laboratory setup, under field conditions, HOC mass transfer occurs in a quiescent fashion, where continuous and complete mixing are not guaranteed. In this case, sorption-retarded contaminant transport through the pore space among sediment particles towards the AC particles also becomes a limiting kinetic process for overall HOC mass transfer. To explain this inter-particle transport processes, a model system is formulated by stacking small sub-volumes (cubes) vertically and horizontally (Figure 11.5). This stacking comprises some sub-volumes with and some without AC particles, where the kinetics of the local sorption process of the HOC within

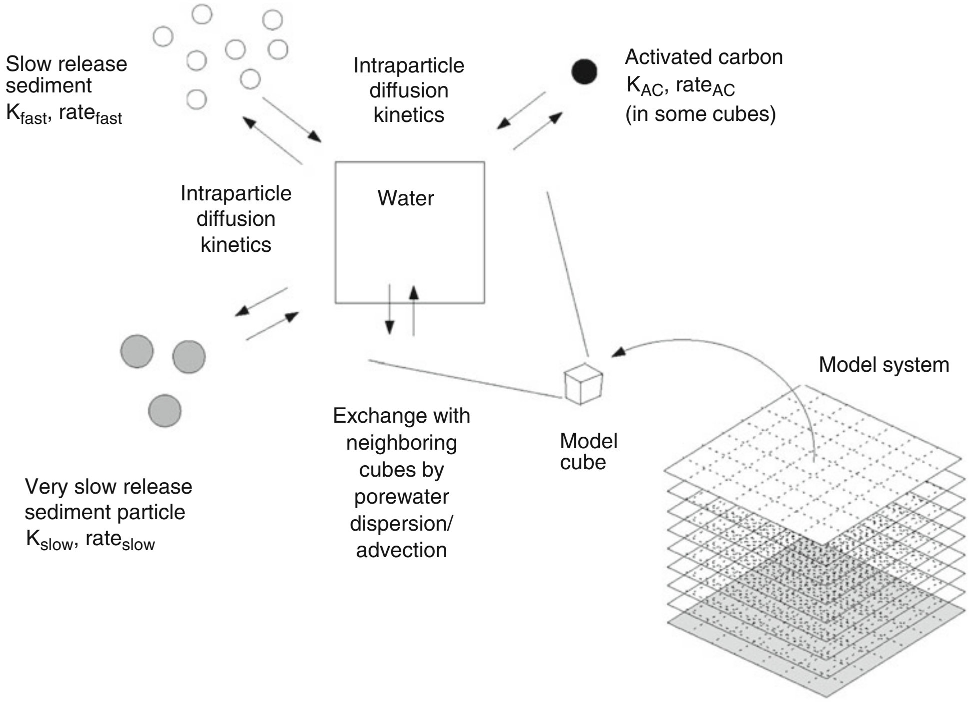

Figure 11.5. The conceptual framework for a model of HOC transport for a minimally mixed sediment system. Movement of contaminants between neighboring cubes can occur by molecular diffusion in porewater, porewater dispersion, or advective flow (Cho, 2009).

each cube is simulated based on the well-mixed model described in Section 11.4.1. HOC movement between cubes is dependent on mass transport by either diffusion in the sediment porewater alone or assisted by porewater flow or dispersion. The distribution of AC particles in a system can be determined either by random selection or by a specific assignment process to account for a statistical or measured heterogeneity in AC distribution. In addition to the simulation of each cube, the model considers the exchange of contaminants between neighboring cubes as may be driven by the porewater movement in the form of either dispersion or advective movement. The change in the aqueous concentration, S_{aq} (g/cm^3), at location x,y,z and at time, t (seconds [s]), is:

$$\begin{aligned}\frac{dS_{aq}(x,y,z,t)}{dt} &= D_{disp}\left[\frac{\partial^2 S_{aq}(x,y,z,t)}{\partial x^2}+\frac{\partial^2 S_{aq}(x,y,z,t)}{\partial y^2}+\frac{\partial^2 S_{aq}(x,y,z,t)}{\partial z^2}\right]\\ &\quad -\left[u_x\frac{\partial S_{aq}(x,y,z,t)}{\partial x}+u_y\frac{\partial^2 S_{aq}(x,y,z,t)}{\partial y}+u_z\frac{\partial^2 S_{aq}(x,y,z,t)}{\partial z}\right]\\ &\quad -\frac{V_{sed}(x,y,z)}{V_{aq}}\cdot\frac{d}{dt}\left[3\int_0^1 q^2 S_{sed\_fast}(x,y,z,q,t)dq+3\int_0^1 q^2 S_{sed\_slow}(x,y,z,q,t)dq\right]\\ &\quad -\frac{V_{AC}(x,y,z)}{V_{aq}}\cdot\frac{d}{dt}\left[3\int_0^1 q^2 S_{AC}(x,y,z,q,t)dq\right]\end{aligned}$$

(Eq. 11.9)

where D_{disp} (cm^2/s) denotes the dispersion coefficient, and u_i (centimeters per day [cm/d]) the porewater advective flow rate in i direction (x,y,z) (Hale and Werner, 2010; Cho, 2009).

Other variables and parameters are the same as described for the well-mixed model. The dispersion coefficient and porewater advective flow rate should be carefully evaluated to apply to the model due to the highly site-specific characteristics that influence dispersion and porewater movement.

11.4.4 Model Extension

The HOC models described in Sections 11.4.1 and 11.4.3 for different mixing regimes may be extended to consider possible contaminant uptake into passive samplers (semi-permeable membrane devices and polyethylene devices) or biodegradation in the form of first-order rate degradation in the aqueous phase. A discussion of such extensions can be found elsewhere (Werner et al., 2006; Hale and Werner, 2010).

11.5 EFFECTS OF MIXING REGIME, PARTICLE SIZE, AND DOSE OF AC SORBENTS IN SEDIMENT FOR *IN SITU* STABILIZATION

11.5.1 Mixing Regime

To demonstrate the effect of mixing regime on the *in situ* stabilization of an organic contaminant by AC sorbent, three theoretical scenarios of AC-sediment-porewater contact mode are assessed by HOC mass transfer model simulations (Figure 11.6). The first scenario is a complete and continuous AC-sediment-porewater contact as shown in Figure 11.6a, where AC particles randomly and continuously contact with sediment particles and porewater molecules in the system. This model framework predicts well the qualitative trends in contaminant aqueous concentration observed as a function of time, AC size, and dose in laboratory experiments wherein complete mixing between AC and sediment is assured (Werner et al., 2006). However, K_{AC} values measured in clean water systems had to be adjusted to consider the attenuative effect by natural organic matter of sediment. For example, K_{AC} was reduced by an average factor of 16 to achieve good quantitative agreement between model and experimental results for PCB congeners in Hunters Point and Lake Hartwell sediments (Werner et al., 2006). The second scenario (Figure 11.6b) assumes HOC mass transfer in a quiescent system, wherein

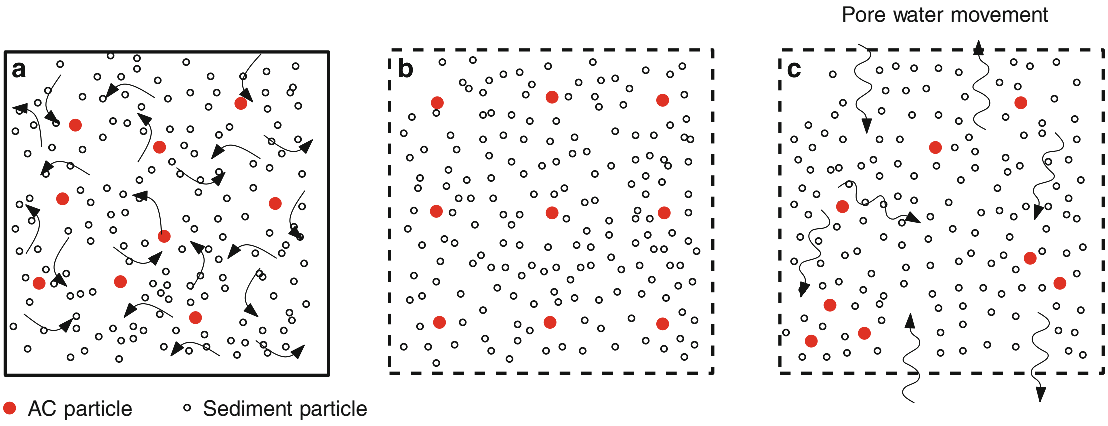

Figure 11.6. Three scenarios for sediment-AC contact: (a) complete mixing system, (b) quiescent system with uniformly distributed AC particles, (c) quiescent system with non-uniform AC distribution and porewater movement by tidal pumping (Cho, 2009).

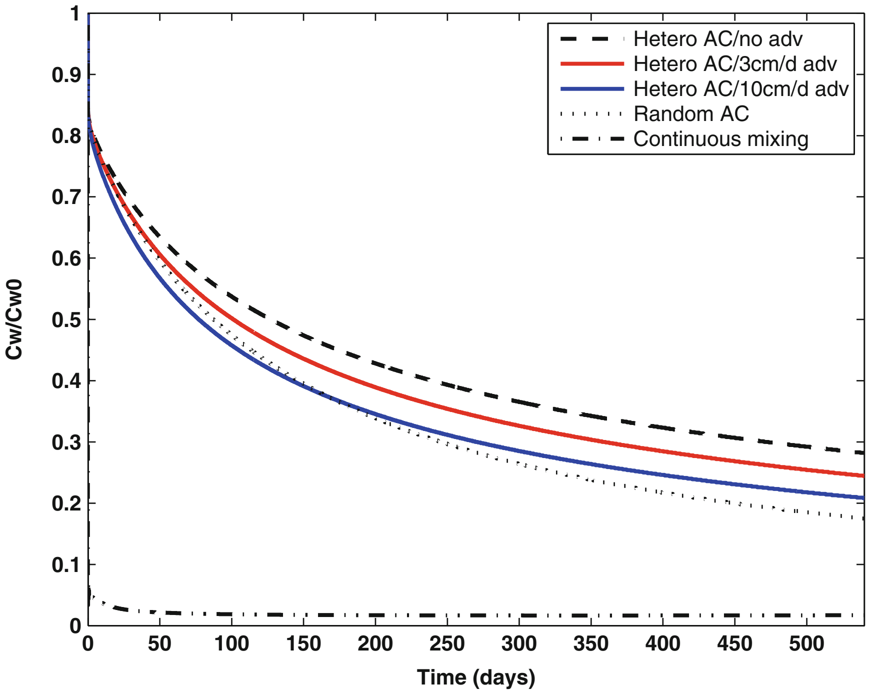

Figure 11.7. PCB 101 congener mass transfer simulation results with various mixing regimes, AC distribution, and hydraulic conditions (advective movement) and with 3.4 wt% AC dose. The y-axis represents the ratio of aqueous PCB 101 congener concentration to the initial concentration and the x-axis represents the sediment-AC contact time (Cho, 2009).

molecular diffusion between solid particles (sediment and AC sorbent) is the only dominant transport process in sediment porewater, and AC particles are distributed uniformly (or randomly). This scenario seems more plausible than the well-mixed scenario for assessments of the field application of AC amendment, where a continuous mixing assumption is inapplicable. Furthermore, this model scenario can be adjusted to account for additional considerations of field-specific conditions. Adjustments would be especially significant for uneven AC distribution and possible porewater advective movement to achieve more realistic model simulations. The uneven AC distribution may retard the HOC mass transfer further. On the other hand, the possible advective movement and mechanical dispersion driven by field hydraulic conditions, as for example by tidal pumping, may facilitate HOC mass transfer (Cho, 2009). The last scenario applies these two additional field conditions (Figure 11.6c).

The model simulation results for the three scenarios are summarized in Figure 11.7. Model parameters are selected for a polychlorinated biphenyl (PCB 101) with 3.4 wt% AC dose, and sediment characteristics are optimized for an inter-tidal mudflat on Hunters Point Shipyard, San Francisco, California, where a field-scale trial of AC amendment was tested for *in situ* stabilization of PCBs (Cho et al., 2007; Cho, 2009). The advective flow velocity at the site was quantified by Cho et al. (2010) and Cho (2009) giving a few centimeters per day (cm/d) downward porewater flow velocity for AC-treated sediment. The distribution of AC was estimated based on the assumption that the distribution of 2-in. core average total organic carbon (TOC) contents throughout the AC-treated area would be similar to the AC distribution in a model system. Although this assumption is rather simple, it nevertheless provides a reasonable basis for assigning AC heterogeneity compared to an arbitrary random distribution or uniform distribution.

In Figure 11.7, the bottom dash-dot line represents the change of the ratio of aqueous PCB 101 concentrations after AC addition relative to the initial aqueous PCB concentration in untreated sediment for a completely mixed system (scenario 1). In this case, as soon as AC-sediment contact starts, aqueous PCB concentration drops below 10% of the initial concentration. The initial drop in concentration is a consequence of sediment particles and porewater being in full contact with the accessible sorption sites on the surface of AC particles by continuous mixing. In contrast, this prompt absorption by AC is greatly retarded without mixing, as other simulations in the graph show much slower decreasing concentration patterns than the complete-mix case (dash-dot line). Next in importance to the mixing condition in terms of approach to a quasi-equilibrium state, the distribution of AC plays an important role as a kinetic barrier for PCB mass transfer. Compared to a random distribution of AC (dotted line), a heterogeneous distribution of AC (dashed line) shows a delay in approach towards equilibrium. After 18 months of AC-sediment contact, the difference in reduction of aqueous PCB 101 congener concentration is more than 10% between a random AC distribution and heterogeneous AC distribution. Further, the incorporation of a modest amount of advective porewater movement of 3 or 10 cm/d (solid red and blue lines) results in a greater reduction in aqueous PCB 101 concentration than the diffusion only system (dashed line). This difference is predicted to be about 5–10% reduction in aqueous PCB 101.

The simulations for the long-term behavior of aqueous PCB 101 congener concentration under field conditions predict that more than two decades of AC-sediment contact time is needed to reach an equilibrium state. However, near-equilibrium condition (>90% reduction) is attained within about 10 years with only very gradual changes occurring subsequently.

These model predictions are well aligned with empirical data from field studies. Although *in situ* pore-water PCB concentration data in the field were not available due to analytical difficulties, *in situ* PCB uptake data into semi-permeable membrane devices (SPMDs) were measured, as this generally correlate well with aqueous phase concentrations. It was found that reductions of *in situ* field PCB uptakes into SPMDs after 1 and 7 months of AC amendment were 37% and 62% respectively (Cho et al., 2007). Similar extent of reductions can be predicted by this mass transfer model with 3.4 wt% AC dose (Figure 11.7). With less AC dose (1.7–2.1 wt%), 50–67% of reduction in SPMD uptakes with time spans between 6 and 18 months were observed (Cho et al., 2009), which also aligned with model prediction results with lower AC dose.

11.5.2 Particle Size

The HOC mass transfer models described in Sections 11.4.1 and 11.4.3 can be used to consider the effect of AC sorbent particle size on *in situ* stabilization through use of a particle-size dependent estimation of the diffusion kinetic rate of contaminant uptake by AC, rate_{AC}. According to Equation 11.8, a large AC particle will take longer to equilibrate than a small, fine AC particle. These assumptions are in general agreement with the experimental observations illustrated by Zimmerman et al. as shown in Figure 11.8, where decreasing AC particle size significantly increases the effectiveness in reducing aqueous PCB concentrations in 1-month contact experiments (Zimmerman et al., 2005; Tomaszewski et al., 2007).

In an un-mixed AC-sediment system, sorbent particle size may also affect the benefit of AC. With fixed dosing, increasing particle size would increase average distances between sediment particles and a nearest AC particle, which will retard PCB mass transfer due to the limiting kinetics in aqueous phase. However, further study needs to explore the sorbent particle size effect under field conditions.

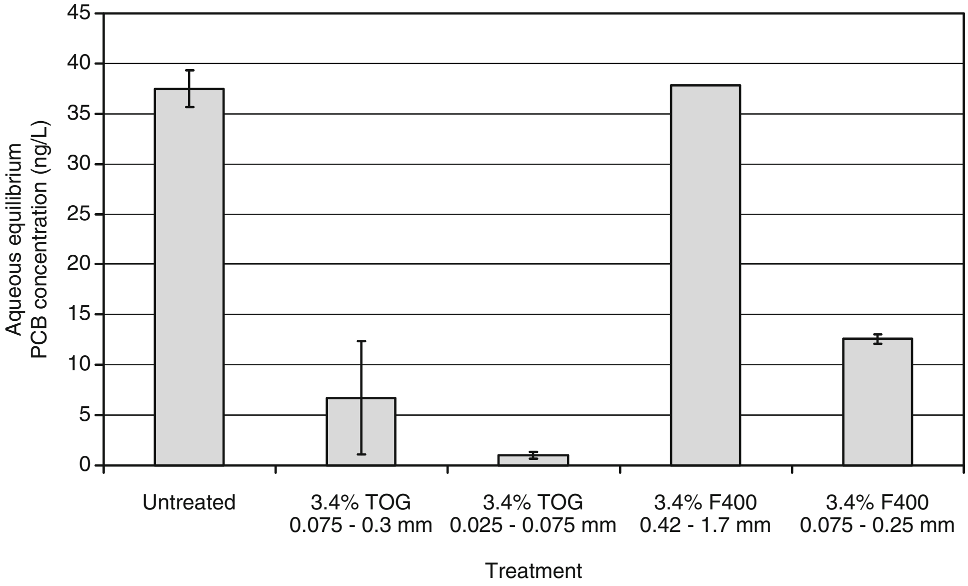

Figure 11.8. Aqueous PCB concentrations for Hunters Point (San Francisco Bay, CA, USA) sediment contacted with varying sizes of TOG and F400 carbon for 1 month (Zimmerman et al., 2005).

11.5.3 Dose of Sorbents

A clear AC dose-response is observed in laboratory well-mixed systems in that increasing the carbon dose increases the benefit of AC amendment. A series of physico-chemical tests and bioassays observed this dose-response relationship (Zimmerman et al., 2005; McLeod et al, 2008). For example, Figure 11.9a, b show the total PCB and total PAH aqueous equilibrium concentrations for untreated sediment and sediment from Hunters Point, California, contacted with 0.34%, 1.7%, and 3.4% 75–300 micrometers (µm) activated carbon (TOG) for 1 month. In the case of PCBs, the aqueous equilibrium concentrations gradually decreased by 44%, 74%, and 87% with increasing dose. The reductions of the aqueous concentrations vary for the individual PCB and PAH compounds. For both PCBs and PAHs, aqueous concentrations of the less hydrophobic compounds are reduced to a greater extent than that for the more hydrophobic compounds. The aqueous concentration reduction differences among homolog groups are likely due to slower mass transfer kinetics. Similar trends are observed in passive sampler uptake and quiescent flux experiments (Zimmerman et al., 2005). The results of 56-day PCB bioaccumulation tests using *N.arenaceodentata* and *L.plumulosus* also show a dose-response in decreasing PCB body burdens with increasing AC additions for both species (Figure 11.10).

The HOC mass transfer model for an un-mixed AC-sediment system also tells a similar story about the effect of AC dose on the ultimate (thermodynamic) benefit of AC amendment. Furthermore, the model provides insight into the kinetic aspects of AC dose that relates to the possible short-term benefit of AC application. As shown in Figure 11.11, after 5 years of AC-sediment contact time, aqueous PCB 101 concentration is predicted to be reduced to 20% of the initial concentration with 2.1 wt% AC dose for sediment in Hunters Point Sediment, California. When the dose was doubled to 4.2 wt%, the residual PCB 101 congener concentration was halved. With 80% reduction in aqueous PCB concentrations as a cleanup goal, 4.1 wt% AC dose would achieve the goal within 18 months based on the model simulation, while about a 5-year

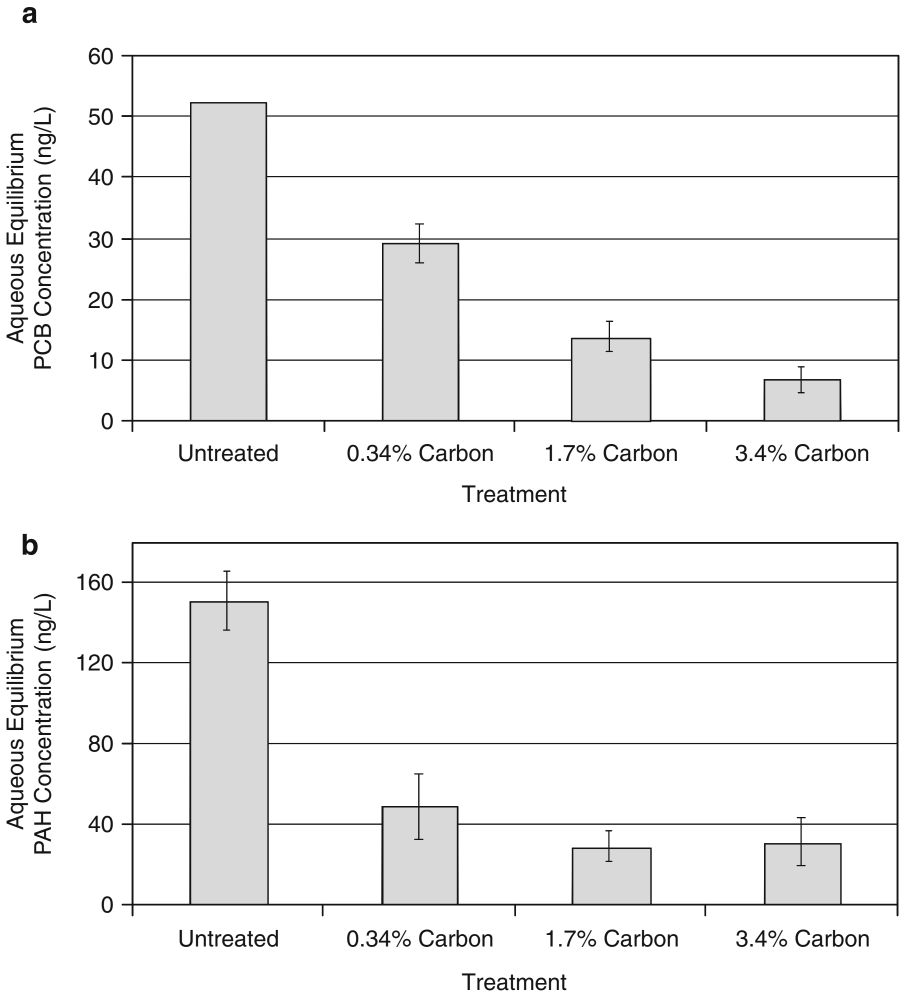

Figure 11.9. Aqueous PCB (a) and polycyclic aromatic hydrocarbon (*PAH*) (b) concentrations for Hunters Point (San Francisco Bay, CA, USA) sediment contacted with varying doses of activated carbon for 1 month. The activated carbon is coarse (75–300 μm) type TOG (Zimmerman et al., 2005).

monitoring plan is needed to confirm the success of the remediation with an AC dose of 2.1 wt%. In 5 years, the 4.2% AC dose is expected to attain over 90% reduction in PCB aqueous concentration. This kinetic effect can be explained by the shorter mean length of the pathway between sediment particles and AC particles in sediment amended with a higher AC dose.

11.6 CONCLUSIONS

From both laboratory tests and model simulations, it is concluded that increasing the activated carbon dose increases both the short-term (kinetic) and the long-term (thermodynamic) treatment effectiveness. It appears that there may be different dose responses for different compound classes, which would depend on the distribution of specific contaminants in the sediment and their association among sediment particle types. For consideration of application of activated carbon at any particular contaminated sediment site, a series of tests and model simulations would most likely be needed to determine an appropriate dose and form

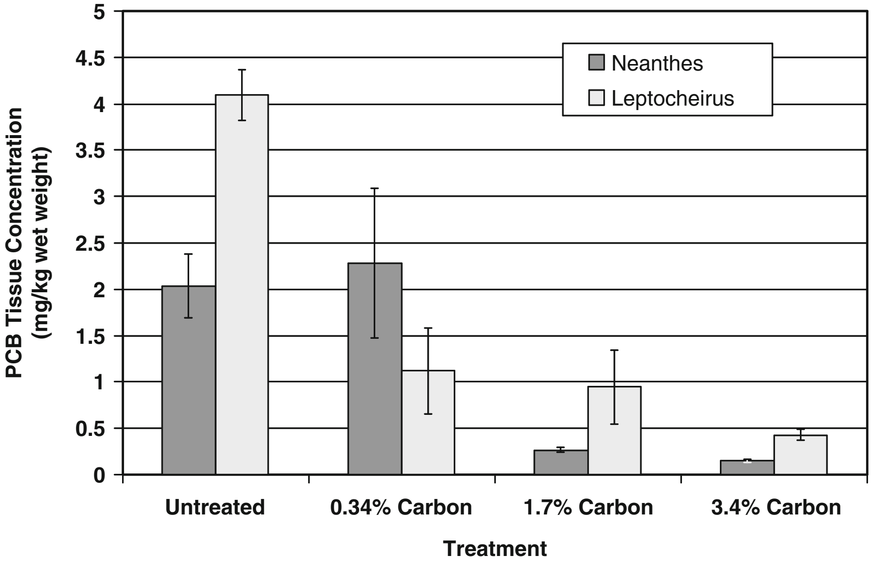

Figure 11.10. PCB bioaccumulation by *Neanthes arenaceodentata* and *Leptocheirus plumulosus* during 56-day exposure tests. The sediment was contacted for 1 month with varying doses of 75–300 μm type TOG carbon before the bioaccumulation tests (Zimmerman et al., 2005).

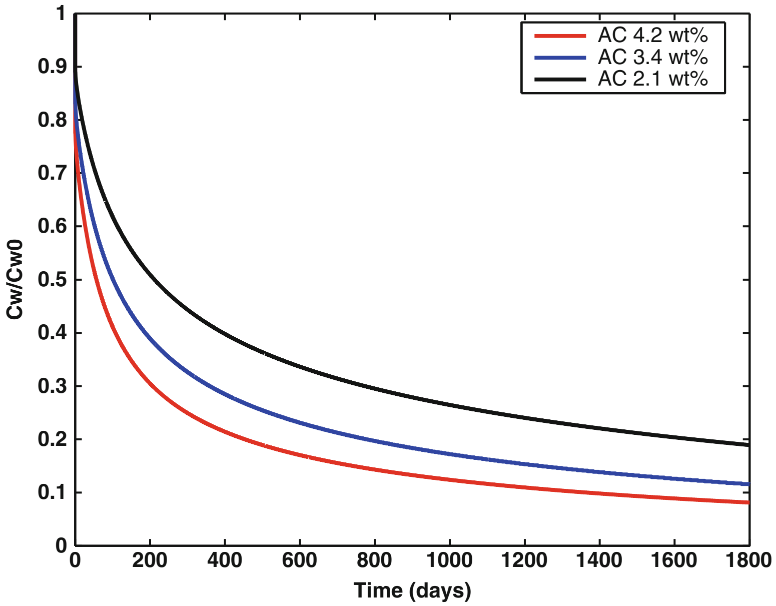

Figure 11.11. Effect of AC dose on aqueous concentration of PCB101 congener. The model simulation results with heterogeneous AC distribution with 3 cm/d porewater velocity. The y-axis represents the ratio of aqueous PCB 101 congener concentration to the initial concentration and the x-axis represents the sediment-AC contact time (days) (Cho, 2009).

of application for a desired endpoint within a specified time period. The modeling framework outlined in this chapter points the way for laboratory and field tests to support one another to improve predictive capabilities and advance the design of effective *in situ* sorbent amendment applications.

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CHAPTER 12

CAPPING FOR REMEDIATION OF CONTAMINATED SEDIMENTS

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12.1 INTRODUCTION

The historical release of contaminants into the environment has generated a legacy of contaminated sites throughout the world. For years, the sediments in water bodies adjoining these pollution sources served as sinks for contaminants, particularly hydrophobic organic compounds (HOCs) and heavy metals. Many of these original sources have been eliminated, but the sediments that formerly served as a pollutant sink now serve as sources of contamination and residual environmental risk. Assessment and remediation of these contaminated sediment sites have been the subject of much scientific analysis, public debate and technological innovation (NRC, 2001). There are few economically viable options for management of contaminated sediments. Capping sediments with a layer of clean material is one of few alternatives with a proven record of success for sediment remediation. This chapter is intended to describe the tools and techniques that are applicable for 55 assessment, design, implementation and monitoring of capping as a remedy for contaminated sediment sites. Capping is designed to achieve one or more of the following objectives depending upon the cause of exposure and risk at a site:

1. Contain contaminated sediments to eliminate sediment re-suspension risk
2. Contain contaminants in sediments and reduce migration and release
3. Separate a benthic community from interacting with and processing the underlying contaminated sediments

The first objective is achieved by designing a cap that is sufficiently armored to reduce or eliminate erosion of the underlying sediment and is most effective when contaminants are strongly solid associated as is typically the case. The sorption characteristics of such a cap are largely irrelevant since it is designed to only contain the underlying sediments and sand; gravel and/or stone are typically used in such cases. The second objective is often also achieved by this type of cap although in some instances, such as when there is significant groundwater upwelling through the cap, an alternative cap material might be chosen. This alternative or amended cap might be chosen to control upwelling (low permeability cap), to absorb or sequester contaminants (sorptive caps) or encourage degradation and fate processes of the contaminants (reactive caps). The final objective is a particularly important advantage of a cap in that the interaction of a benthic community with the contaminated sediments leads to particularly rapid contaminant transport (through bioturbation) and can lead to bioaccumulation and trophic transfer of the contaminants. The separation of the benthic community from the contaminated sediments reduces or eliminates contaminant exposure by either of these mechanisms.

Capping contaminated sediments following dredging operations and for capping dredged material has been a common practice by the U.S. Army Corps of Engineers since the 1970s

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(Bokuniewicz and Liu, 1981; O'Connor and O'Connor, 1983). Some field studies were performed on the long-term effects of caps on contaminant levels at these sites (Fredette et al., 1992; Sumeri et al., 1994). Sampling performed in these studies utilized sediment cores and revealed sharp gradient in concentration between the underlying material and the caps. However, it must be noted that analysis based on bulk solids was inherently biased due to differences in partitioning between the sediment and sand (Reible et al., 2006).

The application of sand and sediment caps as a remediation technology for contaminated sediments was subsequently investigated. Thibodeaux et al. (1991) proposed using capping with clean sediments to create a diffusive barrier for reducing the concentrations and fluxes from sediments contaminated with polychlorinated biphenyls (PCBs). Wang et al. (1991) found that a layer of clean sediment successful reduced concentrations of the HOC 2,4,6-trichlorophenol in the laboratory and later utilized a sorption-diffusion model to predict the observed behavior (Thoma et al., 1993). Based on initial successes, other studies were employed using clean sands and other "active" materials that attempted to sequester or enhance degradation of the contaminants.

This chapter is intended to describe the tools and techniques that are applicable for assessment, design, implementation and monitoring of capping as a remedy for contaminated sediment sites. The chapter presents some background on the literature associated with capping to serve as a reference for specific applications, then various processes and concepts relevant in caps followed by a discussion of the information needed to perform cap assessments. Some design models and guidance on their implementation are then presented. The final section describes the monitoring of caps.

12.2 CAPPING MATERIALS

An inert material such as sand can be effective as a capping material where contaminants are strongly solid-associated and where the operative site-specific transport mechanisms do not lead to rapid contaminant migration through such a material. Sand caps may not be sufficient for achieving remedial goals in sites where contamination levels are high or transport rates are fast due to porewater upwelling or tidal pumping effects. Additional contaminant containment can often be achieved through the placement of clean sediment, e.g., dredged material from a nearby location. The placement of clean sediment as an *in situ* cap can be difficult when the material is fine-grained or has a low density. Other materials as cap layers or amendments may be useful to address particularly mobile contaminants or when particular degradative mechanisms can be exploited. The most common situation encouraging the use of amended caps is when groundwater upwelling or other advective processes encourage significant chemical mobility.

Metals migration is very site dependent due to the potential for many metals to complex with other species in the interstitial water and the specific metal speciation present at a site. Often, the strongly reducing environment beneath a cap renders many common metals unavailable through the formation of metal sulfides. In such cases, a simple sand cap can be very effective. Amended caps for metal contaminated sediments may be advantageous when site-specific conditions lead to elevated metals mobility, but should be supported with site-specific testing.

For hydrophobic organic contaminants, cap amendments that directly control groundwater upwelling or sorbents that can remove migrating contaminants from that groundwater have been successfully employed. Examples include clay materials such as AquaBlok™ for permeability control, and sorbents such as activated carbon for truly dissolved contaminants, and organophilic clays for separate phase contaminants.

Although a variety of materials have been proposed for sediment caps, a far smaller number of options have been successfully employed in the field. The following subsections discuss the performance and feasibility of various capping materials for sediment remediation.

12.2.1 Sand

Capping with clean sand provides a physical barrier between the underlying contaminated material and the overlying water, stabilizes the underlying sediment to prevent re-suspension of contaminated particles, and can reduce chemical exposure under certain conditions (USEPA, 2005). Sand primarily provides a passive barrier to the downward penetration of bioturbating organisms and the upward movement of sediment or contaminants. Zeman and Patterson (1997) demonstrated that a sand cap could be effectively placed in Hamilton Harbor, Ontario, Canada. A capping project in the St. Paul Waterway near Tacoma, Washington, successfully demonstrated habitat restoration using sand as the capping material (Ficklin et al., 1989). Ten years of monitoring showed minimal cap disturbance and successful containment of contaminants. As an added benefit, sand capping restored shallow-water habitat that had been reduced by 90% over the past 100 years (yrs). Simpson et al. (2002) found that capping was successful at reducing metal fluxes, particularly due to organism-induced mixing (bioturbation) in the clean cap material rather than in the sediments. As indicated previously, even a sand cap will enhance chemical reduction in the sediments, stabilizing metals through metal sulfide formation.

Although conventional sandy caps can often be an effective means of managing contaminated sediments, there are conditions when sand caps may not be capable of achieving design objectives. Some factors that reduce the effectiveness of sand caps include:

1. Erosion and loss of cap integrity,
2. High groundwater upwelling rates,
3. The presence of tidal influences,
4. Mobile (low sorption) contaminants of concern (COCs),
5. High COC concentrations,
6. The presence of nonaqueous phase liquids (NAPLs),
7. Unusually toxic COCs and
8. High rates of gas ebullition.

In these cases, it may be possible to offset these issues by increasing the thickness of the cap. However, the required thickness can reach infeasible levels in shallow streams or navigable water bodies. In addition, increased construction costs associated with thick caps may become prohibitive. As a result of these issues, caps that use alternative materials to reduce the thickness or increase the protectiveness of a cap may be utilized (active caps). The materials in active caps are designed to interact with the COCs to enhance the containment properties of the cap.

12.2.2 Apatites

Apatites are a class of naturally-occurring minerals that have been investigated as a sorbent for metals in soils and sediments (Chen et al., 1997; Peld et al., 2004). Apatites consist of a matrix of calcium phosphate and various other common anions, including fluoride, chloride, hydroxide, and occasionally carbonate. Metals are sequestered either through direct ion exchange with the calcium atom (Miyake et al., 1986; Takeuchi and Arai, 1990) or dissolution of hydroxyapatite followed by precipitation of lead apatite (Ma et al., 1993; Xu and Schwartz, 1994). Crannell et al. (2004) investigated pilot-scale apatite caps and found reductions in lead (Pb), cadmium (Cd) and zinc (Zn) porewater concentrations and reduced bioaccumulation of Cd versus control (sand) caps. Reible et al. (2006) discuss the successful implementation of an apatite cap for control of metals in the Anacostia River in Washington, D.C. Solid-phase concentration profiles suggested effective containment of the underlying contaminated metals 6 months after cap implementation.

12.2.3 Zeolites and Organoclays

Jacobs and Forstner (1999) proposed the concept of an active barrier system for containment of metals using zeolites, which are microporous aluminosilicate minerals with a high cationic exchange capacity (CEC). A subsequent study found that Zn and iron (Fe) were effectively demobilized using a zeolite-based active capping system (Jacobs and Waite, 2004).

By exchanging a cationic surfactant onto the surface of clays such as zeolites and bentonites, it is possible to create a hydrophobic, sorbing layer for non-polar organics. Organoclay is a modified bentonite containing such substitutions that has been evaluated for control of NAPLs and other organic contaminants (Reible et al., 2007). An organoclay cap has been implemented for sediment remediation at the McCormick and Baxter site in Portland, Oregon (Parrett and Blishke, 2005; Reible et al., 2005). Pernyeszi et al. (2006) found that 2,4-dichlorophenol was adsorbed effectively onto organoclay in laboratory isotherm experiments and were able to model transport of the solute through an organoclay column using the convection–dispersion equation. A similar organic sorbing phase can be formed by treating zeolites with surfactants, but to-date this approach has not been used for contaminated sediments.

12.2.4 Activated Carbon

Activated carbon is a strong sorbent of the hydrophobic organic compounds that are commonly associated with sediments. Activated carbon as an *in-situ* sediment treatment is discussed in Chapter 11 and in Rakowska et al. (2012). Placement of activated carbon for sediment capping or as an *in-situ* treatment is difficult due to the near neutral buoyancy of the material. Various approaches for placement are summarized in Rakowska et al. (2012). McDonough et al. (2007) describe a procedure for placing a thin layer of near neutral buoyancy material using a reactive core mat. Using the mat, a thin layer of coke (an inexpensive, moderately sorbing material) was placed in a capping demonstration in the Anacostia River (Reible et al., 2006).

Murphy et al. (2006) modeled the transport of organic contaminants through thin-layer activated carbon caps and found that activated carbon could isolate PCB-contaminated sediment for >60 yrs even with high groundwater upwelling rates (1 centimeter per day [cm/d]). McDonough et al. (2008) assessed the potential of activated carbon for sediment capping through batch adsorption experiments in the presence of natural organic matter, which is to be expected in sediment environments. The natural organic matter significantly lowered adsorption capacity of the carbon, although the sorption of PCBs onto the carbon was still sufficient to warrant further study as a capping material.

12.2.5 Clay Materials

As an alternative to a sorptive capping amendment, low-permeability cap amendments have been proposed to enhance cap design life by decreasing porewater advection. Low permeability clays are an effective means to divert upwelling groundwater away from a contaminated sediment area but are difficult to place in the aqueous environment. Bentonite clays can be placed in mats similar to what is done to provide a low permeability liner in landfills. There are also commercial products that can place clays directly. AquaBlok^{TM} is a bentonite clay and polymer-based mineral around an aggregate core, as a sediment capping material. AquaBlok^{TM} is capable of settling to the bottom of the water column and forming a cohesive boundary with minimal intermixing with the underlying contaminated sediment with permeabilities of the order of 10^{-9} centimeters per second (cm/s). Reible et al. (2006) discuss the successful implementation of an AquaBlok^{TM} cap for permeability control in the Anacostia River in Washington, D.C. The AquaBlok^{TM} cap effectively reduced the porewater advection rates to zero versus a control area and a sand cap, at least initially after placement. As will be discussed later, gas accumulation and ultimate release led to substantial movement of the low permeability layer and potentially a reduction in long-term containment (Reible et al., 2006).

12.2.6 Nutrients

Sediment caps become colonized by microorganisms from the sediments and surface water and potentially become a zone of pollutant biotransformation over time (Himmelheber et al., 2009). This was demonstrated in laboratory column tests in which the polycyclic aromatic hydrocarbons (PAHs) naphthalene and phenanthrene were biotransformed in a sand cap under aerobic conditions (Hyun et al., 2006). However, such aerobic degradation occurs only near the solids-water interface in which benthic organisms are active and thus there might still be significant benthic organism exposure to contaminants. Biotransformation in the anaerobic zone of a cap, which typically extends well beyond the zone of benthic activity, could significantly reduce the risk of pollutant exposure. Smith et al. (2012) has investigated that potential at a particular site. Sun et al. (2010) showed that it may be possible to modify the typical anaerobic conditions through application of an electric potential. This approach has not been demonstrated beyond the laboratory.

The addition of materials for enhancing the attenuation of HOCs through biodegradation has also been assessed. Murphy et al. (1995) reported significant reduction in PAH concentrations following addition of calcium nitrate within a year. Xu and Obbard (2004) found the addition of slow-release fertilizers to contaminated beach sands enhanced degradation rates of two- to six-ring PAHs significantly. Jackson and Pardue (1999) and Shin et al. (2000) showed that nutrient addition can aid in the degradation of petroleum hydrocarbons (PHCs) in marsh sediments. These studies are not intended to be comprehensive but illustrate that short-term improvements in biodegradation rates can be achieved through tailoring of conditions or addition of nutrients. There have been few applications of nutrient amendments for biodegradation enhancement in the field to date, however, primarily due to the difficulty of introducing amendments and the need, in principle, to replenish the nutrients after some time.

12.2.7 Zero-Valent Iron

Zero-valent iron (ZVI) nanoparticles are effective amendment for soil remediation for specific applications (Li et al., 2006). ZVI particles possess a reactive surface that can reduce and subsequently immobilize a variety of compounds. Complete degradation of mixtures of

PCBs and other chlorinated solvents have been reported through reactions with ZVI (Wang and Zhang, 1997). Other laboratory-scale feasibility assessments have shown potential for ZVI for treating nitroaromatic compounds (Agrawal and Tratnyek, 1996), arsenic (Kanel et al., 2005), chromium (VI) and lead (II) in aqueous solutions (Ponder et al., 2000) and dichlorodiphenyltrichloroethane (DDT) and related compounds (Sayles et al., 1997). More pilot and field-scale demonstrations are likely necessary to assess the long-term feasibility of ZVI as a sediment capping amendment. Preliminary laboratory studies suggest that the passivation of the iron in the aqueous environment may preclude its use as a sediment cap. In principle, however, burial of the iron in the reducing zone before significant oxidation has occurred could lead to an effective application.

12.3 SORPTION OF CONTAMINANTS TO SEDIMENTS AND CAP MATERIALS

Sorption phenomena largely control the performance of cap materials. Sorption of contaminants to the underlying sediments defines the mobile interstitial or porewater concentration of contaminants that might migrate through a cap. Sorption onto cap materials largely defines the rate of contaminant migration through a cap. Sediments are formed as a result of the natural processes of weathering and erosion, precipitation and deposition of organic detritus and are constantly transported. As a result of these processes, the chemical composition of sediments and some cap materials varies greatly from location to location and the partitioning relationships between sediment and contaminants are complex and variable. Contaminants become associated with sediments through a variety of mechanisms. The ratio of the mass of a contaminant between particulate matter and the neighboring water is often expressed as using a distribution coefficient K_d:

$$q = K_d C \qquad \text{(Eq. 12.1)}$$

where C and q are the concentrations in the porewater and particle, respectively. The value of K_d is a function of the site, the compound and sometimes the concentration. The nature of the interaction between the particle and water phases depends on a great many factors. Organic and inorganic contaminants behave very differently as discussed below.

The effect of sorption is primarily to slow porewater processes such as diffusion and advection. If we consider a strongly sorbing contaminant whose mass is primarily sorbed to the solid with a dry bulk density, ρ_b, then a retardation factor can be defined as:

$$R = \rho_b K_d \qquad \text{(Eq. 12.2)}$$

which is effectively the ratio of the contaminant mass in the porewater (or mobile phase) to the total mass in the system (essentially all sorbed to the solid). The effective advection velocity and diffusivity of the contaminant through the sediment or cap is:

$$U_{eff} = \frac{U}{R} \qquad D_{eff} = \frac{D_s}{R} \qquad \text{(Eq. 12.3)}$$

where U and Ds are the velocity and diffusivity in the absence of sorption. Since R for common strongly sorbing compounds can be of the order of 10^3–10^6, this can dramatically slow the migration of contaminants through the sediment and cap layer.

12.3.1 Organic Compounds Sorption to Sediments and Capping Materials

Early studies of sorption of organic compounds in sediments revealed that the organic matter in the sediments was primarily responsible for the accumulation onto soils and sediments (Goring, 1962). The organic carbon fraction of sediment (f_{OC}) is responsible for most of the organic compounds, particularly those of a hydrophobic nature. Organic matter in sediments is composed of a complex mixture of different biochemical compounds including proteins, nucleic acids, lipids, cellulose and lignin. The processes of degradation, rearrangement and recombination of the original compounds (diagenesis) create new compounds in sediment environments. As a result, natural organic matter in sediment contains many different domains with varying degrees of hydrophobicity and sorption characteristics. In addition to the natural organic matter present in sediments, other organic sorbents that are derived from anthropogenic sources can also be present. An increasing body of evidence suggests the so-called “black” or “hard” carbon fraction, which is derived from incomplete combustion processes, significantly affects sorption processes in sediments.

A widely accepted model for sorption of HOCs onto sediments is the linear sorption model onto the f_{oc} (Karickhoff et al., 1979). In this case, K_d is constant and is related to the organic carbon normalized partition coefficient K_{oc}:

$$K_d = K_{oc} f_{oc} \qquad \text{(Eq. 12.4)}$$

The values for K_{oc} have been found to correlate with octanol-water partition coefficients, K_{ow} (Seth et al., 1999). Schwarzenbach et al. (2003) present a summary of empirical correlations for estimating the value of K_{oc} for various classes of compounds.

Desorption of organic contaminants from sediments has been observed to be very different from sorption. Observed porewater concentrations are often much less than those predicted using measured values of q and values for K_d predicted using Equation 12.4. Several hypotheses exist to explain this phenomenon, including interaction with black carbon, hole filling and physical entrapment within the organic matter (Accardi-Dey and Gschwend, 2002; Lohmann et al., 2005). The release of organic contaminants from sediments remains an important research topic. Many capping materials also have the potential to sorb organic contaminants. Schwarzenbach et al. (2003) reported that even in sands with low organic carbon content that some sorption onto minerals surfaces can occur, with an effective lower-bound equivalent to an organic carbon content of 0.01–0.1%. Organoclays strongly absorb organic compounds into the aliphatic hydrocarbons on their surfaces. Sorption onto long-chain organoclays generally increases with K_{ow} and remains linear over a wide range of concentrations consistent with sorption onto sediments (Groisman et al., 2004; Lee et al., 2004). The value of K_d for a given compound can be determined using batch adsorption experiments and can often be estimated using analytical tools.

The value of K_{oc} can be estimated through correlations with K_{ow} as described by Schwarzenbach et al. (2003). A broadly applicable correlation is (Baker et al., 1997):

$$\log K_{oc} = 0.903 \ \log \ K_{ow} + 0.09 \qquad \text{(Eq. 12.5)}$$

K_{ow} is a well characterized parameter that is readily available for most COCs including PCBs (Hawker and Connell, 1988) and PAHs (Mackay, 2006). In the absence of an experimentally-measured value, literature methods are available for estimating K_{ow} (Lyman et al., 1990).

Dissolved natural organic matter in the interstitial porewater in sediments and sediment caps can interact with organic compounds and should be considered when assessing caps. The following relationship has been used to describe the partitioning between the freely dissolved concentration of a contaminant C, the dissolved organic matter concentration ρ_{DOC}, the concentration of the contaminant on the dissolved matter C_{DOC} and the dissolved organic carbon (DOC) partition coefficient K_{DOC} (Burkhard, 2000):

$$C_{DOC} = \rho_{DOC} K_{DOC} C \qquad \text{(Eq. 12.6)}$$

The value of ρ_{DOC} can be determined by standard methods, and the partition coefficient can be estimated using the correlation provided by Burkhard (2000):

$$\log K_{DOC} = \log K_{ow} - 0.48 \qquad \text{(Eq. 12.7)}$$

Sorption to activated carbon is very strong for HOCs and is often quite nonlinear and as a result the value of K_d is a function of concentration. The Freundlich model is frequently used to predict q from C for activated carbon:

$$q = K_F C^{1/n} \qquad \text{(Eq. 12.8)}$$

where K_F is the adsorption capacity at unit concentration and 1/n is the adsorption intensity. For a given carbon, it is possible to estimate the Freundlich parameters using Polanyi adsorption theory (Manes and Hofer, 1969). However, in most cases it is necessary to use series of batch adsorption experiments over the desired range of equilibrium concentrations to determine the Freundlich (or other model) parameters. These experiments have illustrated the effects of competition with other contaminants and the potential for fouling with natural organic matter or with biofilms (McDonough et al., 2008; Sharma et al., 2009). In general, it appears that the effect of such competition may be to reduce the sorption capacity of activated carbon approximately an order of magnitude. This is in contrast to natural organic matter and organophilic clays, which exhibit absorption-like phenomena, linear sorption and minimal competition effects.

12.3.2 Metals Sorption to Sediments and Capping Materials

Metals and other toxic inorganic pollutants are often associated with contaminated sediments. The distribution of mass between inorganic compounds and the neighboring water depends on the pH and salinity of the water and the number and type of available sites for binding onto the sediment particle surface. Because of the high degree of variability in the observed distribution coefficients, it is often necessary to make site-specific measurements for the purposes of assessment and remediation. Sorption of cationic metals may be a strong function of the CEC. For sorption onto a limited number of specific sites, the Langmuir model is often used to predict sorption of contaminants:

$$q = \frac{q_{max} b C}{1 + bC} \qquad \text{(Eq. 12.9)}$$

where q_{max} is the maximum sorption capacity and b is the relative intensity of sorption. Xu et al. (1994) found that Langmuir model fit sorption of Zn and Cd onto apatite surfaces. However, adsorption of the compounds onto apatite varied with pH as is typically true of metal sorption on most cap materials. As a result, the parameters are a function of the aqueous solution and not only the apatite itself, which is in contrast to sorption of hydrophobic compounds. As a result, it is often necessary to experimentally determine sorption of pollutants onto solid surfaces. Bentonite clays possess relatively high CEC and thus may adsorb metals such as Pb, Cd, copper (Cu) and Zn to their surfaces (Bereket et al., 1997; Mellah and Chegrouche, 1997; Donat et al., 2005).

Chemical speciation of the metals may also render them immobile or biologically unavailable. Most commonly, the presence of excess sulfides in a reducing environment will lead to the formation of metal sulfides that exhibit low solubility, mobility and availability (e.g., DiToro et al., 1992; Hong et al., 2011). The presence of sulfides can also modify mercury behavior in that the presence of high sulfide concentrations may inhibit mercury methylation while low sulfide levels may enhance methylation behavior (Johnson et al., 2010).

12.4 SITE CONDITIONS AND CHARACTERIZATION

The design of a cap for contaminated sediment management is a complex process due to natural heterogeneity, the inherently transient nature of sediments and the rich diversity of biological life in benthic environments. Each site presents unique challenges that must be overcome if a cap design is to be successful. A crucial component in the design process is the site characterization. Appropriate site characterization requires identifying remedial objectives, characterizing site hydrodynamics, assessing biological effects, characterizing geotechnical properties of the sediment and cap materials and estimating relevant chemical properties for the contaminants. This section briefly introduces the relevant concepts and parameters needed to perform screening level assessments of sediment caps.

12.4.1 Remedial Objective Identification

The first step in the design of a cap for contaminated sediment management is to identify the appropriate contaminants of concern (COCs) and the remedial objectives for the site. The remedial objectives should in the first instance identify the desired outcome of any remedial efforts including potential uses for the water body and the desired qualities, characteristics and future uses. Capping may be preferred for some end states, such as improved habitat qualities, or discouraged by specific water depth requirements. In addition, quantitative goals could be set for specific COCs but a specification of such cleanup goals should not be in lieu of the desired qualitative characteristics of a water body. Quantitative goals that might be used to design a cap might include not-to-exceed concentration levels or maximum contaminant fluxes in the surficial sediment layers at a specified time (e.g., for a 100-yr design life). Typically, it is expected that natural attenuation processes, such as sediment deposition or natural degradation, will eventually detoxify contaminants and a finite but long design half-life will allow time for these processes to occur and ensure that the cap is protective indefinitely. Alternatively, in some cases, it is possible to design a cap that is protective under steady conditions (i.e., over a long period of time) even without additional natural attenuation processes. A design under steady conditions, however, is conservative and not always possible.

Quantitative design performance criteria might be set on the basis of a bulk solids concentration or an interstitial water concentration. Bulk solids criteria may be easily met with capping but may be misleading since the cap material may not sorb contaminants to a significant extent. In such a situation, the cap material may never exhibit a significant contamination concentration even with substantial contaminant migration through the cap. A major difficulty with setting interstitial water concentrations, however, is lack of directly applicable regulatory framework. In lieu of such a framework, interstitial water concentrations are sometimes compared to surface water quality standards, although the application of surface water concentration criteria to interstitial water is very conservative in that it does not consider the dilution and mixing in the overlying water.

12.4.2 Hydrodynamic Characterization

Characterizing a site's hydrodynamic conditions is an important component in a remedial assessment of capping. Benthic environments lie at the interface of groundwater and surface water, and it is necessary to assess the flow of both when evaluating capping. To estimate the potential effects of erosion and deposition of sediments and capping materials, it is necessary to determine expected surface water flows and velocities. For modeling fate and transport of contaminants in a cap, it is necessary to characterize the flow of groundwater through a cap.

12.4.2.1 Surface Water Hydrodynamics

Sediments are continually transported through aquatic systems, and at a given time a site may be net deposition or erosional. It is crucial that the integrity of a cap is maintained during high flow erosional events. To successfully design an erosion-prevention layer requires estimates of flows and velocity for various flood events for the site. Episodic storm events, tidal fluctuations and bottom currents can all potentially cause re-suspension and erosion of a cap and must be carefully evaluated. The application of a cap can alter existing hydrodynamic conditions in some cases. For example, in harbors the changes in depth or bottom geometry can affect current patterns and in riverine environments reductions in depth may significantly alter the flow in the channel. Changes in channel geometry may affect flow velocities and shear stresses on a cap. As a result, historic flow data may not be sufficient to characterize velocities post-cap application. In such cases, modeling studies may be utilized to assess the potential hydrodynamic impacts of a cap. The information needed to evaluate surface water hydrodynamic conditions includes currents, waves, flood flows and flood depth. Predictive methods and models may be used, and may be the only way to predict the effects of a potential future storm if a sufficient historical record is unavailable.

12.4.2.2 Groundwater Upwelling

Because sediment caps are designed to contain pollution from benthic receptors and the overlying water bodies, it is critical that accurate predictions of contaminant migration in caps can be made. Groundwater upwelling at a site is potentially one of the most important processes of contaminant migration through a cap. The application of a sediment cap rarely has a significant impact on groundwater flow as most capping materials are course-grained and highly permeable. Some materials, such as AquaBlok^{TM} are designed to divert groundwater flow away from contaminated areas.

The flow of water in a cap may be upward or downward, or both in the case of tidal systems. The nearshore portions of lakes and rivers are common groundwater discharge areas. For direct measurement of groundwater flux, seepage meters such as the one described by Lee (1977) may be used to measure the groundwater seepage rate. Alternatively, Cook et al. (2003) describe methods for estimating flux using different kinds of tracers. In the absence of direct measurements, the flow may be modeled using Darcy's Law, which relates the flow per unit area (Darcy velocity) V through a porous medium subject to a hydraulic gradient i though the empirical parameter k_h, the hydraulic conductivity of the medium. For one-dimensional flow (normally applicable to sediment caps), Darcy's Law can be expressed as:

$$V = k_h i \tag{Eq. 12.10}$$

At sites where flow is to be modeled, an assessment of the hydrogeology of the area including the hydraulic conductivity of the sediment/groundwater system and the local groundwater levels driving the flow rate is required. In some cases, it may be necessary to extend the flow modeling into multiple dimensions (e.g., the placement of a flow control cap such as AquaBlok$^{\mathrm{TM}}$). Many excellent texts have been written on the subject of groundwater flow and transport (Freeze and Cherry, 1979; Charbeneau, 2000).

Because of natural heterogeneity, the flow of porewater through sediments is non-uniform. Thus, the microscopic flow paths that water follows through sediments and caps have different lengths. On a macroscopic scale, the contaminants that move with the water are scattered. This phenomenon, hydrodynamic dispersion, is often modeled as a Fickian diffusion process where the flux of compound F_{disp} with concentration C associated with dispersion coefficient D_{disp} in the x-direction is:

$$F_{disp} = -D_{disp}\frac{\partial C}{\partial x} \qquad \text{(Eq. 12.11)}$$

The dispersion coefficient is often expressed as the product of the Darcy velocity V and a dispersivity α that is indicative of the heterogeneity of the medium:

$$D_{disp} = \alpha V \qquad \text{(Eq. 12.12)}$$

Because dispersion is the result of the averaging on a macroscopic scale of the microscopic differences in the media, α is often claimed to be dependent on the length scale of the problem. As a result, the dispersivity for transport through 1 foot (ft) of sediment is different than that for transport through 10 ft of the same material. In general, the value of α must be determined empirically through a tracer study. For a uniform material such as sand, the flow may be closer to ideal and dispersivity may be similar in magnitude to the particle diameter. In the absence of site specific information, generally conservative estimate would be to scale the dispersivity with the cap thickness, e.g. 10% of the cap thickness (Clarke et al., 1993).

12.4.3 Biological Characterization

Benthic ecosystems possess rich levels of degradable organic matter and organisms. Because the biological active zone is limited to the near surface (5–15 cm), surficial sediments typically exhibit sharp gradients in nutrients and dominant electron acceptors and redox zonation. The upper few millimeters or centimeters of the benthic zone are characterized by the presence of oxygen (the most energetically favorable electron acceptor) and other nutrients from the overlying water. Oxygen from the overlying water is consumed near the surface; beneath the aerobic zone other zones develop that are characterized by the reduction of nitrate, iron, sulfate and other electron acceptors consistent with redox energetics. The presence of these zones can be measured through the use of voltammetry (Brendel and Luther, 1995) and can have important effects on the fate and transport of many pollutants.

The activity of microorganisms in fully anaerobic sediments often produces gases including methane. Gases produced beneath the sediment surface migrate upwards through a process known as gas ebullition. Gas ebullition is often driven by degradation of newly deposited organic matter and a cap can effectively eliminate this deposition into contaminated sediment layers. Without new labile organic matter, the rate of degradation and the rate of gas ebullition will slow rapidly over a period of months to years. Shortly after placement, however, a cap can enhance gas ebullition as a result of consolidation after placement and due to the development of anaerobic sediments in what had previously been surficial aerobic sediments.

Organisms present in sediments mix particles through activities such as burrowing and sediment ingestion. Some filter feeding organisms also build burrows and pump the overlying waters through the burrows. The mixing processes by benthic organisms are collectively termed bioturbation. Bioturbation processes affect the fate and transport of nutrients, electron acceptors and contaminants in benthic environments. The mediators of bioturbation are typically annelid worms, mussels, clams and other infaunal or epifaunal organisms.

The application of a cap alters the depths at which bioturbation and the various redox zones take place. The resulting changes have important effects on the fate and transport of various species within a sediment/cap system. For example, mercury methylation has been linked to sulfate reduction, and the application of a cap has the potential to encourage methylation (Himmelheber et al., 2008; Johnson et al., 2010). Degradation of many compounds occurs only under aerobic conditions; some examples include PAHs (Johnsen et al., 2005) and chloroaromatics (Olaniran and Igbinosa, 2011). Over time, as new sediments are deposited on the surface of a cap, the depths previously associated with various redox states re-develop and the benthic ecosystem is restored at the surface of the cap. The re-colonization of the cap surface must be considered in the design of a cap since bioturbation can compromise the cap surface (Lampert et al., 2011).

One of the primary purposes of a cap is to physically isolate benthic organisms from the contaminated sediments. It is also important to understand the role of bioturbation processes in the fate and transport of contaminants through a cap layer. To appropriately address these issues, it is necessary to characterize the expected depth and mixing intensity of bioturbation. Various approaches are available for modeling solute fate and transport due to bioturbation in sediments (Lampert et al., 2011). A common approach is to assume the mixing is random and that it can be modeled as a Fickian diffusion process with a compound- independent biodiffusion coefficient. The flux F_{bio} of a solute with a total (solid + porewater) concentration W in the x direction due to bioturbation with a coefficient D_{bio} is:

$$F_{bio} = -D_{bio}\frac{\partial W}{\partial x} \qquad \text{(Eq. 12.13)}$$

The total concentration for sediment with a bulk density ρ_b and porosity ε can be related to the porewater concentration through a retardation factor R:

$$R = \varepsilon + \rho_b K_d \qquad \text{(Eq. 12.14)}$$

Thus, Equation 12.13 can be re-written in terms of the porewater concentration C:

$$F_{bio} = -D_{bio} R\frac{\partial C}{\partial x} \qquad \text{(Eq. 12.15)}$$

It is possible to measure the flux of radioactive tracers in sediment cores and estimate D_{bio} (Gerino et al., 1998; Kershaw, 1985). The flux from bioturbation often dominates the overall solute transport in the biologically-active layer (Goldhaber et al., 1977) and thus it is important to make appropriate characterizations of the role of bioturbation in the design of sediment caps. Thoms et al. (1995) present a summary of various measurements of the biodiffusion coefficient and the depth of bioturbation at a number of sites throughout the United States. For freshwater systems, the mean value of D_{bio} was 3.3×10^{-8} cm^2/s and the mean depth of bioturbation was 4.8 cm. For estuarine systems, the mean value of D_{bio} was 3×10^{-7} cm/s^1 and the mean depth of bioturbation was 7.90 cm. Values from these literature surveys may be the best estimates in the absence of direct measurements.

12.4.4 Geotechnical Characterization

The geotechnical conditions of a site are an additional component in the analysis of sediment capping. Some considerations include stratification and stability of underlying sediment layers, the depth to bedrock, the potential for consolidation of the underlying sediment layers after cap placement and the hydrogeological parameters of the site such as the hydraulic conductivity. The thickness of the contaminated sediment layer and the physical properties of the soil underlying this layer need to be determined in order to evaluate potential consolidation of the sediment due to the cap loading. The degree of potential consolidation should be evaluated based on consolidation testing procedures The porewater expressed by sediment consolidation can lead to enhanced contaminant migration into a cap although any sorption in the cap may render this effect negligible. In addition, this enhanced migration is only transient and only speeds the achievement of steady conditions in a cap. Melton and Prieto (2008) and Prieto et al. (2009) evaluated the effect of consolidation on capped sediments.

Consolidation of a sediment containing NAPL may pose special problems due to the expression of NAPL. Erten et al. (2011) provide a consolidation testing method to evaluate NAPL expression as a result of cap loading. Shear strength of the contaminated sediment layer should be considered for evaluation of the stability of the cap during placement.

12.4.5 Gas Ebullition

Gas ebullition can be an important component of fate and transport of contaminants in sediments and sediment caps in some cases. The contaminant migration associated with gas ebullition may be the result of sorption of contaminants to the surface of a migrating gas bubble (especially important for strongly hydrophobic contaminants and migration through NAPL layers), partitioning into the vapor phase of the bubble (especially important for volatile organic compounds) or loss of integrity of the cap layer due to mechanical disruption by bubble passage.

Yuan et al. (2007) observed that a sand cap can significantly reduce the contaminant migration from exposed sediment due to gas ebullition. In addition, since gas ebullition is often driven by degradation of newly deposited organic matter and a cap effectively eliminates deposition into contaminated sediment layers, the rate of degradation and the rate of gas ebullition slow after a period of months to years. Gas ebullition can still be important in the short term if gas migrates through a NAPL layer or if a low permeability cap is used to control groundwater upwelling. Reible et al. (2006) report an accumulation of gas underneath an impermeable capping layer, which led to cap uplift and a rapid gas release on regular intervals from a portion of the cap in the first season after cap placement. This likely led to decreased permeability control in that portion of the cap even though the gas release apparently stopped within 1 yr after cap placement.

The long-term importance of gas ebullition is likely to be significant only when the source of the gas is degradation of the contaminants or contaminant-bearing phases (e.g., NAPL). The lifetime of gas generation, then, is of the order of the lifetime of the contaminant (and therefore the design lifetime of the capping layer). In such a case, an estimate of the flux F_{gas} that must be contained by a cap is given by:

$$F_{gas} = V_{gas}HC \tag{Eq. 12.16}$$

where V_{gas} is the volumetric flux of gas, H is the Henry's Law constant of the compound of concern (the equilibrium partition coefficient between gas and water) and C is the porewater concentration. This approach assumes that the primary mechanism of contaminant migration by gas ebullition is due to partitioning into the gas bubble from the surrounding porewater in the contaminated sediment. If the gas were migrating through a layer of NAPL (assumed an ideally mixed phase), this equation should be modified to:

$$F_{gas} = V_{gas}xP_vM_w/RT \tag{Eq. 12.17}$$

where x is the mole fraction of the COC in the NAPL (assumed to be an ideal mixture of contaminants) and P_v is the pure component vapor pressure of that contaminant. M_w is the molecular weight of the COC and RT represents the product of the ideal gas constant and absolute temperature. Note that this represents the flux into the cap layer and therefore represents the flux that must be managed by the cap.

If the estimated flux leads to unacceptable migration through the cap or if the long-term gas ebullition may lead to compromising the physical integrity of the cap (as in the case of the ebullition into the low permeability cap described by Reible et al., 2006), then the cap must be designed to collect and divert the generated gas. A coarse layer or even a piping system oriented in a manner to divert gas to a collection or treatment process may be desirable.

12.5 DESIGN OF CAPS FOR SEDIMENT REMEDIATION

The primary consideration in the assessment and design of sediment caps is to reduce contaminant concentrations and fluxes to minimize bioaccumulation. Other important considerations are minimizing erosion and providing appropriate thickness to account for consolidation of the surficial sediments. To determine the most appropriate cap for a given site, each of these components should be considered. In many cases, a simple sand cap can be used to meet all the design criteria. Under certain conditions it may be necessary to consider other approaches. The following sections outline approaches that can be used to determine the most appropriate cap for a site.

12.5.1 Contaminant Transport Modeling Concepts

To appropriately assess and design caps, models are needed that predict the relationship of design parameters and remedial objectives (i.e., reduced contaminant fluxes and concentrations). Predicting chemical migration in porous containment layers is normally accomplished using transient advection–diffusion models. There are many well-established models (e.g., MODFLOW) for predicting fate and transport in groundwater. However, such models are not typically applied to sediment caps for several reasons. The benthic layer that develops at the cap surface is subject to significantly different transport processes and rates than those seen in groundwater or in the underlying cap and sediment layers. Among the applicable conditions and transport processes are sharp gradients in redox conditions, sharply defined sediment and cap layering, the presence of bioturbation processes, the effects of erosion, deposition and consolidation, and interactions with the overlying benthic boundary layer and water.

The small vertical scale of interest suggests that the fate and transport of contaminants in sediment caps can generally be modeled using the locally one-dimensional advection diffusion reaction equation with sorption. Variations across a site are often simulated by considering multiple one-dimensional realizations of the model. Two-dimensional models have primarily been used to evaluate the significance of not achieving lateral homogeneity in groundwater flow. Local sorption processes are often assumed to occur instantaneously since transport through sediment caps is typically slow (on the order of years).

12.5.1.1 Governing Equations

It is generally appropriate to assume a cap is composed of multiple homogeneous layers that can be modeled with a series of equations of the form:

$$R_i \frac{\partial C_i}{\partial t} - U \frac{\partial C_i}{\partial z} = D_i \frac{\partial^2 C_i}{\partial z^2} - \varepsilon_i \lambda_i C_i \qquad \text{(Eq. 12.18)}$$

The subscript refers to the layer number and the variables are:

C_i = porewater concentration in Layer i
z = depth downward from the cap-water interface
t = time
R_i = retardation factor in Layer i (ratio of total concentration to mobile phase concentration as defined previously)
U = effective advective velocity (assumed upward, though can be negative)
D_i = effective diffusion coefficient in Layer i
ε_i = porosity in Layer i
λ_i = decay rate constant in Layer i (assumed only in the porewater)

The importance of the various terms in Equation 12.18 and their relationships to site and chemical parameters are discussed below.

12.5.1.2 Sorption Processes

The first term in Equation 12.18 represents accumulation in a control volume and incorporates sorption of the contaminant onto the media. Due to the hydrophobic nature of sediment contaminants, the majority of the mass resides on the solid phase. It is necessary to utilize the appropriate sorption relationship in this term and to make appropriate estimates of the sorption model parameters. When partitioning is nonlinear, such as a Langmuir or Freundlich isotherm, the parameter R_i varies with concentration (and also in time and space) and must be handled appropriately. In the most general case of nonlinear sorption and partitioning to colloidal organic matter, the following equation can be used:

$$R_i(z,t) = \frac{\varepsilon_i + \varepsilon_i \rho_{DOC} K_{DOC} + \rho_i \frac{\partial q(z,t)}{\partial C}}{1 + \rho_{DOC} K_{DOC}} \qquad \text{(Eq. 12.19)}$$

When partitioning is linear, the derivative term in Equation 12.18 has a constant value of K_d. This approach assumes that ρ_{DOC} is constant throughout and that the colloidal matter is advected along with the porewater.

12.5.1.3 Advective Processes

The second term in Equation 12.18 represents the fluxes associated with advective processes. The primary advective process is porewater flow (V), although additional processes that are sometimes modeled as advective include erosion and deposition. The porewater upwelling rate should be conservatively estimated since upwelling can rapidly compromise cap performance. Erosion is a positive flux (increases transport) while deposition is negative since it buries contamination. A simplistic approach to incorporate erosion/deposition into a model is to take a coordinate system fixed to the sediment-water interface. In the case of deposition with a velocity V_{dep}, the net advective velocity is:

$$U = V - RV_{dep} \qquad \text{(Eq. 12.20)}$$

This approach is accurate if R is a constant throughout the cap. If variable, the value of R in should be selected conservatively since deposition increases predicted cap design life. Typically the value from the layer in a cap with the lowest sorption capacity (e.g., sand) is recommended. In numerical models, it is possible to directly simulate the effect of sediment deposition by considering the growth of the surface layer.

12.5.1.4 Diffusive Processes

The third term in Equation 12.18 represents the fluxes associated with diffusive processes. The relevant processes vary from site to site and with the layer but potentially important processes include molecular diffusion, hydrodynamic dispersion and bioturbation. In the most general case where all the processes are important, the effective diffusion coefficient for a layer is:

$$D_i = \varepsilon_i D_w / \tau_i + \alpha_i V + D_{bio} R_i \quad \text{(Eq. 12.21)}$$

Here ε_i is the porosity and τ_i is the tortuosity of layer i. The tortuosity is the length of the average diffusion path in the layer divided by the vertical coordinate distance. The final term in this equation is associated with bioturbation, which typically involves particle reworking rather than just porewater movement and thus is multiplied by R_i, the retardation factor. The typical range of values of the bioturbation diffusion coefficient is discussed in Chapter 2.

12.5.1.5 Decay Processes

The final term in Equation 12.18 represents the decay of contaminants. The decay is assumed to occur in the porewater only, and seemingly large decay rate constants may have only a minimal impact on mass degradation rate since only a small fraction of the contaminants resides in the porewater. The strong sorptive nature of most sediment contaminants limits the rate of degradation due to limited bioavailability. In cases where degradation can occur directly on the solid or the rate constant is an effective constant based upon the measured disappearance of solid phase concentration, the term can be multiplied by R_i. The approach in Equation 12.18 assumes first-order decay, which is the most commonly employed methodology. In a system where decay is of substantial significance, it may be necessary to utilize a more complicated model to predict transformation rates.

12.5.1.6 Auxiliary Conditions

To solve the governing equations, it is necessary to impose boundary and initial conditions for each layer. For continuity of mass, the porewater concentration and flux at the interface of any two layers must be the same. Note that while porewater concentration is continuous across a boundary, the associated solid phase concentration is typically not continuous due to the different sorption characteristics of the different layers. The advective fluxes are equal if the concentrations are equal. However, the diffusive fluxes are a function of D_i in each layer. The following boundary conditions apply at the interface of the i th and i + 1th layers at depth $h_{interface}$:

$$C_i(z = h_{interface}) = C_{i+1}(z = h_{interface}) \quad \text{(Eq. 12.22)}$$

$$D_i \frac{\partial C_i(z = h_{interface})}{\partial z} = D_{i+1} \frac{\partial C_{i+1}(z = h_{interface})}{\partial z} \quad \text{(Eq. 12.23)}$$

The bottom boundary at depth h_{tot} of the bottommost layer is often assumed to maintain a constant concentration of C_b:

$$C_i(z = h_{tot}) = C_b \quad \text{(Eq. 12.24)}$$

It is also possible to use a flux-matching boundary condition such as commonly employed for modeling columns (Danckwerts, 1953):

$$UC_i(z = h_{tot}) + D_i \frac{\partial C_i(z = h_{tot})}{\partial z} = UC_b \qquad \text{(Eq. 12.25)}$$

The top boundary condition is often taken as a flux-matching relationship between the top of the sediment cap and the benthic boundary layer. The flux through the benthic boundary layer is the product of the concentration difference between the top of the sediment column and the concentration in the overlying water C_w times the benthic boundary layer mass transfer coefficient k_{bl} (Boudreau and Jørgensen, 2001). The matching flux from the sediment column is from diffusive processes characterized by Fick's first law. The top boundary condition of the topmost layer i at $z = 0$ is:

$$D_i \frac{\partial C_i(z = 0)}{\partial z} = k_{bl}(C_i(z = 0) - C_w) \qquad \text{(Eq. 12.26)}$$

The initial condition in a layer must also be specified. Most often it is uniform value of C_0:

$$C_i(t = 0) = C_0 \qquad \text{(Eq. 12.27)}$$

12.5.2 Parameter Estimation

12.5.2.1 Molecular Diffusion

Molecular diffusion (migration due to random molecular motion) may be an important component in the transport of a contaminant through a cap. The migration rate from molecular diffusion is a function of temperature, viscosity of the fluid and the size of the molecule. Molecular diffusion produces a net flux F_{diff} in the x-direction from a region of higher concentration to one of lower concentration that is often described by Fick's first law:

$$F_{diff} = -D_w \frac{\partial C}{\partial x} \qquad \text{(Eq. 12.28)}$$

where D_w is the molecular diffusion coefficient of the compound in water. Equation 12.28 is only applicable for transport in a continuum (i.e., aqueous solutions). Molecular diffusion in a porous medium such as a sediment cap must be corrected for tortuosity and porosity of the diffusion pathways. Millington and Quirk (1961) suggest a combined correction factor of the porosity to the four-thirds power to account for these effects:

$$F_{diff} = -\varepsilon^{\frac{4}{3}} D_w \frac{\partial C}{\partial x} \qquad \text{(Eq. 12.29)}$$

Boudreau (1997) suggests an alternative correction that may be more applicable to fine-grained sediments:

$$F_{diff} = -\frac{\varepsilon D_w}{1 - ln\varepsilon^2} \frac{\partial C}{\partial x} \qquad \text{(Eq. 12.30)}$$

Values of D_w are typically 10^{-5}–10^{-6} cm^2/s for sediment contaminants. The following relationship can be used to estimate the molecular diffusion coefficient in water (adapted from Hayduk and Laudie, 1974):

$$D_w = \frac{1.326(10)^{-5}}{\mu_w^{1.14} V_m^{0.589}} \qquad \text{(Eq. 12.31)}$$

Where:

D_w = molecular diffusion coefficient in water (cm^2/s)
μ_w = viscosity of the water (centipoise)
V_m = molar volume of the compound (cm^3/mol)

12.5.2.2 Benthic Boundary Layer Mass Transfer Coefficient

Transport of mass through the sediment-water interface or benthic boundary layer is commonly modeled with a mass transfer coefficient (Boudreau and Jørgensen, 2001). It is often necessary to characterize this compound and site-specific parameter in the assessment and design of sediment caps. The mass transfer coefficient is a function of the turbulence and velocity in the overlying water and has typical values on the order of 1 centimeter per hour (cm/hr). Correlations have been developed based on the mixing intensity in rivers (adapted from Thibodeaux, 1996):

$$k_{bl} = 88.4 v_x n \sqrt{gd} \left(\frac{D_w}{r_H v_w} \right)^{\frac{2}{3}} \qquad \text{(Eq. 12.32)}$$

Where:

k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
v_x = river velocity (m/s)
n = Manning's n
g = gravitational acceleration (m/s^2)
d = river depth (m)
D_w = molecular diffusion coefficient in water (cm^2/s)
r_H = hydraulic radius (m)
v_w = dynamic viscosity of water (m^2/s)

For lakes, wind-driven circulation drives mixing and the following correlation can be used to estimate k_{bl} (adapted from Thibodeaux, 1996):

$$k_{bl} = \frac{11294 \rho_a v_a^2 d^2}{\rho_w MW^{0.5} L_{lake}} \qquad \text{(Eq. 12.33)}$$

Where:

k_{bl} = benthic boundary layer mass transfer coefficient (cm/hr)
ρ_a = density of air over the lake (kg/L)
v_a = mean wind speed (m/s)
d = mean lake depth (m)
MW = molecular weight of the compound (amu)
ρ_w = density of water (kg/L)
L_{lake} = lake fetch in the direction of wind (m)

12.5.2.3 Summary

Specific site conditions, contaminants and cap materials' different processes may be more important than others. For example, molecular diffusion is relatively insignificant compared to hydrodynamic dispersion in high upwelling systems and vice versa. Depending on the degree of conservatism and the level of analysis required, different modeling approaches can be taken. Several examples are provided below to illustrate cap design modeling.

12.5.3 Transient Design Model for a Single Chemical Isolation Layer

The most simplistic approach for modeling transport in a cap is to assume it is a single homogeneous layer. This approach is generally not applicable in systems with bioturbation since rates of transport between the bioturbation layer and the underlying material are different. However, as a first approximation for a single isolation layer it can be informative since analytical solutions are readily available. This approach can also provide an estimate of concentration profiles in a cap before the contamination reaches the bioturbation layer. By assuming the cap is infinitely thick and the concentration in the underlying sediment is a constant C_b, the solution to the transport equation for a single layer of depth h is (Van Genuchten, 1981):

$$C(z,t) = \frac{C_b}{2}\left\{\begin{array}{c} \exp\left[\frac{\left(U-\sqrt{U^2+4\varepsilon\lambda D}\right)(h-z)}{2D}\right]\mathrm{erfc}\left[\frac{R(h-z)-t\sqrt{U^2+4\varepsilon\lambda D}}{\sqrt{4RDt}}\right]+ \\ \exp\left[\frac{\left(U+\sqrt{U^2+4\varepsilon\lambda D}\right)(h-z)}{2D}\right]\mathrm{erfc}\left[\frac{R(h-z)+t\sqrt{U^2+4\varepsilon\lambda D}}{\sqrt{4RDt}}\right]\end{array}\right\}$$

(Eq. 12.34)

The bottom of the layer is at z = b and the cap-water interface is z = 0. If decay is negligible, Equation 12.34 reduces to:

$$C(z,t) = \frac{C_b}{2}\left\{\begin{array}{c} \mathrm{erfc}\left[\frac{R(h-z)-Ut}{\sqrt{4RDt}}\right]+ \\ \exp\left[\frac{U(h-z)}{D}\right]\mathrm{erfc}\left[\frac{R(h-z)+Ut}{\sqrt{4RDt}}\right]\end{array}\right\} \quad \text{(Eq. 12.35)}$$

If there is no advection, Equation 12.34 reduces to:

$$C(z,t) = C_b\ \exp\left(-\frac{\lambda t}{R}\right)\ \mathrm{erfc}\left[\frac{\sqrt{\mathrm{R}}(\mathrm{h}-\mathrm{z})}{\sqrt{4\mathrm{Dt}}}\right] \quad \text{(Eq. 12.36)}$$

If there is only diffusion, Equation 12.34 reduces to:

$$C(z,t) = C_b\ \mathrm{erfc}\left[\frac{\sqrt{\mathrm{R}}(\mathrm{h}-\mathrm{z})}{\sqrt{4\mathrm{Dt}}}\right] \quad \text{(Eq. 12.37)}$$

Note that the assumption of constant concentration in the underlying sediment assumes that mass transfer into the cap does not deplete the contaminant mass in this layer. This assumption will normally provide a very conservative basis if a cap will maintain protective near surface concentrations for a very long time. These exact solutions are easily implemented into a spreadsheet for quick computation. It should be noted that these solutions are based on an infinitely thick cap assumption and do not consider the effects of physical boundaries. As such, they may not apply to predicting concentrations near the cap-water interface. Fluxes are generally controlled by transport processes well away from the surface, however, and thus these equations can be used to provide estimates of flux. Fluxes can be estimated by evaluating the left-hand side of Equation 12.25 at a location of interest, z, such as z = 0.

Example 1 A cap consisting of 12 inches (in.) of sediment that is subject to bioturbation above 12 in. of organoclay is being considered for sediments contaminated with phenanthrene. The underlying porewater concentration is 100 nanograms per liter (ng/L) and regulatory requirements suggest that the concentration 18 in. from the surface must not exceed 10 ng/L. How long will it take for the concentration to exceed the limit assuming that the concentration in the underlying sediment is constant? The organoclay-water partition coefficient for phenanthrene is 10^4 liters per kilogram (L/kg), the expected bulk density of the organoclay is 1.5 kg/L, a conservative estimate of the porewater upwelling velocity is 50 in./yr and the dispersivity of the organoclay has been conservatively estimated at 2 in.

Solution Transport in the s surface sediment layer subject to bioturbation is rapid and unimportant in estimating flux and concentrations as a function of time in the lower layer. Moreover, the regulatory standard is being applied below this layer so a single layer model with a hypothetical cap-water interface at the bottom of the surface sediment layer is appropriate. The value of R is dominated by sorption because of the large K_d:

$$R \approx \rho_b K_d = 1.5\,\frac{\mathrm{kg}}{\mathrm{L}} * 10000\,\frac{\mathrm{L}}{\mathrm{kg}} = 15000$$

The dispersion coefficient is:

$$D = \alpha V = 2\ \mathrm{in.} * 50\,\frac{\mathrm{in.}}{\mathrm{yr}} = \frac{100\ \mathrm{in.}^2}{\mathrm{yr}} * 6.45\,\frac{\mathrm{cm}^2}{\mathrm{in.}^2} * \frac{\mathrm{yr}}{31536000\ \mathrm{s}} = \frac{2(10)^{-5}\mathrm{cm}^2}{\mathrm{s}}$$

The hydrodynamic dispersivity is an order of magnitude larger than typical molecular diffusion coefficients so it is safe to ignore molecular diffusion. Because the 18-in. depth of interest, there is no need to consider bioturbation or the surface layer. Finally, there is no decay mentioned. So, the relevant processes are sorption, porewater advection and hydrodynamic dispersion, and Equation 12.35 can be used to estimate the behavior of phenanthrene in the system. The value of the parameters are $C = 10$ ng/L, $C_0 = 100$ ng/L, $z = 18$ in., $h = 24$ in., $R = 15{,}000$, $D = 100$ in.^{2}/yr, $U = 50$ in./yr.

$$0.2 = \mathrm{erfc}\left[\frac{90000\ \mathrm{in.} - 50\,\frac{\mathrm{in.}}{\mathrm{yr}}\,\mathrm{t}}{2449\mathrm{yr}^{-0.5}\sqrt{\mathrm{t}}}\right] + \exp[3]\ \mathrm{erfc}\left[\frac{90000\ \mathrm{in} + 50\,\frac{\mathrm{in.}}{\mathrm{yr}}\,\mathrm{t}}{2449\ \mathrm{yr}^{-0.5}\sqrt{\mathrm{t}}}\right]$$

Solving iteratively for t using an appropriate goal seek program, the time to exceedance is determined to be 549 yrs.

Characteristic Times

The analytical solution presented in Equation 12.34 can be used to estimate the time for a contaminant to penetrate a chemical isolation layer. Increased groundwater upwelling rates and diffusion coefficients decrease the transport time through a layer while sorption increases transport time. Lampert and Reible (2009) derived a characteristic time $t_{adv/diff}$ for breakthrough through a layer of thickness h using the characteristic advection time t_{adv} and characteristic diffusion time t_{diff} and assuming advection and diffusion act as parallel processes:

$$t_{adv/diff} \approx \frac{1}{\frac{1}{t_{diff}} + \frac{1}{t_{adv}}} \approx \frac{1}{\frac{16D}{Rh^2} + \frac{U}{Rh}} \approx \frac{Rh^2}{16D + Uh} \qquad \text{(Eq. 12.38)}$$

For a single layer, this time corresponds to the time required before the flux or concentration is approximately 1% of the flux or concentration at the bottom of the layer (± 20%). The penetration time for multiple layers can be roughly estimated summing the characteristic times of the individual layers. However, it is often necessary to make more accurate assessments in systems with multiple layers.

The modeling approach presented thus far can be extended to more complex problems as needed. A source for analytical solutions for diffusion and some advection–diffusion problems that arise in sediment cap modeling including diffusion/reaction in multiple layers is Choy and Reible (2000). Other sources for solutions to diffusion and advection–diffusion problems are Crank (1983) and Carslaw and Jaeger (1986).

12.5.4 Steady-State Design Model for Two Layers

In a system with two chemical isolation layers or an isolation layer and an overlying bioturbation layer, it may be desirable to predict concentrations or fluxes in the upper layer. To do so, it is necessary to simultaneously consider the effects of both layers to appropriately assess the potential applicability of a cap. Lampert and Reible (2009) developed a modeling approach to predict performance of such a two-layer system. The performance of the cap can be estimated using Equation 12.34 until the penetration time given by Equation 12.38. After contaminant penetration of the chemical isolation layer, an exact solution to the steady state transport equation that incorporates porewater advection and diffusion, sediment erosion and deposition, sediment re-working and porewater pumping via bioturbation and reaction can be used. The steady-state model allows the complexities of the upper of biologically active layer to be considered while maintaining an analytical form for convenient and rapid evaluation. The assumption of steady state to consider the concentration in the two layer system is appropriate if the upper layer rapidly approaches steady state behavior as in the case of the rapid mixing processes in the bioturbation layer. The steady-state model for a chemical isolation layer (Layer 1) with a bioturbation layer (Layer 2) with thicknesses h_1 and h_2 and transport parameters of the form of Equation 12.18 is (written for convenience in dimensionless form):

$$C_1 = \frac{C_{bio}e^{-\frac{Pe_1}{2}} - C_b e^{-\beta}}{2\sinh\beta}\exp\left[\left(\frac{Pe_1}{2}+\beta\right)\frac{h_1+h_2-z}{h_1}\right] + \frac{C_b e^{\beta} - C_{bio}e^{-\frac{Pe_1}{2}}}{2\sinh\beta}\exp\left(\frac{Pe_1}{2}-\beta\right)\frac{h_1+h_2-z}{h_1} \quad \text{(Eq. 12.39)}$$

$$C_2 = \frac{C_{bl}e^{-\frac{Pe_2}{2}} - C_{bio}e^{-\gamma}}{2\sinh\gamma}\exp\left[\left(\frac{Pe_2}{2}+\gamma\right)\frac{h_2-z}{h_2}\right] + \frac{C_{bio}e^{\gamma} - C_{bl}e^{-\frac{Pe_2}{2}}}{2\sinh\gamma}\exp\left[\left(\frac{Pe_2}{2}-\gamma\right)\frac{h_2-z}{h_2}\right] \quad \text{(Eq. 12.40)}$$

where C_{bio} is the concentration at the interface of the chemical isolation and bioturbation layers and C_{bl} is the concentration at the cap-water interface. The values are:

$$C_{bio} = \frac{C_b\frac{Pe_2}{Pe_1}e^{\frac{Pe_1}{2}}\beta\sinh\gamma}{\frac{Pe_2}{Pe_1}\beta\cosh\beta\sinh\gamma + \gamma\ \sinh\beta\cosh\gamma - \frac{\gamma^2\sinh\beta}{\left(Sh+\frac{Pe_2}{2}\right)\sinh\gamma+\gamma\ \cosh\gamma}} \quad \text{(Eq. 12.41)}$$

$$C_{bl} = \frac{C_b e^{\frac{Pe_1+Pe_2}{2}}}{\left\{\left(\frac{Pe_1}{2}+\frac{Pe_1 Sh}{Pe_2}\right)\frac{\sinh\beta\cosh\gamma}{\beta} + \left(\frac{Pe_2}{2}+Sh\right)\frac{\cosh\beta\sinh\gamma}{\gamma} + \frac{Pe_1\gamma\sinh\gamma\sinh\beta}{Pe_2\beta} + \cosh\beta\cosh\gamma\right\}} \quad \text{(Eq. 12.42)}$$

The dimensionless numbers in Equations 12.39, 12.40, 12.41, and 12.42 are:

$$Pe_1 = \text{Peclet number in chemical isolation layer} = \frac{\mathrm{Uh_1}}{\mathrm{D_1}} \quad \text{(Eq. 12.43)}$$

$$Pe_2 = \text{Peclet number in bioturbation layer} = \frac{\mathrm{Uh_2}}{\mathrm{D_2}} \quad \text{(Eq. 12.44)}$$

$$Da_1 = \text{Damkohler number in chemical isolation layer} = \frac{\varepsilon_1 \lambda_1 \mathrm{h}_1^2}{\mathrm{D}_1} \tag{Eq. 12.45}$$

$$Da_2 = \text{Damkohler number in bioturbation layer} = \frac{\varepsilon_2 \lambda_2 \mathrm{h}_2^2}{\mathrm{D}_2} \tag{Eq. 12.46}$$

$$Sh = \text{Sherwood number at cap-waterinterface} = \frac{\mathrm{k_{bl} h_2}}{\mathrm{D}_2} \tag{Eq. 12.47}$$

$$\beta = \sqrt{\frac{Pe_1^2}{4} + Da_1} \tag{Eq. 12.48}$$

$$\gamma = \sqrt{\frac{Pe_2^2}{4} + Da_2} \tag{Eq. 12.49}$$

While the steady-state model (Equations 12.39, 12.40, 12.41, 12.42, 12.43, 12.44, 12.45, 12.46, 12.47, 12.48, and 12.49) may seem complex, it is an analytical solution and can be readily implemented into a spreadsheet or other platform for rapid computation. The general approach for application of the model is as follows:

1. Identify the relevant transport processes for the system.
2. Determine how the relevant processes are implemented into the transport model as described in Section 12.5.1.
3. Determine the values of the transport parameters as described in Section 12.4.
4. Calculate the appropriate values of R_i, U_i, D_i and λ_i for the two equations of the form shown in Equation 12.18, noting that sorption (R_i) is irrelevant at steady-state.
5. Determine the dimensionless parameters Equations 12.43, 12.44, 12.45, 12.46, 12.47, 12.48, and 12.49.
6. Calculate C_{bio} and C_{bl} from Equations 12.41 and 12.42, respectively.
7. Determine concentrations at the depth(s) of interest using Equations 12.39 and 12.40.

This approach can be used to predict concentrations and/or fluxes in the cap based on the given system parameters. For a design approach it is necessary to work backwards. The model is of most use in the assessment of sand caps, although the results apply to active caps as well. Some examples are provided below to illustrate this approach.

Example 2 A sand cap is being considered for remediating a site contaminated with phenanthrene. The site is ecologically significant and the estimated benthic activity levels are $D_{bio} = 10^{-5}$ cm^2/s with $h_{bio} = 10$ cm. The current porewater concentrations in the area are 100 ng/L, and the regulatory agency has determined that concentrations at the bottom of the bioturbation layer must not exceed 10 ng/L. How thick must the cap be to ensure compliance? The sand-water partition coefficient for phenanthrene is 8 L/kg, the expected bulk density and porosity of the sand are 1.2 kg/L and 0.4, respectively, the estimate for k_{bl} is 0.001 cm/s, the tortuosity-corrected molecular diffusion coefficient for phenanthrene is 10^{-6} cm^2/s, the porewater upwelling rate is 1 centimeter per year (cm/yr) and the dispersivity is 10% of the layer thickness.

Solution To ensure compliance, the safest design approach is to use the steady-state model and assume no biodegradation. Equation 12.41 can be used to determine the design thickness. Because there is no decay, $\beta = \frac{Pe_1}{2}$ and $\gamma = \frac{Pe_2}{2}$ and Equation 12.41 simplifies to:

$$\frac{C_{bio}}{C_b} = \frac{e^{\frac{Pe_1}{2}} \sinh\frac{Pe_2}{2}\left(\left(\mathrm{Sh} + \frac{\mathrm{Pe}_2}{2}\right)\sinh\frac{Pe_2}{2} + \frac{Pe_2}{2}\cosh\frac{Pe_2}{2}\right)}{\left(\left(\mathrm{Sh} + \frac{\mathrm{Pe}_2}{2}\right)\sinh\frac{Pe_2}{2} + \frac{Pe_2}{2}\cosh\frac{Pe_2}{2}\right)\sinh\frac{Pe_1+Pe_2}{2} - \frac{Pe_2}{2}\sinh\frac{Pe_1}{2}} \tag{Eq. 12.50}$$

While the expression is complex, the dimensionless concentration is a function of only Pe_1, Pe_2 and Sh, and the latter two can be readily calculated. Because of the low upwelling rate, the effective diffusion coefficient in the containment layer is primarily due to molecular diffusion (the assumption is checked later):

$$D_1 = \varepsilon^{\frac{4}{3}} D_w + \alpha V = \frac{10^{-6}\text{cm}^2}{\text{s}} + \frac{1\ \text{cm}}{\text{yr}} h_1 \approx \frac{10^{-6}\text{cm}^2}{\text{s}} \quad \text{(Eq. 12.51)}$$

The retardation factor in the bioturbation layer (Layer 2) is needed to assess bioturbation:

$$R_2 = \varepsilon + \rho_b K_d = 0.4 + 1.2 \frac{\text{kg}}{\text{L}} * 8 \frac{\text{L}}{\text{kg}} = 10 \quad \text{(Eq. 12.52)}$$

Due to rapid mixing, the effective diffusion coefficient in the bioturbation layer is assumed dominated by biodiffusion:

$$D_2 = \varepsilon^{\frac{4}{3}} D_w + \alpha V + D_{bio} R_2 \approx D_{bio} R_2 \approx 10 * \frac{10^{-5}\text{cm}^2}{\text{s}} \approx \frac{10^{-4}\text{cm}^2}{\text{s}} \quad \text{(Eq. 12.53)}$$

This is two orders of magnitude greater than molecular diffusion, which is safely neglected in the bioturbation layer. The Peclet number in Layer 2 is:

$$Pe_2 = \frac{Uh_2}{D_2} = \frac{1\ \text{cm}}{\text{yr}} * 10\ \text{cm} * \frac{\text{s}}{10^{-4}\ \text{cm}^2} * \frac{\text{yr}}{31557600\ \text{s}} = 0.00317 \quad \text{(Eq. 12.54)}$$

The small value implies the bioturbation layer is dominated by diffusion processes (i.e., bioturbation) relative to advection processes (porewater upwelling). The Sherwood number is:

$$Sh = \frac{k_{bl} h_2}{D_2} = \frac{0.001\ \text{cm}}{\text{s}} * 10\ \text{cm} * \frac{\text{s}}{10^{-4}\ \text{cm}^2} = 100 \quad \text{(Eq. 12.55)}$$

The large value implies transport is rapid at the sediment-water interface and as a result the concentration in the boundary layer is near that in the overlying water (zero). Equation 12.50 can be solved iteratively using an appropriate technique for the required value of Pe_1 using the values for Pe_2 (0.00317), Sh (100), C_{bio} (10 ng/L) and C_0 (100 ng/L):

$$Pe_1 = \frac{Uh_1}{D_1} = 0.0293 \quad \text{(Eq. 12.56)}$$

The required thickness of the chemical isolation layer can easily be determined using the provided values of D_1 (10^{-6} cm^2/s) and U (1 cm/yr):

$$h_1 = 0.0293 * \frac{10^{-6}\text{cm}^2}{\text{s}} * \frac{\text{yr}}{1\ \text{cm}} * \frac{31557600\ \text{s}}{\text{yr}} = 0.92\ \text{cm} \quad \text{(Eq. 12.57)}$$

Thus, a 1-cm isolation layer (and an 11-cm cap thickness) is sufficient to meet remedial objectives in this case. The hydrodynamic dispersivity for a cap of this thickness is ~10^{-9} cm^2/s, so the assumption of negligibility is reasonable. The thin layer is quite effective in this case because of the low upwelling velocity (1 cm/yr).

Example 3 Examine the performance of an 11-cm cap using the information from the previous example but with porewater upwelling velocities of 100, 400 and 1,000 cm/yr. Plot the steady-state concentration profiles for the different rates. Then develop a curve of the required design thickness versus upwelling rate.

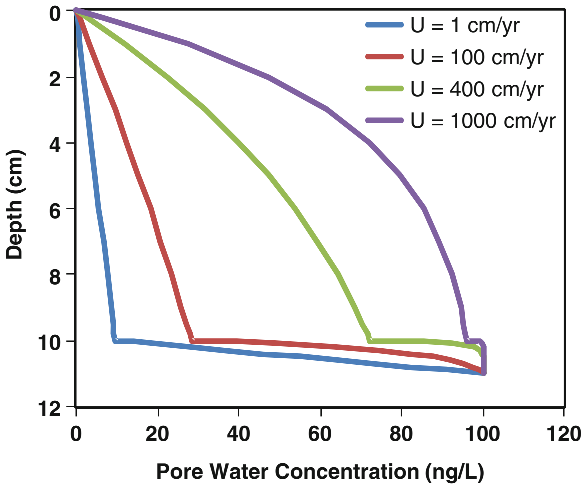

Figure 12.1. Effects of porewater upwelling on an 11-cm sand cap.

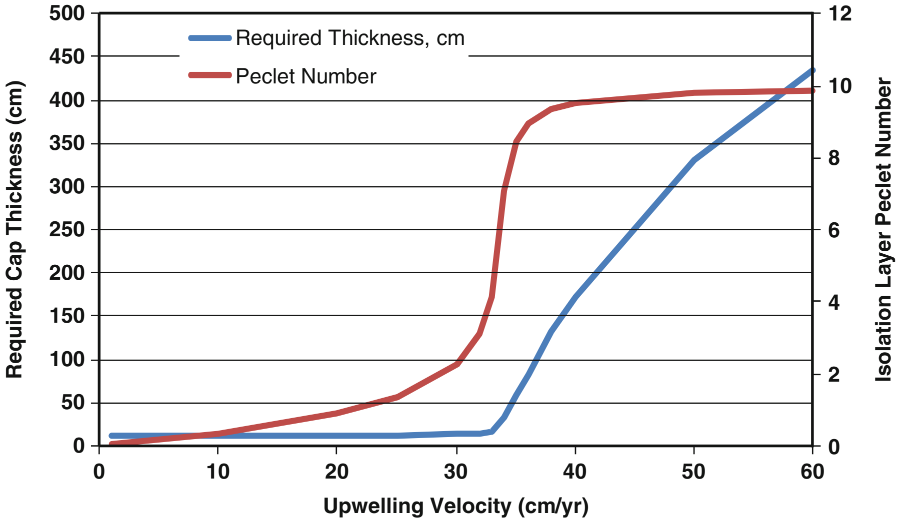

Figure 12.2. Effects of upwelling velocity on required cap thickness.

Solution The concentration profiles can be determined following the procedure outlined above for the different Darcy velocities. Figure 12.1 shows the results. The concentrations throughout the cap increase substantially at the higher Darcy velocities. The upwelling velocity is one of the most important parameters in a design. At high upwelling rates, sand capping is much less effective and sorbent amendments are required to effectively retard contaminant migration.

Following the procedure used in Example 2, it is possible to determine the requisite cap thickness for different Darcy velocities from 1 to 1,000 cm/yr. The hydrodynamic dispersion coefficient becomes significant at higher upwelling rates, which slightly complicates the calculation. However, using a goal seek function, it is still easily handled in a spreadsheet. The results are plotted in Figure 12.2. For upwelling rates that result in Peclet numbers in the isolation layer that are >1, the required thickness is large. In such cases, sorbent amended capping is likely to be considered.

12.5.5 Numerical Modeling

In many instances it is not possible to find exact solutions to the transport equations of the form shown in Equation 12.18 and a numerical model is necessary. Using a numerical modeling approach removes the limitations and allows for consideration of consolidation, nonlinear sorption and an unlimited number of layers in addition to the processes of porewater upwelling, diffusion, etc. Such a model has been developed specifically for the purpose of cap design and is available from the authors (CAPSIM). A brief description of the model is presented below.

12.5.5.1 Model Overview

The model platform uses a graphical-user interface and can simulate an arbitrary number of layers. Nonlinear sorption, deposition, consolidation and bioturbation can all be incorporated in addition to groundwater upwelling, molecular diffusion, hydrodynamic dispersion and reaction. Simulations can also be performed in a batch when a large number of simulations are needed. Contaminant properties are stored in a database that can be used to estimate the needed physical and chemical properties. The user can create input files that can be used to run similar simulations and save the inputs for re-use (e.g., two simulations that differ only in upwelling rates). The platform can generate a report with the input and output parameters, a comma-separated value file of the output and generates plots of the simulation results. The model is distributed as an executable installer file. The governing equations are of the form shown in Equation 12.18, the interfacial boundary conditions of the forms shown in Equations 12.22 and 12.23, the bottom boundary can be the form of either Equation 12.24 or 12.25, the top boundary is of the form shown in Equation 12.26 and the initial concentrations in the layers are assumed constant as in Equation 12.27. Additional details of the model are described below.

12.5.5.2 Numerical Solution Method

The model uses finite differencing with the Crank-Nicolson method to approximate the solutions to the governing equations. The spatial discretization Δz is uniform and ensures stability for the governing equations for each layer using the following (Morton, 1996):

$$\Delta z_{max} = \frac{2D_i}{U} \qquad \text{(Eq. 12.58)}$$

The maximum grid spacing is determined for each layer, and then the smallest spacing is used for all layers to ensure none exceeds this stability requirement.

The maximum time step size is determined for each layer using the Courant-Friedrichs-Lewy condition:

$$\Delta t_{max} = \frac{R_i \Delta z}{2D_i} \qquad \text{(Eq. 12.59)}$$

The user has the option to utilize the Δt from the layer with the smallest Δt, the largest Δt or the geometric mean of the two.

12.5.5.3 Sorption

Sorption in each layer can be characterized by specifying the partition coefficient K_d, specifying K_{oc} and f_{oc} (to determine K_d), or using a nonlinear Langmuir or Freundlich isotherm. For a Freundlich isotherm, the derivative term required by Equation 12.19 is:

$$\frac{\partial q(z,t)}{\partial C} = NK_f C(z,t)^{N-1} \qquad \text{(Eq. 12.60)}$$

For a Langmuir isotherm the derivative term is:

$$\frac{\partial q(z,t)}{\partial C} = \frac{q_{max} b}{(1 + bC(z,t))^2} \qquad \text{(Eq. 12.61)}$$

The value of the derivative term is constant for linear partitioning. When a nonlinear isotherm is used, the value of the term varies with space and time. The model calculates the value of the derivative term using concentrations at each point at the beginning of each time step and then again at the end of the time step. The average of the two is then taken and used to compute the concentrations at the next time step.

12.5.5.4 Consolidation

The net advective velocity U in the model is the sum of the groundwater upwelling rate and upwelling due to consolidation. Consolidation-induced flow is time-dependent and assumed to be of the form:

$$V_{cons}(t) = V_0 e^{-k_{cons} t} \qquad \text{(Eq. 12.62)}$$

The consolidation parameters V_0 and k_{cons} are fitted using the time to 90% consolidation and the total consolidation. Diffusive processes include molecular diffusion, hydrodynamic dispersion and bioturbation and decay is assumed first-order.

12.5.5.5 Bioturbation and Diffusion Terms

The diffusion coefficient in each layer is assumed to be the sum of hydrodynamic dispersion and molecular diffusion. Molecular diffusion can be modeled using the tortuosity correction (Equation 12.29 or 12.30). Bioturbation is added into the topmost layer as an effective diffusion term and provides the capability for both particle reworking and porewater mixing. Porewater mixing rates are less well known than particle reworking rates but are generally important for strongly sorbing contaminants.

12.5.5.6 Deposition

Deposition is incorporated into the model by adding additional layers at the top of the cap given an average deposition rate specified by the user. The user is cautioned that even small deposition rates may give rise to physically unrealistic cap depths over long periods of time. That is, it is unrealistic to assume that deposition rates of 1 cm/yr will continue over hundreds of years. In such cases it is preferably to define what might be viewed as an equilibrium sediment surface and use that as the cap dimensions throughout the simulation.

Example 4 A cap consisting of 2 cm of activated carbon and 60 cm of sand is being considered for a 30-cm layer of sediment contaminated with phenanthrene at a porewater concentration of 100 ng/L. The bioturbation depth is conservatively assumed to be 20 cm with $D_{bio} = 10\ \text{cm}^2/\text{yr}$ and the upwelling velocity is 100 cm/yr. The Freundlich parameters are $K_F = 10^5\ \text{ng/kg/(ng/L)}^N$ with $N = 0.8$, K_d in the sand is 100 L/kg, the f_{oc} of the sediment is 0.01 and the overlying water is clean. Predict the transport of phenanthrene within the system. A schematic is shown in Figure 12.3. Let us consider the time until a concentration of 20 ng/L is achieved at the bottom of the bioturbation zone (20 cm).

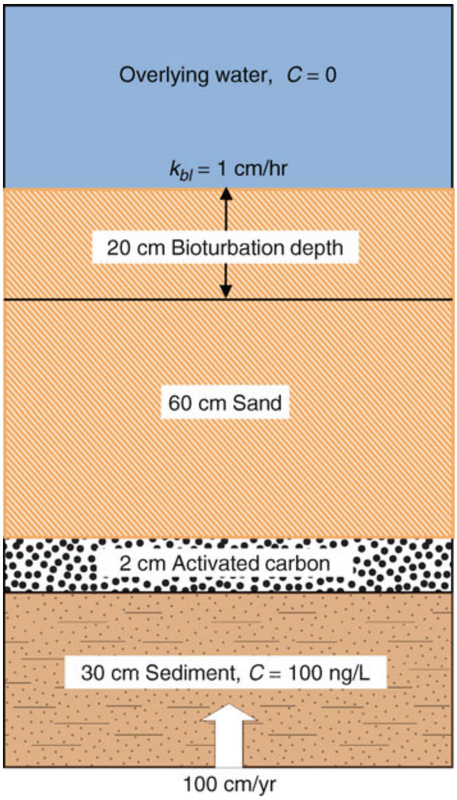

Figure 12.3. Cap system for simulation example.

Solution To appropriately address all the processes and layers, it is necessary to use a numerical model. The model can simulate transport (depletion) in the top 30 cm of sediment; the bottom of this layer is assumed to maintain a constant concentration of the initial value (100 ng/L). The activated carbon and sand sorption properties are given and K_{oc} is estimated using the built-in model correlations to be $10^{4.16}$ L/kg. With the bioturbation layer, a total of four layers are simulated. Since no geotechnical parameters are given, for simplicity they are assumed $\rho_b = 1.5$ kg/L and $\varepsilon = 0.5$ for all layers. Consolidation and deposition are ignored. The benthic mass transfer coefficient could also be estimated from hydrodynamic data using the model but for simplicity it is assumed to be 1 cm/hr. Molecular diffusion coefficient is estimated using the built-in correlation for the program to be $4.9(10)^{-6}$ cm^2/s before correction using the Millington and Quirk tortuosity model (built in to the program). Hydrodynamic dispersion is not presented but is assumed to be 10% of the layer thickness.

The results for a 1,000-yr simulation are shown in Figure 12.4. The concentration in the sediment is depleted in the bottom of the cap. The 2-cm activated carbon layer prevents significant migration for the first ~100 yrs, after which the contaminant breaks through rapidly to the surface. Because of the discontinuity in the diffusion at the bioturbation layer, the profile abruptly changes slope. The concentration at the bottom of the bioturbation layer reaches 20 ng/L at about 150 yrs as shown in the bottom part of Figure 12.4. A numerical model allows for the addition of many complexities that analytical models must ignore. However, analytical models can be sufficient in many cases.

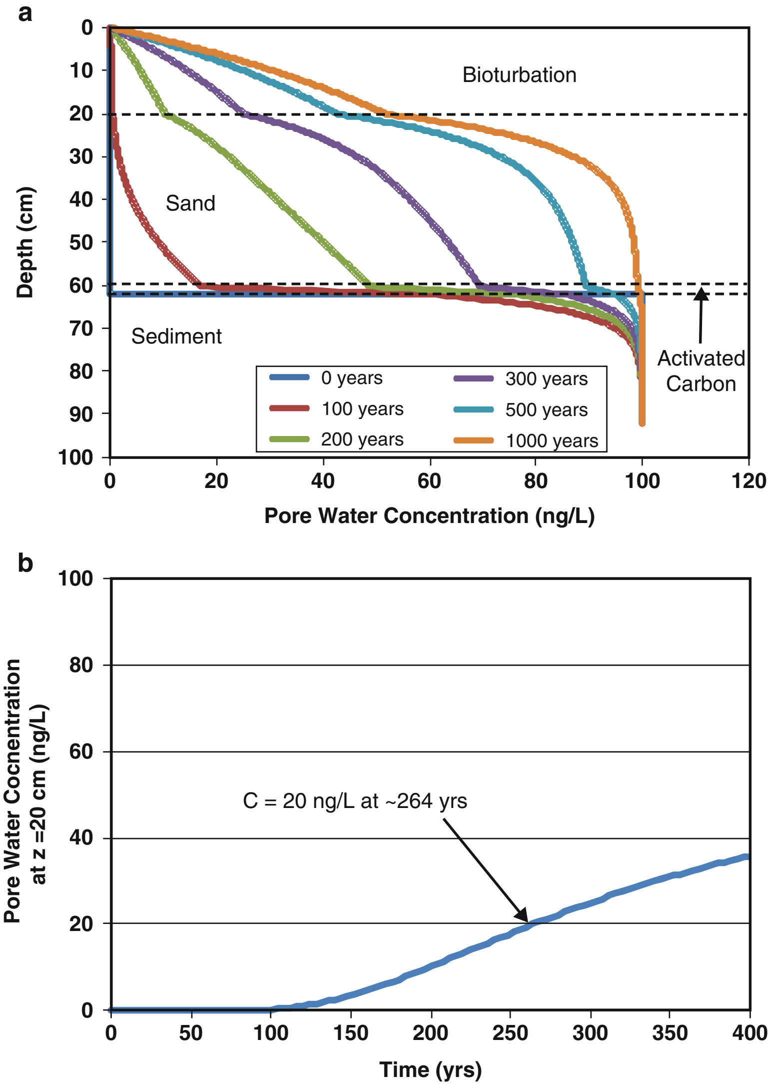

Figure 12.4. Two hundred-year simulation results; (a) porewater profiles; (b) concentration at z = 20 cm.

12.5.6 Additional Design Considerations for Active Caps

The use of any material exhibiting greater containment effectiveness than sand is often referred to as active capping, even if such a material is also a passive barrier. The primary objectives of an active cap are one or more of the following:

- Reduction in permeability at the sediment-water interface to reduce interstitial water exchange processes such as groundwater upwelling or tidal pumping
- Increases in sorption capacity of the cap layer to increase sorption-related retardation of contaminant migration
- Enhancement of contaminant transformation and degradation processes to reduce or eliminate contaminant release into the overlying water

In this section, conditions that limit the effectiveness of conventional sand capping are analyzed and materials or cap amendments that can achieve one or more of the above objectives will be identified. Key design characteristics and the status of the technologies will also be identified.

12.5.6.1 Permeability Control Layers

The primary means of permeability control at contaminated sediment sites is through the introduction of low permeability clay layers (e.g., AquaBlok$^{\mathrm{TM}}$ or Bentomat$^{\mathrm{TM}}$). Clays typically do not maintain their integrity when introduced directly into a water column and, thus, clays are typically placed within a needle-punched or laminated mat (Bentomat$^{\mathrm{TM}}$), or bound on a granular core (AquaBlok$^{\mathrm{TM}}$). A mat ensures retention of the clay fines during placement at the sediment-water interface while being bound to a granular core ensures sufficiently fast settling to avoid loss of the permeability controlling material.

Alternative approaches have also been used at particular sites. At Thea Foss Waterway in Tacoma, Washington, a sheet of high-density polyethylene was used to cut off gas bubbling up through a NAPL-contaminated layer. At a variety of sites, sheet pile walls and grout walls have been used to limit groundwater movement into an adjoining water body. Although these approaches are typically used to control an upland-contaminated groundwater or NAPL plume, they also serve to reduce upwelling through contaminated sediments in the adjoining water body.

The primary limitation to permeability control approaches is that they divert rather than eliminate groundwater upwelling. Without active control of groundwater levels, water levels will migrate around or overtop the low permeability layer or wall or find an alternative path. If the groundwater is not contaminated, this may not pose a problem and the low permeability layer may achieve its desired effect of hindering groundwater movement through the contaminated sediment layer. In the example of the Thea Foss Waterway, the presence of the impermeable high-density polyethylene sheet was designed to divert gas and groundwater flow away from the existing NAPL seep zones. In this way, the flow path was increased allowing additional time for contaminant degradation and sorption onto sediment or cap materials. In general, the groundwater response to the presence of a low permeability layer should always be evaluated before placing a low permeability layer. This may be done by explicit modeling of groundwater behavior or by simply recognizing likely alternative paths for the diverted groundwater.

12.5.6.2 Permeable Sorptive Layers

The most common approach to implementing an active cap layer is the incorporation of sorptive materials that increase the capacity of a cap and retard the flux of any contaminants. As indicated by Equation 12.38, the time required for migration of a contaminant through a cap is decreased linearly with the degree of sorption onto the cap materials. Knox et al. (2008) summarized the performance of a variety of sorbents for both metals and organic contaminants. In addition to the sorbents identified therein, activated carbon has often been considered as a sequestering agent in a cap.

The first efforts to improve the capacity of a cap and therefore slow the migration of contaminants through the cap were through the addition of organic matter. Clean sand has a sorption capacity that is approximately equivalent to a soil or sediment containing 0.01–0.1% organic carbon. Normal surface soils and surficial sediments typically have organic carbon contents of 1–10% making them at least 10–1,000 times more sorbing than clean sand for the HOCs.

Thus, sediment composed of topsoil theoretically exhibits 10–1,000 times more protectiveness than a clean sand cap, based upon the time until significant contaminant release at the top of a cap. Because natural organic matter is mostly associated with fine silts and clays, however, this theoretical increase may not be observed in practice due to the tendency of the fines to be lost or separated during placement through the water column. That is, the actual organic carbon contained within the capping layer after the attempted placement of topsoil may be 50% or less than observed in the original topsoil. Efforts to place 1% organic carbon topsoil in Silver Lake, Massachusetts, for example, led to the realization of approximately 0.5% organic carbon in the sediment cap (ARCADIS, 2008). This still suggests that the capacity of the placed topsoil cap is substantially greater than that which would be expected if clean sand were to be placed over the sediment and this provides a longer period of protectiveness of a cap containing organic matter or other sorbent.

Note that sorption-related retardation of the migration of contaminants is purely a transient phenomenon. Once the sorption capacity of a cap layer is saturated, the effect of the sorptive capacity is negligible and the migration of a contaminant through the sorptive cap is effectively identical to that of a sand layer. The significantly greater time until complete penetration of a sorbing cap relative to sand, however, provides greater opportunities for natural fate or recovery processes to attenuate the contaminant. Degradation processes may render the contaminant harmless over the longer timeframe or deposition of new, clean sediment may effectively bury the contamination before complete penetration of the originally placed cap layer.

An alternative to simply boosting the organic carbon fraction of the placed cap materials is use of materials that are specifically designed to preferentially absorb organic compounds. Activated carbon, organo-modified clays and sorptive resins, such as Ambersorb, have all been proposed as permeable sorptive barriers to organic compounds. These materials exhibit a high affinity for organic compounds, increasing the organic sorption capacity of a cap made from such materials by orders of magnitude over sand or even typical topsoils and sediments. They are substantially more expensive than sand or other natural materials, however, and are often difficult to place and retain in or on the sediments. The most important of these materials are discussed below.

12.5.6.3 Activated Carbon

Activated carbon is routinely used for water treatment as a final polishing step and, thus, there is extensive experience and understanding of its use and capabilities. Sorption capacity of activated carbon can be quite high for HOCs. Walters and Luthy (1984) reported the sorption of a variety of PAH compounds onto activated carbon (Filtrasorb 400, Calgon Corp. with a surface area of 998 square meters per gram [m^2/g]). The value for the distribution coefficient for phenanthrene at 10% of saturation using the reported isotherms is $K_d \sim 10^6$ L/kg, which is approximately 50% than the estimated K_{oc} of $10^{4.16}$. Thus, a 1-cm layer of activated carbon layer has potentially the equivalent breakthrough time of a 50 meter (m) layer of sediment with an f_{oc} of 1% or 500 m of sand with an effective f_{oc} of 0.1%.

Activated carbon exhibits two significant limitations in applications as a contaminated sediment cap: a tendency for fouling by NAPL or natural organic matter (DOC) that will reduce the sorptive capacity (Sharma et al., 2009) and a difficulty in placing the carbon in water due to its low density. The wet density of activated carbon is only slightly greater than that of water, and so the carbon can settle and be retained at the sediment-water interface although the potential for resuspension and erosion is substantially greater than soil or sediment grains of a similar diameter. The reduction in sorption capacity of activated carbon due to fouling by natural organic matter is not predictable at the current time but measurements at specific sites show the potential for reductions of an order of magnitude or more. Fouling by NAPL can have an even greater influence on activated carbon capacity.

To overcome the difficulties in placement, activated carbon has normally been considered as a capping material when contained within a laminated mat such as demonstrated by Reible et al. (2006) in the Anacostia Active Capping Demonstration using coke rather than activated carbon. Coke, a nonporous carbon product, exhibits a similar density as activated carbon but has substantially less sorption capacity due to its nonporous nature. Activated carbon was placed in similar mats in Duluth, Minnesota, in 2006 at the Stryker Bay site. The mats were constructed of a high void fraction core with a filtering layer on each side of the core to physically contain the cap amendment. The nominal thickness of the mats from CETCO is approximately 1 cm and they contain approximately 0.4 pounds per square foot (lb/ft^2) of activated carbon (or about 2 kilograms per square meter [kg/m^2]). Additional efforts are under development that would allow incorporation of activated carbon into caps without placement in a mat (Rakowska et al., 2012).

12.5.6.4 Organo-modified Clays

Organo-modified clays are clays that have been treated to cation exchange Na for organic molecules that can serve as organic sorbents. In sediment applications, the organo-modified clays that have been employed are quarternary amines with long-chain alkyl groups that make them effective for sorption of hydrophobic organic compounds and particularly for NAPLs. The sorptive capacity of organo-modified clays is less than that of activated carbon, although the potential for fouling with natural organic matter is also less. The sorption of PAH compounds to a tallow based organo-modified clay is given essentially by K_{ow} (Reible et al., 2007). The sorption is generally linear, suggesting an effectively constant K_d and an absorptive process into the volume of the sorptive phase rather than a surface-area-driven process. Assuming $K_d = K_{ow}$, the effective partitioning coefficient for phenanthrene onto organo-modified clay is about five times K_{oc}, and thus the organo-modified clay behaves (for phenanthrene and similar PAH compounds) as though it were a sediment containing 500% organic matter. This sorption onto organoclays is at least ten times less than clean activated carbon but more similar in capacity to activated carbon fouled by natural organic matter at a particular site. In general, however, activated carbons are more effective sorbents of dissolved HOCs and organo-modified clays are more effective sorbents for NAPLs.

Organo-modified clays are substantially denser than activated carbon with a dry bulk density of the order of 0.8 grams per milliliter (g/mL) and a wet density of about 1.5 g/mL. As a result, organo-modified clays will settle rapidly in a water column and can be placed in a manner similar to sands, although their somewhat lower density may give rise to enhanced dispersion of the organo-modified clay relative to sand. A bulk organo-modified clay layer 12 in. thick was placed at the McCormick and Baxter Superfund Site in Portland, Oregon, without significant loss of organo-modified clay to the water column (Parrett and Blishke, 2005).

Organo-modified clays can also be placed with mats when only thin layers are needed. At the McCormick and Baxter site, organo-modified clay in mats was placed over gas ebullition areas that were leading to contaminant seeps and NAPL sheens. The organo-modified clays can be placed in both laminated mats as with activated carbon but also in needle-punched mats, which likely provides more uniform loading of the clays in the mat. Due to the greater density of organo-modified clays, commercial mats contain densities of up to 0.8 lb/ft^2, almost double that of activated carbon.

An important attribute of organo-modified clay is the ability to absorb NAPL. Reible et al. (2007) observed NAPL sorption capacity for organo-modified clays under field-simulated conditions of the order of 1 g NAPL/1 g organo-modified clay. If NAPL is present, and particularly if NAPL has the potential to migrate, the organo-modified clay is an effective means of eliminating that facilitated transport process. As with sorption of dissolved contaminants, however, the capacity of the organo-modified clay is finite and upon saturation of that capacity, the organo-modified clay may provide little or no barrier to additional contaminant migration. Because the organo-modified clays are organophilic, they swell upon sorption of NAPL and then reduce in permeability. As a result, NAPL-impacted organo-modified clay deters further NAPL migration through the clay. It is important for the cap to be designed such that NAPL is not diverted outside of the capped area when the permeability is affected.

12.5.6.5 Degradative Caps

The final objective of an active cap could be to enhance contaminant fate processes including degradation. This has proven to be the most elusive of the active cap attributes because capping will reduce the natural flux of organic matter to the underlying sediments and the microbial processes typically depend upon labile organic matter to degrade contaminants. In addition, a cap will tend to cause the entire sediment layer to become anaerobic, reducing the microbial degradation rates of important compounds such as PHCs, which degrade rapidly under aerobic conditions. As indicated previously, however, development of the strongly anaerobic conditions will generally encourage metals containment and sequestration. For organics, however, any reservoir of nutrients may be depleted over time, further slowing microbial activity. No approach has yet been identified that can effectively deliver nutrients or other degradation agents after cap placement without substantial disruption of the cap although some recent research shows promise (Harper et al., 2011). Some degree of degradation can occur naturally in caps and techniques for their evaluation has been identified (Smith, 2011). Degradation processes in caps have also been studied in a small number of environments (Hyun et al., 2006; Himmelheber et al., 2008, 2009). The encouragement of sustained conditions conducive to contaminant degradation has also been attempted using the application of electricity (Sun et al., 2010). All of these efforts have been largely confined to laboratory studies, however, and degradation has not normally been used as a component of the design of a cap.

12.5.7 Design of Erosion Control and Habitat Layers

An important component in the design of a cap is the prevention of re-suspension of cap materials and contaminated sediments through erosion. Design of a cap for longevity requires that it be maintained in place until other natural attenuation processes render its presence as unnecessary. Since a cap is generally composed of non-cohesive granular material, its resistance to shear stresses is generally well understood. A more difficult problem is often definition of the shear stresses that are likely to occur. Past history may provide a clue as to possible shear stresses but changes such as dam removal and climate change may give rise to events and shear stresses that are unprecedented. For this reason, erosion control design is often extremely conservative, for example, using the threshold of erosion as a design criteria rather than allowing for a small amount of erosion in an expected event or even allowing for erosion and building in monitoring and maintenance plans that allow replacement of a portion of a cap after a major event. A more difficult problem is often the design of a cap to be stable in the face of anthropogenic influences, e.g., recreational and commercial vessel traffic.

The top layer of a cap may have a dual purpose: to protect the cap and to provide a suitable habitat for a healthy benthic community or aquatic species. These goals are rarely consistent with each other and instead an armoring layer may be placed immediately above a chemical isolation layer of a cap for erosion control and an appropriate habitat layer may be placed above the armoring layer. One effect of this is that the habitat layer may be lost in a high-flow event for which the armoring layer is designed. In such a situation, however, a habitat layer would have been lost whether a cap was present or not. Ultimately, the surface of a cap will likely return to the surficial sediment conditions present prior to cap placement.

Design of an erosion control layer or a habitat layer is beyond the scope of this chapter. Little general guidance exists for habitat layers specifically for caps although appropriate habitat information for bottom sediments is widely available that is applicable.

12.6 MONITORING CAP PERFORMANCE

Evaluating the performance of remedies for the management of contaminated sediments is challenging regardless of the approach employed. Typically, monitoring includes both evaluation of remedy implementation, long-term stability and both short- and long-term risk reduction. Remedy implementation monitoring and long-term stability monitoring for capping normally entails bathymetric surveys, coring and sub-bottom profiling where conditions are conducive to such approaches to document both placement of the desired thickness of a cap and the maintenance of that thickness over time. Short-term risk reduction is usually indicated by reductions in surficial sediment concentrations, which can commonly be achieved relatively quickly and effectively by capping relative to other sediment remedial approaches. More difficult is the assessment of long-term risk reduction. Since many caps contain non-sorptive material, concentrations within the cap layer may remain low indefinitely, even if significant contaminant migration is occurring. A more effective approach is to collect interstitial water concentrations of the contaminant within the cap and compare the measured concentrations to the design expectations and modeling results. Passive sampling with polymer sorbents for *in situ* evaluation of interstitial water concentration with 1 cm vertical resolution and detection limits of sub-ng/L has been developed for the purpose of evaluating cap performance (Reible and Lotufo, 2012). Lampert et al. (2011) employed this approach to evaluate the performance of a thin-layer cap in the laboratory and showed that cap performance and organism bioaccumulation at the top of the cap could be directly assessed employing passive sampling. The same approach was also applied to field monitoring of caps in Lampert et al. (2013). The combination of low detection limits and high vertical resolution means the method can be used to evaluate the mobile and bioavailable fraction of contaminants during very early stages of the design life of a sediment cap. The method can be a much more effective early warning indicator of cap performance than traditional bulk solids.

More traditional approaches can also be employed, e.g., the use of constructed screened wells within a cap. This might be especially appropriate in a heavily armored cap in which insertion of sampling tool or coring tool from the surface may be difficult and it is not desirable to temporarily remove armoring. This method results in a significant loss of vertical resolution, however, and therefore makes it difficult to compare results to model predictions of future cap performance. Instead of a traditional screened well, multiple polymer-sorbent passive samplers could also be inserted within a cap during placement and individual samplers retrieved as needed to monitor contaminant migration in a cap over time.

By either method, water concentrations changing over time require comparison to some criteria of success or failure. As indicated above, this could be comparison to design model predictions for performance at any time. Alternatively, the interstitial water concentration measured within the cap or, particularly, at the near surface, could be used to compare to quantitative concentration criteria. Although no quality standards exist for interstitial water concentration, a common comparison criteria is a surface water quality criteria. If surface water quality criteria are maintained within the capping layer, it is clear that the migration of contaminants through the cap could never lead to exceedance of surface water quality criteria in the overlying water. This may be a particularly conservative criterion, however, and a criterion that is rarely applied to dredging remedies, but it remains a useful and increasingly used comparison criteria.

12.7 SUMMARY

This discussion has highlighted that capping is a viable contaminant containment technology and has a role, with other remedial approaches, in managing contaminated sediments. Capping with even inert materials such as sand can be effective for many metal-contaminated sites and sites contaminated with HOCs when groundwater upwelling is not a significant factor. For more challenging sites, a variety of cap amendments have been proposed and are beginning to be used to enhance contaminant containment. Modeling tools exist for the design of caps and for identification of conditions that require cap materials other than sand. The modeling tools can be used to project forward in time and can be most effectively used to evaluate the sensitivity of future projects of performance to uncertainties in cap or site conditions. Capping continues to be a useful tool for contaminated sediment remediation that will see increasing use either alone or in concert with other remedies such as dredging in the future.

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CHAPTER 13

SEDIMENT DREDGING, TREATMENT AND DISPOSAL

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13.1 INTRODUCTION

Removal of contaminated sediments from the water body with subsequent treatment and/or disposal of the contaminated dredged sediment is the most common approach for contaminated sediment remediation. Various excavation equipment types and approaches have been used, including both dredging (excavation underwater) and excavation of the sediments in the dry. Excavation can be used as the sole active remediation approach or can be used in combination with monitored natural recovery (MNR) and/or capping. This chapter focuses primarily on environmental dredging as a contaminated sediment remedy component. The various treatment and disposal options available for contaminated sediments are also described in this chapter with a description of how they relate to the environmental dredging process, but these options are not covered in detail.

The U.S. Army Corps of Engineers (USACE), U.S. Environmental Protection Agency (USEPA) and others have developed detailed technical guidelines and guidance documents for evaluation of environmental dredging, sediment treatment and processing and dredged sediment disposal (NRC, 1997, 2001, 2007; Palermo et al., 2008; PIANC, 1996, 1998, 2002; USACE, in publication; USACE/USEPA, 2004; USEPA, 1994, 2002, 2005). Much useful information is also available on the USACE Dredging Operations Technical Support (DOTS) website[1] and at the USEPA Superfund Contaminated Sediments website.[2] In addition, experience with constructed remediation projects involving dredging and sediment disposal are extensively documented in the literature. USEPA guidelines (USEPA, 2005; Palermo et al., 2008) are summarized and referenced extensively in this chapter, with a focus on the technical considerations for each aspect of evaluation. The detailed procedures for conducting design evaluations cannot be adequately addressed here due to limitations on length, therefore the more detailed guidelines and guidance documents in the reference list should be referred to for detailed evaluations.

13.1.1 Sediment Removal as a Remediation Approach

A removal option for remediation involves more than environmental dredging. Components of a removal remedy include sediment removal, transport, staging, treatment (both pretreatment and treatment of water and sediment, as necessary) and disposal (liquids and solids). Figure 13.1 illustrates the possible components in a dredging or excavation alternative. The simplest dredging or excavation projects may consist of as few as three of the components,

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[1] http://el.erdc.usace.army.mil/dots/. Accessed April 10, 2012.

[2] http://www.epa.gov/superfund/health/conmedia/sediment/index.htm. Accessed April 10, 2012.

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Figure 13.1. Components of a sediment removal remedy.

but more complex projects may include most or all of these components. There may also be other required actions at the excavation site to ensure remediation of the site.

There is a range of considerations in selecting sediment removal as a remediation approach, and the decision to dredge should be based on a clear evaluation of all the possible remedy options and their associated risk reduction benefits. The evaluation, design and application of a sediment removal remedy involves many different aspects, and much of the cost and complexity for a removal remedy is inherent to the disposal/treatment components as opposed to the dredging component. However, the effectiveness of the environmental dredging process itself continues to be a major subject of debate for these projects (USEPA, 2005; NRC, 2007).

13.1.2 Definitions and Objectives

Environmental dredging can be defined as the removal of contaminated sediments from a water body for purposes of sediment remediation. Figure 13.2 is a conceptual illustration of environmental dredging and related processes of importance: **removal** (dislodging and removing the sediments from the dredge cut), **resuspension** (dispersion of sediments in the water column), **release** (loss of contaminants from the porewater or from resuspended sediment particles into the water column or air) and **residuals** (sediments remaining in or adjacent to the dredging footprint after completion of the removal/dredging operation). These processes are often referred to as the "Rs" of environmental dredging (Bridges et al., 2006, 2008). The objectives of an environmental dredging operation are related to these processes and normally include one or more of the following:

- Dredge with sufficient accuracy such that targeted contaminated sediment is removed and sediment cleanup levels (CULs) are met without excessive removal of clean sediment;
- Dredge the sediments in a reasonable period of time and in a condition compatible with subsequent transport for processing treatment or disposal;

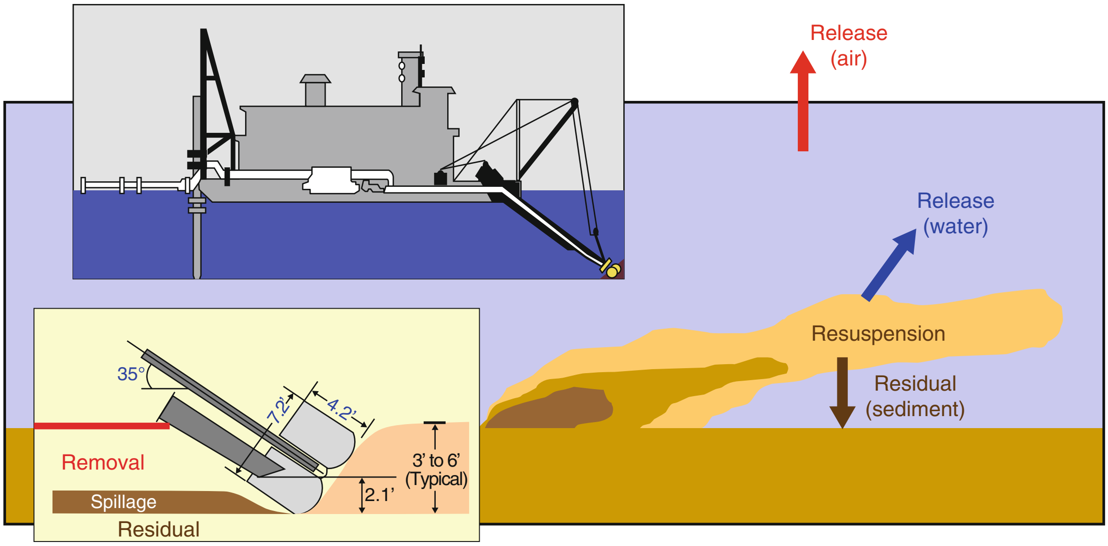

Figure 13.2. Conceptual illustration of environmental dredging and processes (from Palermo et al., 2008).

- Reduce and/or control resuspension of contaminated sediments, downstream transport of resuspended sediments and releases of contaminants of concern (COCs) to water and air; and
- Dredge the sediments such that generation of residuals is reduced and/or controlled.

As defined in USEPA (2005), a hierarchy of objectives for most contaminated sediment remediation projects can be described in terms of remedial action objectives (RAOs), remediation goals (RGs), and CULs. It is important to recognize that, from an engineering standpoint, active remedies for contaminated sediment sites (such as environmental dredging) are formulated and designed to achieve sediment CULs.

The above objectives point to the differences between environmental dredging and navigation dredging, which has as its primary objective the creation or restoration of navigable depths. Evaluation of environmental dredging involves an engineering and environmental assessment of site and sediment conditions; the selection of equipment and operational approach; evaluation of complex processes such as sediment resuspension, contaminant release and residual sediment generation; and development of monitoring and management plans for implementation. There is a strong interdependence between all these components of an environmental dredging project. Each of these aspects are discussed in more detail in the following sections, based on *Technical Guidelines for Environmental Dredging* developed for the USEPA by the USACE (Palermo et al., 2008).

13.1.3 Initial Evaluations

Initial evaluations of environmental dredging should be done as part of the screening of alternatives for a feasibility study or as part of a remedial design. An early initial evaluation of the potential feasibility of dredging would allow for tailoring the site and sediment investigations to collect necessary data for further evaluation of dredging for feasibility evaluations. The initial evaluations include a comparison of known site conditions, sediment characteristics and project requirements to those conducive to a dredging remedy; consideration of the advantages and disadvantages of environmental dredging as compared to other remedy approaches or combinations of approaches; consideration of environmental dredging as a component of a complete dredging and treatment/disposal remedy approach; and identification of significant project requirements and constraints. It is particularly important to identify major constraints at an early stage, such as the non-availability of onsite disposal, bedrock or hard substrate, boulders, debris, etc. If site conditions or institutional constraints indicate that a full dredging remedy is not a potentially feasible option, other remediation options or combined remedies such as partial dredging followed by capping and/or MNR could be considered.

Environmental dredging is only one component of a dredging/disposal remedy. The environmental dredging process must be fully integrated and compatible with other components such as transportation of the dredged sediment and the subsequent treatment and/or disposal or reuse of the sediment. Further, environmental dredging may be a component of a combined remedy or a remedy involving other actions within the water body itself (NRC, 2001; USEPA, 2005). For example, dredging may be selected as a remedy component to ensure navigational depth is maintained or to remove the most highly contaminated sediments, then combined with capping or MNR to achieve the final CUL. The preliminary evaluation should determine whether dredging is potentially feasible at the site, whether a full dredging remedy should be considered, whether a combination remedy with partial dredging should be considered (e.g., to a set elevation to make room for a capping component of the remedy), what areas and volumes should be considered, and whether mechanical dredging, hydraulic dredging or both approaches should be evaluated.

13.2 SITE AND SEDIMENT ASSESSMENT CONSIDERATIONS

Site conditions and sediment characteristics should be evaluated as they relate to potential feasibility and effectiveness of environmental dredging. These evaluations entail design of the field and laboratory investigations that will be essential to evaluation of dredging as a remedial alternative, identification of data gaps needed for dredging feasibility evaluations and conceptual level cost estimates, and/or identification of dredging-specific laboratory tests or modeling efforts needed for detailed design of a selected environmental dredging remedy. There are other aspects of site characterization that are important for other remediation approaches not discussed in this chapter (e.g., groundwater intrusion conditions critical to capping evaluations). Depending on the data gaps identified at a particular phase of evaluation, the conditions for the contaminated sediment site under consideration for remediation must be defined or refined. This includes gathering the needed data on physical characteristics of the water body (water depths, bathymetry [especially slopes], currents, wave energies, etc.), water body uses (navigation, recreation, water supply, wastewater discharge, etc.), the presence and nature of major infrastructure (bulkheads, piers, abandoned pilings, bridges, utility crossings, pipelines, etc.), the presence and nature of debris in the sediments and information on geotechnical conditions (stratification of underlying sediment layers, depth to bedrock, physical properties of foundation layers, etc.). It is particularly important to identify site conditions critical to dredging implementability such as potential to undermine the shoreline or shoreline structures. The process of filling data gaps on site characterization may be iterative in that several tiers or phases of investigation may be warranted.

In a similar manner, the contaminated sediments under consideration for dredging must be characterized, filling any data gaps critical to evaluation of environmental dredging. This includes the physical and chemical characteristics of the sediments. These characteristics should be determined both horizontally and vertically, considering stratification, etc. The results of the characterization, in concert with the CUL defined for the remedy, will determine the potential aerial extent and depths to be dredged. As with evaluation of site conditions, the process may be iterative. Uncertainties in site characterization must be considered in design. For example, depth of contamination cannot be determined precisely by sediment coring due to core compression and incomplete cores.

Positioning – Evaluation of dredging requires site and sediment data tied to a location (in three dimensions) at an acceptable level of precision. The vertical position of sediment samples should be tied to elevations, based on a standard vertical datum. State of the art electronic positioning (specifically Real Time Kinetic Differential Global Positioning Systems [RTK-DGPS]) and/or survey control should therefore be a central part of all field data collection efforts and subsequent implementation of environmental dredging.

Physical Conditions – The physical characteristics of the water body (water depths, bathymetry, slopes, currents, wave energies, etc.), water body uses (navigation, recreation, drinking water supply, wastewater discharge, etc.) and the presence and nature of major infrastructure (bulkheads, piers, abandoned pilings, bridges, utility crossings, pipelines, etc.) will influence the selection of dredging equipment and the approach for dredge operation.

Debris – The presence and nature of debris in the sediments is an especially important consideration because debris in the sediments results in an increase in sediment resuspension, contaminant release and generated residuals. A survey of debris should be conducted and, if necessary, a debris management plan developed for debris removal, decontamination and disposal that is consistent with and supports the plan/equipment for removing and handling contaminated sediment.

Geotechnical Conditions – Information on geotechnical conditions (stratification of underlying sediment layers, depth to bedrock, physical properties of foundation layers, etc.) and sources of contamination are important considerations. The potential to undermine the shoreline or shoreline structures is a critical issue and may limit the practical depth of dredging.

Access and Compatibility for Disposal – It is particularly important to identify site conditions critical to dredging implementability such as access to the water body and potential interface points for subsequent transport and disposal. Key considerations include potential locations of sites for rehandling and/or disposal, potential sites and acreage near the dredging area for rehandling or disposal, locations for offloading facilities for barges, potential hydraulic dredge pipeline routes and potential truck routes.

Sediment characteristics – The physical and chemical characteristics of the sediments should be determined both horizontally and vertically. It is critically important to characterize the limiting elevation of contamination (i.e., the lowest elevation that contaminants exceed the anticipated cleanup standards) accurately so that the dredging prism and dredging volumes can be appropriately determined. The physical characteristics should always include grain size distribution and *in situ* water contents – both critical to dredging evaluations and treatment/disposal evaluations. The importance of a quality characterization of the extent of contamination is critical to the success of environmental dredging. Inadequate characterization has been the underlying cause in the failure to meet removal goals at major projects. Samples are usually obtained by borings, and the potential inaccuracies of boring data due to core compression and losses should be appropriately considered.

13.3 PERFORMANCE STANDARDS

Performance standards are sometimes needed to satisfy project objectives related to short-term and long-term effectiveness, environmental protection, project duration and overall costs, forming the basis for determining feasibility, costs and needs for controls. Performance standards may also be used to evaluate the execution of the environmental dredging component of the remedy. Therefore, identifying or determining appropriate performance standards is sometimes a necessary early step in conducting feasibility evaluations or developing remedial designs and controls for environmental dredging (Palermo et al., 2008).

Performance standards for environmental dredging may include:

- Removal of all sediment having contaminant concentrations above a specific action level.
- Reduction of the surface-weighted average concentration (SWAC) to achieve the sediment CUL.
- Removal of sediments to a specified elevation within specified areas.
- Limits on the surficial contaminated sediment mass remaining as residuals following dredging.
- Limits on sediment resuspension generated by the operation.
- Limits on the release of dissolved contaminants reaching some distance downstream from the dredging operation.
- Limits on contaminant releases to air.
- Limits on solids content and/or volume throughput for subsequent treatment or disposal.
- Constraints on allowable time for project completion.

The above list shows that there is an inherent conflict in setting performance standards for environmental dredging with the desire to achieve an economically efficient remedy through efficient production and timely project completion, potentially conflicting with the desire to minimize resuspension, release and residuals. The setting of performance standards, therefore, requires a balance between multiple needs. Performance standards should be directly related to achieving the RAOs and all CULs for the remediation project, not to the expected capabilities of the dredging operations for the given site conditions and sediment characteristics.

13.4 DREDGING EQUIPMENT CAPABILITIES AND SELECTION

With site conditions and sediment characterization data available and performance standards defined, dredge equipment type(s) and size(s) can be selected for evaluation. Selection should be made considering pertinent equipment capabilities and selection factors related to the capabilities of equipment and the compatibility of equipment with site and sediment conditions, transport and rehandling requirements and disposal options (USEPA, 2005; Palermo et al., 2004, 2008). A preliminary operational strategy (to include a dredging sequence, depths of cuts, cut slopes, consideration of allowable overdredging, debris management, etc.) can be developed at an early stage. Multiple dredge types and operational approaches may be initially selected for evaluation, but the selection is usually narrowed for more detailed evaluations.

Figure 13.3 illustrates some of the basic dredge types and specialty dredges used for environmental dredging. Both hydraulic and mechanical equipment have been successfully used for environmental dredging. Equipment used for environmental dredging is usually

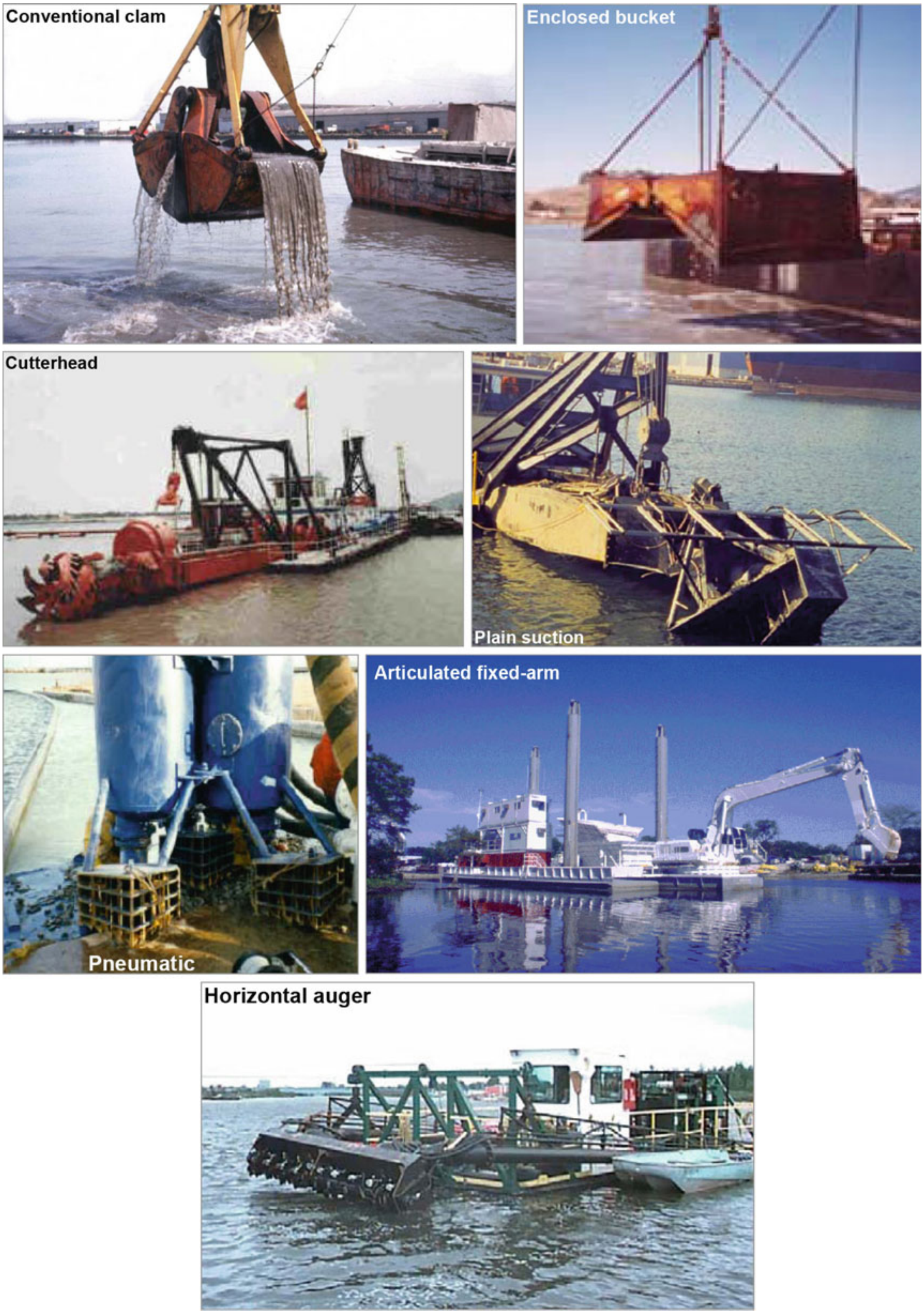

Figure 13.3. Photos of environmental dredging equipment types.

Figure 13.3. (continued)

smaller than that commonly used for navigation dredging, because the removal volumes tend to be smaller, dredging cut depths tend to be shallower and require more accuracy, precision and control of resuspension, release and residuals, and the operation may be coupled with other processes of limited capacity, such as a dewatering plant. Larger dredges are sometimes used; however, they often must operate at less than full capacity or intermittently and/or with less precision, decreasing their cost-effectiveness.

The tradeoffs between mechanical and hydraulic dredging approaches are often a major focus of equipment selection evaluations. Both dredging approaches are evaluated and compared in many cases. Sediment management options are often the primary influence in the selection of dredge type and may even limit those that can be considered.

Field pilot studies are often considered to confirm the applicability and capability of selected equipment for the site-specific conditions prior to a full-scale effort. Field pilot studies can be useful, but tend to be expensive and the results difficult to scale to the full-scale project. Thus, care should be taken to ensure that any pilot studies are conducted in such a manner as to provide useful information, e.g. design data, for a full-scale operation. Results from smaller-sized dredging equipment are often not scalable to larger equipment.

Within given dredge types, specific designs also differ and have varying capability. Equipment designed specifically for environmental dredging continues to be developed, allowing better performance for remediation than equipment originally designed for navigation dredging. In general, the dredge types listed above reflect equipment that is readily available and used for environmental dredging projects in the United States.

The type and size of dredge equipment selected for a particular project depends on a number of factors, including: volume to be dredged; site conditions such as water depth and current and wave climate; physical and chemical characteristics of the sediment; presence of debris, vegetation or loose rock; physical site constraints such as bridges or waterway widths; distance to the disposal site; treatment and disposal methods; availability and cost of equipment; and the performance standards for the operation. Details on evaluation of the various equipment selection factors are available in the USACE guidelines on environmental dredging (Palermo et al., 2008). Because the dredge must be capable of meeting the performance standards in an efficient manner, all these factors should be considered, and the environmental and operational trade-offs should be clearly identified and appropriately balanced.

13.5 RESUSPENSION AND CONTAMINANT RELEASE

Evaluation of sediment resuspension, contaminant release to the water column, and residual sediments are important considerations for environmental dredging (Bridges et al., 2006, 2008). Sediment resuspension occurs by direct resuspension of sediment by the operating dredgehead. Recent experience has also indicated that erosion of generated residuals is a major issue for resuspension and release and may be a greater resuspension source than direct resuspension by the dredgehead in many circumstances. Other activities associated with the dredging operations, such as barge overflow or prop resuspension from tug or work boats, may also result in significant sediment resuspension.

Evaluations of resuspension and release are critical in determining the potential short-term and long-term effectiveness of environmental dredging for the site. Resuspension evaluations usually rely on an estimate of the resuspension “source strength,” i.e., the mass of sediment resuspended per unit time, coupled with a model for prediction of suspended solids concentrations as a function of distance and time. These estimates can be based on field experience (a number of published papers have summarized resuspension data for completed dredging projects), or empirical or analytical models. Results can then be compared to performance standards for resuspension or water quality standards for suspended sediments or turbidity. The need for control measures (such as restrictions on the rate and timing of operations or deployment of silt curtain containments) can then be determined.

Releases of COCs in dissolved phase to water and releases of volatile contaminants to air are directly related to sediment resuspension. At early stages of evaluation, the estimates of contaminant release may be based on simple partitioning models. Effects of non-equilibrium partitioning and dispersion should also be evaluated. For detailed evaluations, estimates could be based on laboratory tests such as the Dredging Elutriate Test (DRET) or flux chamber tests for volatilization. Results of both release evaluations and sediment resuspension evaluations can be used in combination to estimate concentrations of contaminants in the water column or volatilized to air, and these can be compared to water quality standards or air quality limits established for the project. As with sediment resuspension, these comparisons will determine the need for control measures.

13.6 RESIDUAL SEDIMENTS

No removal technology can remove every particle of contaminated sediment from the water body, and residuals are one of the more significant limitations of environmental dredging effectiveness. Post-dredging residual contamination levels have often not met desired CULs (NRC, 2007). Inherent inaccuracies of the dredging operation, inaccuracies of sediment characterization and sediment contaminant distribution with higher concentrations at depth all contribute to potentially unacceptable levels of residuals that require management. The nature and extent of post-dredging sediment residuals are related to dredging equipment, dredging methods, sediment geotechnical and geophysical characteristics, the variability in contaminant distributions, and physical site conditions (including hydrodynamics).

Field experience gained in recent years has contributed to a better understanding of residuals processes, factors affecting residuals, and considerations for prediction of residuals (Palermo and Patmont, 2007; Patmont and Palermo, 2007; Bridges et al., 2008). Because there are numerous potential sources of residual sediment contaminants, residuals can be broadly grouped into two categories: (1) undisturbed residuals and (2) generated residuals. **Undisturbed residuals** are contaminated sediments found at the post-dredge sediment surface that have been uncovered by dredging but not fully removed. **Generated residuals** are contaminated post-dredge surface sediments that are dislodged or suspended by the dredging operation and are subsequently redeposited on the bottom of the water body. Undisturbed residuals and generated residuals may pose different risks, may require different methods for prediction, and may require different monitoring and management responses.

Undisturbed residuals result from: dredging in areas where removal is difficult such as directly over bedrock or hardpan, uneven surfaces, debris or boulders that are left in place, near piers or pilings, near infrastructure left in place; incomplete or inaccurate characterization of the extent of contaminants and/or over-reliance on geostatistical models to adequately represent the distribution of contaminants; inappropriate selection of a target dredge cut design elevation; inherent inaccuracy of dredging equipment; and dredge plans that intentionally do not target complete removal of contaminated sediments (e.g., due to engineering limitations). As a result of these potential causes, undisturbed residuals can be thin or thick layers of sediments that remain below the dredge cut elevation at a higher dry bulk density than generated residuals, and the dry bulk density would be similar to those of the *in situ*/native sediments.

Generated residuals result from: sediments dislodged but left behind by the dredgehead that fall to the bottom without being widely dispersed (commonly called fallback); sediment dislodged but left behind by debris-removal operations; attempting to dredge sediment in settings that limit the operation of the dredge (e.g., in debris fields), including preventing complete closure of the bucket; sediment that sloughs into the dredge cut from adjacent undredged areas; sediment moved by slope failures caused by the process of dredging or innate slope instability; sediments resuspended by the dredgehead that quickly resettle; sediments resuspended by dredging or other dredging-related activities that resettle within or adjacent to the dredging footprint; and fall back from bucket overpenetration and overfilling. As a result of these potential causes, generated residuals accumulate at the sediment/water interface in thin layers and at relatively low dry-bulk density.

13.6.1 Predicting Dredging Residuals

The quantity and quality of post-dredging generated residuals are related to dredging equipment, dredging methods, sediment characteristics and physical site conditions. Data compiled in recent years from a number of completed projects (Patmont, 2006) indicate that residuals contain 5–9% of contaminant mass removed in the last dredging pass. These masses of residuals are much larger than the observed masses of resuspension, indicating that fallback, slumping, sloughing and spillage are major sources of residuals. Based on these field data, the residual contaminant concentration can be estimated as equal to the depth-averaged contaminant concentration of the sediment removed in the last pass, which would include residuals from the previous pass (Hayes and Patmont, 2004; Desrosiers et al., 2005). The residuals volume from the previous pass would be 5–20% of the volume of the previous pass, depending on equipment type, sediment properties, water depth and other site conditions. These approaches for estimating generated residuals concentration and volume were adopted in the USACE technical guidelines for environmental dredging, which also contains example calculations of residual concentrations for multiple pass scenarios (Palermo et al., 2008).

13.7 DREDGING OPERATIONS

A number of strategies, methods or approaches can be considered related to design and implementation of environmental dredging projects. Operations refers to aspects such as how the project is delineated and sequenced and how the dredge will operate with respect to vertical depth increments, production and cleanup passes, overdredging allowances, etc.

Operations and Monitoring Plans – Operations aspects should be documented in an Operations Plan, a written document describing mobilization and demobilization needs, description and specifications for all dredging related equipment, methods of operation of equipment, logistics for rehandling and transport of dredged material, delineation of any subareas or management units used for the work, horizontal and vertical sequence of work, and management actions and contingencies for all operational aspects of the work. In some cases, the Monitoring Plan might be combined with the Operations Plan because the monitoring needs are contingent on the operations.

Management Units – Subdividing the site into management units is often desirable for purposes of remedial investigation and design and implementation. Such subdivisions or subareas are particularly useful for management of operations, monitoring and compliance. Subdivisions could include horizontally defined subareas used for projecting annual resource requirements, improving accuracy of material balance calculations, specifying sequence of removal, providing data to bidders on sediment types for each unit, or monitoring remedial progress or compliance with performance requirements. In some cases, subareas may correspond to defined dredge cut areas, each with a specified unique final target cutline elevation.

Production Cuts – The dredging operations within specific areas or subareas should be planned in terms of the areas to be cut and the types and numbers of dredge cuts. Dredges typically operate in lanes cutting across the dredge area. The largest size for a dredge cut area is often tied to operational factors for the selected dredging equipment. For example, the width of a production cut or pass might be the limiting swing width for a cutterhead dredge or the limit of reach for a clamshell, and length of the dredge cut would be restricted by the anchor placements. The thickness of sediment to be removed for a dredge cut may require several production cuts or passes to reach the final target cut elevation. The use of lifts not exceeding 5 ft (1.5 m) is recommended for sediment remediation. Most dredges are designed to target relatively level dredge cut design elevations, although the actual final surface is a function of equipment and operation. Depending on the optimal cut thickness for the dredge, multiple full cuts or production passes may be necessary to meet the final target cut elevation.

The objective of a production pass is bulk removal of the targeted sediment to achieve the dredge cut as efficiently as possible. The cutline elevation of the final production cut is usually set at the lowest elevation with concentration of the COC higher than the action level. However, the cutline elevation may also include a tolerance for the accuracy and precision of vertical positioning as well as uncertainty in the depth of contamination. Inaccuracies of positioning and uncertainties in characterization of the depth of contamination should be considered in setting the target cutline. Depth of contamination is normally determined by coring, which can yield large errors (as much as 50% or more) due to incomplete penetration, incomplete recovery, core compression and rodding; therefore, selection of proper coring equipment and appropriate interpretation of coring data is essential.

A few dredge designs allow for the dredgehead to make an inclined cut along a sloping bottom, but most dredges – both hydraulic and mechanical – make level cuts and cannot easily follow slopes in removing sediments. For environmental dredging, a series of box cuts or "step cuts" is sometimes used as the basis of defining a dredge prism for an area with sloping bottom. Since the contaminant removal neat line corresponding to the action level generally follows the slope, use of box cuts requires increased sediment removal as compared to a cut paralleling the slope because the entire box cut must fall below the neat line.

Overdredging Allowances – Overdredging is a common practice used in navigation dredging to permit the dredge to increase productivity and efficiency, and also provides benefits for environmental dredging with respect to meeting a CUL, minimizing residuals and increasing dredging effectiveness. Therefore, some overdredging is recommended for projects in which contaminated sediments overlie clean dredgeable sediments and in which the sediments at the interface have relatively high contaminant concentrations. However, excessive overdredging is less desirable for production cuts when dredging contaminated sediments because it increases the volume of dredged material to be treated and disposed. Overdredge allowances should be tighter (smaller) for environmental dredging as compared to navigational dredging and based on the precision of the dredge. The overdredging is only that thickness below the target cutline allowed for payment, not to be considered an accuracy allowance. Some dredging inefficiencies result from the need to locate the dredgehead as precisely as possible to the design cutline to minimize removal of clean underlying material. Due to the high unit costs of sediment management, incentives and/or disincentives might be considered in developing contract requirements for environmental dredging. Considering the water depths at most contaminated sediment sites, the size of dredges normally employed, and the precision attainable for positioning the dredgehead, an overdredge allowance for environmental dredging projects of 6 in. is the current "state of the practice."

Cleanup Passes – If performance standards for environmental dredging include meeting a CUL after dredging, the generation of residuals and/or the degree of undredged inventory may require further management actions, even if some overdredging is conducted in the production cuts. Possible management actions may include placement of a residuals cap (see below) or additional dredging in the form of cleanup passes. A cleanup pass (sometimes called a sweep pass) is a thin cut taken by the dredge in an attempt to remove residuals with limited removal of clean underlying sediments. Different dredging equipment may be more effective for the cleanup passes if the residuals are limited to a thin, loose layer of disturbed sediment generated by resuspension, and fallback. A thicker residuals layer resulting from sloughing, interference from debris and previously unidentified contamination may require an additional production pass rather than a cleanup pass. Some recent projects have applied "two-stage" dredging programs. In this type of program, a first dredging effort is employed utilizing equipment and approaches designed to remove the bulk of the contaminated sediment. Whether this approach involves one or more dredging passes, the objective is to remove sediment down to, or close to, the interface with the non-contaminated sediment as efficiently as possible. A second stage is then implemented, sometime called a cleanup pass, that removes the remaining relatively thin layer of impacted material, including any residual material that has been generated by the first stage dredging. The second stage may include the planned over-dredge thickness and is intended to remove remaining contaminated sediment while limiting the removal of the underlying non-contaminated sediment. It may also utilize different equipment than the first stage.

Sequencing – Appropriate sequencing of the dredging operation between subareas can improve effectiveness of operations and avoid recontamination of completed subareas. Horizontal sequencing should generally be from upstream to downstream with respect to the predominant flow or circulation pattern. Sequencing may also consider initial removal of hot spots, dedicated operations for removal of nonaqueous phase liquid (NAPL)-impacted sediments, partial removals over the entire area and performing all production cuts in a given area or reach before performing any cleanup passes if there is a high potential for recontamination. Vertical sequencing of production cuts would be from top to bottom, and for slopes, cuts from higher elevation to lower elevation along the slope is the usual sequence to reduce potential of recontamination. Data from a recent environmental dredging project (Fuglevand, 2012) also shows that contaminant release may be strongly related to the time partially dredged areas are left exposed. Thus, every effort should be made to complete areas expeditiously and close them as quickly as possible.

13.8 MONITORING

A monitoring program for environmental dredging should be designed to measure effectiveness or success of the environmental dredging component of the remedy, and provide feedback to the dredging contractor that can be used to adaptively manage their operations to improve project outcome. Some of the same tools used for field monitoring and sampling during and following project implementation overlap those for site and sediment characterization but the tools are applied in different ways for the two purposes. Monitoring during project implementation should focus on those elements and components needed to measure compliance with the project requirements to include production, sediment resuspension and contaminant release, and residuals. The monitoring program should be designed to determine the cause of any non-compliance as well as the lack of compliance. Components of the monitoring may include the bathymetry of the dredge cut prism to ensure that the identified contaminated sediment has been removed, contaminant concentration and thickness of the dredging residuals to ensure compliance with the cleanup goals and to determine the need for residuals management, contaminant concentrations and total suspended solids concentration or turbidity in the downstream water column to determine compliance with standards, and in some cases contaminant concentrations in the air. A written monitoring plan for environmental dredging operations should be completed in detail to include details monitoring approaches, equipment, data management and interpretation, etc. If monitoring determines performance standards for production, resuspension/contaminant release or residuals are not met, management actions may be necessary to bring the operation into compliance.

13.9 MANAGEMENT ACTIONS AND CONTROLS

Design evaluations or monitoring results of dredging production rates, sediment resuspension, contaminant release and dredging residuals may determine the need for any management actions or control measures on the dredging operations. Both operational controls and engineered controls can be considered, depending on the requirements and site conditions. Operational controls include actions that can be undertaken by the dredge operator to reduce the impacts of the dredging operations. Engineered controls require a physical construction technology or modification of the physical dredge plant to cause the desired change in conditions. The most commonly considered control measures are described here, and the USACE and USEPA guidelines should be used for detailed evaluations (Palermo et al., 2008).

13.9.1 Production Management Actions

Dredge production rates, i.e., the rate at which sediment is removed, logically takes a secondary position to environmental protection in environmental dredging projects. Production rates, however, directly affect project duration and costs. Thus, they are usually crucial to overall project success. For this reason, production standards or expectations usually exist in the form of average hourly, daily, weekly production goals and/or limitations on overall project duration. If performance standards or production goals will not be met for overall production, possible management actions include: increasing operating hours or shifts, reducing or eliminating operational controls, using a larger dredge size, changing dredge type, using multiple dredges, or increasing sediment processing and transport capacity.

13.9.2 Resuspension/Release Controls

Management actions for resuspension and contaminant release include both operational and engineered controls. Possible operational controls for resuspension/release include: increasing monitoring to assess impacts, changing the method of operation, implementing a temporary work stoppage, slowing down the operation or changing equipment types. Changes to the method of operation may include reducing the penetration of the dredgehead, eliminating overflow from barges, reducing bucket hoist speed, changing cutterhead swing speed, changing the sequence of work, adding rinse tanks or spillage aprons, and use of foams, skimmers, etc. for control of volatiles or NAPLs. However, there is little data available to support the effectiveness of most of the above operational modifications in reducing resuspension/release (Bridges et al., 2006). Overly constrained dredging operations may increase the total or rate of loss, project duration, and costs.

Silt curtains are probably the most common engineered control for resuspended sediment at dredging projects. Silt curtains may be appropriate when site conditions warrant minimal transport of suspended sediment, e.g., when dredging hot spots of high contaminant concentration. An engineered control such as a silt curtain does not treat turbidity resulting from sediment resuspension; it merely contains or directs the movement of resuspended sediment. The effectiveness of a silt curtain installation is primarily determined by the hydrodynamic conditions at the site, and experience has shown that silt curtains are most effective in relatively shallow, quiescent water, without significant tidal fluctuations. Currents >1–1 ½ knots and

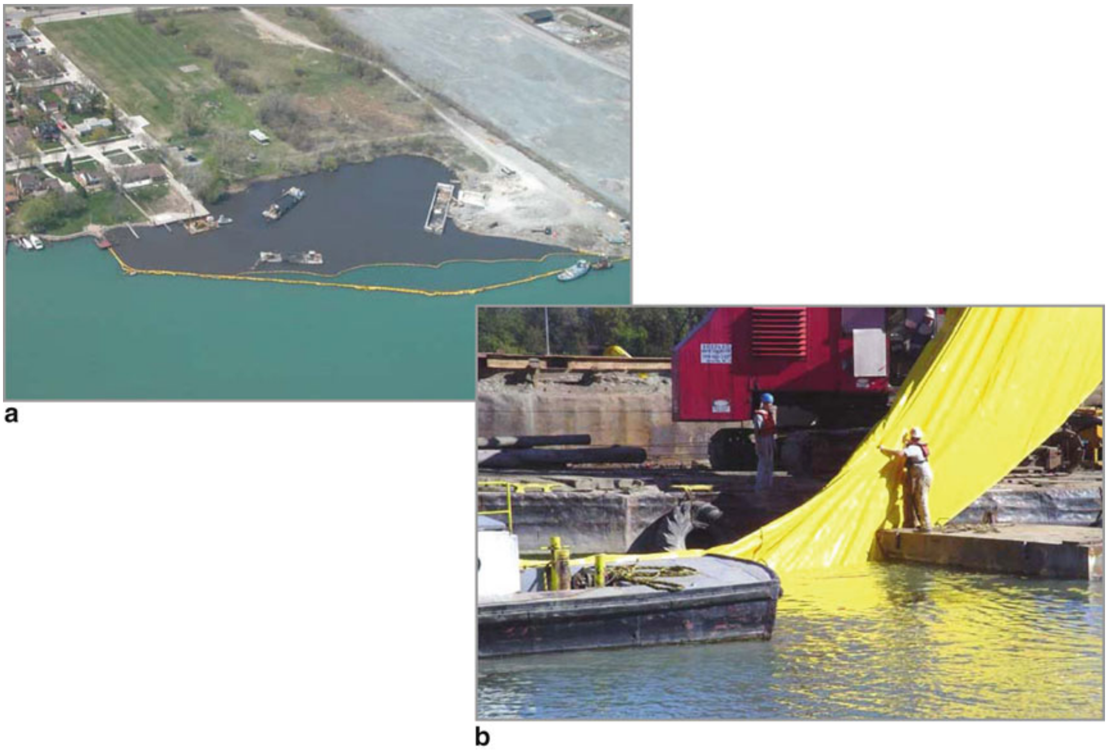

Figure 13.4. Silt curtain installation at Black Lagoon, Detroit River, Trenton, Michigan.

water depths >10–15 ft are problematic and lead to difficult and often expensive silt curtain designs. Application of silt curtains in higher current velocities (>3 knots) and deeper water depths would require special designs and engineered features (Francingues and Palermo, 2005; Palermo et al., 2008).

Structural barriers, such as sheet-pile walls, have been used for sediment excavation and in some cases (e.g., high current velocities) for dredging projects. These measures should be considered when there is a need to contain resuspended sediments that contain highly mobile, highly toxic, or bioaccumulative contaminants, and when there is uncertainty that a silt curtain will be effective. Sheet-pile containment structures likely provide more reliable containment of resuspended sediment than silt curtains, although at significantly higher cost and with additional limitations (Figure 13.4).

13.9.3 Residuals Management and Controls

Undisturbed residuals can be reduced by accurate and precise site characterization (which can be very difficult to achieve), proper establishment of the cut line, accurate and precise positioning of the dredge passes, accurate and precise post-dredging bathymetric surveys and an accurate cleanup pass to remove all sediment above the cut line as defined by initial characterization or confirmation sampling.

A generated residuals layer will be present following production dredging, and some management of these production dredging residuals might be needed if the project objectives include meeting a low CUL for contaminant concentrations. Approaches for managing residuals include both operational controls (actions taken during the production dredging) and post-dredging controls (actions taken following completion of production dredging). The mechanisms and processes that result in generated residuals are poorly understood. Consequently, operational controls for generated residuals are limited to best judgment and their effectiveness is uncertain.

Operational Controls for Residuals – Operational controls for residuals may include: separate debris-removal operations prior to sediment dredging, sequencing the dredging from upslope to downslope and upcurrent to downcurrent, designing and sequencing production cuts to reduce concentrations in residuals, providing for an overdredging allowance for production cuts, overdredging with a cleanup pass, accurate bucket placement with sufficient overlapping, elimination of bucket overpenetration and overfilling and rapid sampling after dredging to provide feedback to dredge operator showing effects of operations.

Post-Dredging Control Measures for Residuals – Post-dredging control options for managing the residuals may be required because of the uncertainty in the effectiveness in operational controls. There are several possible post-dredging management actions for residuals based on the residuals characteristics and site conditions. An engineering/operational evaluation may be required to determine which control measures are most amenable to conditions. The selection of a residuals management approach depends on the nature and extent of the residuals (presence of generated residuals versus undisturbed residuals, residuals thickness, residuals density and COC concentrations) as well as an assessment of site conditions as related to potential management actions (Palermo and Patmont, 2007). Depending on the specific management option selected, additional sediment verification sampling may be required to verify the effectiveness of the action. The need for post-dredging residuals management and controls may also extend outside of the original dredged prism.

Monitored Natural Recovery (MNR) – MNR refers to a remedial approach in which natural processes such as sedimentation, sediment mixing, resuspension and dispersion by erosion and degradation reduce contaminant concentrations over time. Details on MNR as a remedy option are found in Chapter 9. MNR is a potential management approach for post-dredging residuals if the layer thickness and concentrations of the residuals would allow for MNR to achieve risk goals within acceptable timeframes. Essentially, the same considerations that apply to selection of MNR as a primary remedial approach (e.g., as opposed to dredging) would apply in selection of MNR as a post-dredging management approach for residuals.

Cleanup Dredging Pass – At some sites, a cleanup dredge pass has been performed to remove layers of residuals. Such actions have been referred to as a cleanup or sweep pass, and are usually conducted in such a way as to attempt to remove only a thin surficial layer of material, with the intent of removing the residuals layer and a minimal thickness of underlying clean material. Multiple passes of the dredge to achieve a very low residual contaminant concentration can be inefficient and costly. However, a cleanup pass can be effective in removing the required material to meet cleanup objectives. As discussed in USEPA guidance, if cleanup passes are required, project managers should consider limiting the number of passes (to one or two) and providing an option for placement of a residuals cap or cover of clean material to achieve a residuals standard. Limiting the number of cleanup passes also brings more certainty into the process of cost estimating and bidding.

Additional Production Passes – Additional production dredging may be required for thicker layers of residuals, especially undisturbed residuals. This action would typically only be needed for cases where the initial site characterization was incomplete or inaccurate and led to an inaccurate production dredge cutline elevation or dredge positioning or control was poor.

Residuals Cover – "Residuals caps," "sand covers" or "backfill" are terms used to describe a thin layer of clean material (usually a few inches) placed over residuals to provide short-term isolation and long-term reduction in surficial contamination. The clean material used to cover the residuals does not need to be sand; in fact, other materials characteristic of the existing sediment properties with the potential to reduce the bioavailability of the contaminants (such as clay and organics) may be preferable; they may also be more difficult to place accurately. Covers may be an appropriate management action for sufficiently thin layers of residuals with contaminant concentrations sufficiently low that complete mixing of the cover materials into underlying residuals would ensure attainment of the action level. Some mixing of cover materials and layers of residuals will occur upon placement of the cover. As bioturbation and sediment transport processes work the surface, additional mixing may occur. The placement of a cover would thus result in a lower contaminant concentration in the biologically active zone. At some sites, covers may also provide physical and chemical isolation of the residuals, depending on the thickness of the cover, the thickness of the residuals layer and the rate of sediment mixing. Any additional deposition of clean sediment in the short- or long-term may extend and enhance the isolation ability of a cover.

Engineered Isolation Cap – An engineered isolation cap can be considered a residuals management action in cases where substantial layers of residuals, especially undisturbed residuals, cannot be effectively removed. The considerations for evaluating engineered caps as a residuals management option are identical to those for design of engineered caps as a primary remedial option, and USEPA guidance for design of engineered caps is generally followed.

The basis for selection of one or more of the above residuals management approaches should be defined in the monitoring and management plan for the project. In some cases, a project-specific "decision tree" may be developed with specific rules for selection of the management option based on the nature of the layers of residuals as defined by post-dredging verification sampling (Fox et al., 2007).

13.9.4 Adaptive Management

Major sediment remediation projects often take place over a large area, over an extended period of time, and involve a wide range of variable site conditions. Successful completion of such complex projects can be enhanced by a flexible management framework that encourages ongoing adaptation of the remediation methods through continuous gathering and review of performance data, followed by real-time method adjustments to improve the effectiveness of the remedial action. The application of adaptive management to sediment remedial actions provides a mechanism to improve the effectiveness of the planned action by learning from the outcomes of ongoing actions and modifying the actions to achieve the desired outcome, as well as a means to respond quickly to unanticipated conditions.

13.10 EXPERIENCES WITH ENVIRONMENTAL DREDGING

A large number of sediment removal/environmental dredging projects have been described in the literature, and the field experience gained in recent years has contributed significantly to the development of technical guidelines for evaluation and implementation of these projects (USEPA, 2005; Palermo et al., 2008).

The experiences at 26 "megasite" projects were documented in a National Research Council (NRC) study of environmental dredging effectiveness (NRC, 2007), and this comprehensive study serves as a useful summary of field experiences. The key findings pertaining to dredging effectiveness were:

- Available data at most sites is not sufficient to determine if long-term risk reduction goals were met by dredging alone.
- Dredging remains one of the few options available for the remediation of contaminated sediments and should be considered along with other options for managing risk. A remedy should be designed to meet long-term risk-reduction goals, and the design should be tested by modeling and monitoring the achievement of goals.
- Dredging is effective for removal of mass, but mass removal alone may not achieve risk-based goals.
- Dredging will likely have at least short-term adverse effects on the water column and biota, and effectiveness is limited by resuspension and release of contaminants during dredging and the generation or exposure of residual contamination by dredging. Adverse effects of resuspension, release and residuals should be forecast and explicitly considered in expectations of risk.
- Limitations are minimized if site conditions are favorable for dredging (e.g., little or no debris, ability to visually differentiate clean from contaminated sediment, ability to overdredge into clean material, lack of steep slopes or obstacles, absence of NAPL, conditions conducive to natural attenuation following dredging) and the project is appropriately designed.
- Effective design and implementation can be achieved with appropriate and adequate site characterization, identification and control of sources, use of pilot studies where appropriate, application of best management practices to control residuals and resuspension, contracting and procurement mechanisms that focus on achieving RGs and engagement of experienced and innovative environmental-dredging contractors throughout the design and implementation phases of remediation.
- Dredging alone is unlikely to be effective in reaching short-term or long-term goals at sites with unfavorable conditions, because increased contaminant resuspension, release and residual will tend to limit ability to meet CULs and delay the achievement of RAOs unless managed through a combination of remedies or alternative remedies. With unfavorable conditions, pilot tests should be considered for sites with unfavorable conditions to identify optimal remedial approaches and assess their effectiveness.
- The ability of combination remedies to lessen the adverse effects of residuals should be considered when evaluating the potential effectiveness of dredging.
- A good baseline assessment coupled with a well-designed, long-term monitoring plan should be implemented to permit evaluation of dredging effectiveness.
- Well-designed pre-dredging and post-dredging monitoring is necessary to establish effectiveness and indicate achievement of RAOs.
- Monitoring should be conducted to demonstrate achievement of CULs and to confirm that the CULs achieve RAOs.
- An adaptive management approach should be considered for sites where there is uncertainty regarding the potential effectiveness of dredging to achieve CULs.

13.11 DISPOSAL AND TREATMENT OPTIONS

The equipment and approaches used for dredging of contaminated sediment must be compatible with the subsequent transportation, rehandling, treatment and ultimate disposal of the dredged sediments. Disposal options normally considered for contaminated sediments include landfill placement, confined disposal facilities (CDFs) or contained aquatic disposal (CAD) sites. Dewatering and sediment treatment may also be considered. Detailed guidance for design of treatment and disposal options has been developed by the USACE, USEPA, and others (USACE, in publication; USACE/USEPA, 2004; USEPA, 2005; PIANC, 1996, 1998, 2002), and these sources should be used for detailed evaluations. A summary of the major considerations for treatment and disposal of contaminated sediments is provided in this section.

13.11.1 Transport, Staging and Dewatering

After removal, sediment often is transported to a staging or rehandling area for dewatering (if necessary), and further processing, treatment or final disposal. Transport links all dredging or excavation components and may involve several different modes of transport. The first element in the transport process is to move sediment from the removal site to the disposal, staging, offloading or rehandling site. Sediment may then be transported for pretreatment, treatment and/or ultimate disposal. Project design should call for as few rehandling operations as possible to decrease risks and cost. Community concerns regarding these operations (e.g., odor, noise, lighting, traffic and other issues) should also be considered, and health and safety plans should address both workers and community members.

Modes of transportation may include one or more of the following waterborne or overland methods:

- Pipeline – Direct placement of material into disposal sites by pipeline is economical only when the disposal and/or treatment site is located near the dredging areas (typically a few kilometers or less, unless booster pumps are used). Mechanically dredged material may also be reslurried from barges and pumped into nearshore disposal sites or to treatment facilities by pipeline.
- Barge – A rehandling facility located on shore is a commonly considered option. With a rehandling facility, dredging can be accomplished with mechanical (bucket) dredges where the sediment is excavated at near *in situ* density (water content) and placed in a barge or scow for transport to the rehandling facility.
- Conveyor – Conveyors may be used to move material relatively short distances. Materials should be in a dewatered condition for transport by conveyor.
- Railcar – Rail spurs may be constructed to link rehandling/treatment facilities to the rail network. Many licensed landfills have rail links, so long-distance transport by rail is generally an option.
- Truck/Trailer – Dredged material can be rehandled directly from the barges to roll-off containers or dump trucks for transport to a CDF by direct dumping or unloading into a chute or conveyor. Truck transport of treated material to landfills may also be considered. The material should be dewatered prior to truck transport over surface streets. In some smaller sites where construction of dewatering beds may be difficult or the cost of disposal is not great, addition of non-toxic absorbent materials such as lime or cement may be feasible.

Compatibility of the dredging operation with the subsequent transport of the dredged sediment is a key consideration. For example, hydraulic and pneumatic dredges produce contaminated dredged-material slurries that can be transported by pipeline to either a disposal or rehandling site. Mechanical removal methods typically produce dense, contaminated material hauled by barge, railcar, truck/trailer or conveyor systems.

Temporary storage of contaminated sediment may also be necessary in order to dewater it prior to upland disposal or to allow for pretreatment and equalization prior to treatment. For example, a temporary CDF may be designed to equalize flow streams for processing or treatment or to store dredged material for periods when dredging or excavation is not possible due to weather or environmental concerns, while the treatment process may continue on a near 24-hour operating schedule. Storage may be for temporary staging (e.g., pumping onto a barge with frequent off-loading) or more permanent disposal (e.g., moving the sediment to a land-based CDF where it may be dewatered and treated).

Dewatering is usually required prior to landfill disposal. If landfill placement is the anticipated disposal option, hydraulic dredging with mechanical dewatering may be considered. Mechanical dewatering uses a combination of hydrocyclones, belt filter or plate and frame presses, water treatment and other components depending on the requirements. The dewatering plants can also serve to separate sand fractions from fine silt/clay fractions.

Passive dewatering sites have been used for temporary placement of materials that were mechanically dredged. Such sites have used retaining dikes, similar to those for a CDF, or concrete barriers (e.g., so-called "Jersey barriers") to provide lateral containment for the material and for collection of drainage water for treatment. Rehandling sites can also serve as stockpiles for dewatered material from mechanical dewatering operations.

In-barge stabilization has also been used for dewatering and solidification/stabilization of mechanically dredged sediments prior to transport to landfills for disposal. This approach involves injection and mixing of agents in barges, and removal directly to trucks for transport to the landfill site. In-barge stabilization is especially attractive for small-volume removal projects.

CDFs provide an inherent dewatering function through gravity settling of sediment solids. In some instances, CDFs can be used as rehandling sites for temporary placement of dredged sediment prior to transport and disposal at another site. Additional discussion of CDFs as a permanent disposal approach is provided below.

Geotubes fabricated from various geotextile materials have been used for both the dewatering and final disposal of hydraulically dredged or hydraulically transported sediments. These tubes allow for the drainage of excess water through the geotextile and contain the fine-grained sediment solids. In some cases, the tubes may be stacked vertically to further induce drainage. Once drainage of the water is essentially complete, the tubes may be covered in place if the site is intended as a final disposal site, or the tubes may be opened and the dewatered dredged material removed and transported to a permanent disposal site.

Depending upon the quality of the water after it is separated from sediment and upon applicable or relevant and appropriate requirements (ARARs), it may be necessary to treat water prior to discharge. Where water treatment is required, it can be a costly segment of the dredging project and should be included in cost estimates for the alternative. Water treatment costs may also affect choices regarding dredging operation and equipment selection, as both can affect the amount of water entrained.

13.11.2 *Ex Situ* Sediment Treatment

Depending on the contaminants, their concentrations and the composition of the sediment, treatment of the dredged sediment (often referred to as *ex situ* treatment) to reduce the toxicity, mobility or volume of the contaminants before disposal may be warranted. Available disposal options and capacities may also affect the decision to treat some sediment. In general, treatment processes have the ability to reduce sediment contaminant concentrations, mobility and/or sediment toxicity by contaminant destruction or by detoxification, by extraction of contaminants from sediment, by reduction of sediment volume or by sediment solidification/ stabilization.

Treatment of sediment would not normally be considered prior to disposal for sediment sites with widespread low-level contamination. Also, treatment provides little benefit in many cases because end-products typically end up in a landfill. However, treatment is often considered in cases where there are no disposal sites available or when the treated product could be used beneficially.

The treatment of contaminated sediment is not usually a single process, but often involves a combination of processes or a treatment train to address various contaminant problems, including pretreatment, operational treatment and/or effluent treatment/residual handling. Some form of pretreatment and effluent treatment/residual handling are necessary at almost all sediment removal projects. Sediment treatment processes of a wide variety of types have been applied in pilot-scale demonstrations, and some have been applied full-scale. However, the relatively high cost of most treatment alternatives, especially those involving thermal and chemical destruction techniques, can be a major constraint on their use (NRC, 1997). The base of experience for treatment of contaminated sediment is still limited.

Pretreatment, such as particle size separation to distinguish between hazardous and nonhazardous waste disposal options, is common. Also, solidification/stabilization of sediments is often required prior to landfill disposal. High cost, uncertain effectiveness and/or (for onsite operations) community preferences are other factors that lead to treatment being selected infrequently at sediment sites. However, treatment of sediment could be the best option in some circumstances and innovations in *ex situ* or *in situ* treatment technologies may make treatment a more viable cost-effective option in the future.

13.11.3 Pretreatment

Pretreatment modifies the dredged or excavated material in preparation for final treatment or disposal. When pretreatment is part of a treatment train, distinguishing between the two components may be difficult and is not always necessary. Pretreatment is generally performed to condition the material to meet the chemical and physical requirements for treatment or disposal and/or to reduce the volume and/or weight of sediment that requires transport, treatment or restricted disposal. Pretreatment processes typically include dewatering and physical or size separation technologies.

Most treatment technologies require that the sediment be relatively homogeneous and that physical characteristics be within a relatively narrow range. Pretreatment technologies may be used to modify the physical characteristics of the sediment to meet these requirements. Additionally, some pretreatment technologies may divide sediment into separate fractions, such as organic matter, sand, silt and clay. Often the sand fractions resulting from separation contain lower contaminant levels and may be suitable for unrestricted disposal and/or beneficial use if it meets applicable standards and regulations. Selection factors, costs, pilot-scale demonstrations and applicability of specific pretreatment technologies are discussed in detail in USEPA's Assessment and Remediation of Contaminated Sediments (ARCS) Program Remediation Guidance Document (USEPA, 1994).

13.11.4 Sediment Treatment Technologies

Treatment technologies for sediment are generally classified as biological, chemical, extraction or washing, immobilization (solidification/stabilization) and thermal (destruction or desorption). In some cases, particle size separation is also considered a treatment technology. The following treatment technologies are among those that might be evaluated (USEPA, 2005):

- Bioremediation – the process in which microbiological processes are used to degrade or transform contaminants to less toxic or nontoxic forms.
- Chemical Treatment – processes in which chemical reagents are added to the dredged or excavated material for the purpose of contaminant destruction.
- Extraction/Washing – processes to remove organic and, in some cases, metal contaminants from the sediment particles.
- Immobilization or Solidification/Stabilization – processes that alter the physical and/or chemical characteristics of the sediment through the addition of binders, including cements and pozzolans.
- Thermal Treatment – incineration, pyrolysis, thermal desorption, sintering and other processes that require heating the sediment to hundreds or thousands of degrees above ambient temperatures.
- Particle Size Separation – separation of the fine material from the coarse material by physical screening.

It should be noted that most treatment technologies have not seen wide use because of high unit costs and difficulties treating sediments at the rate at which they are removed. Particle size separation and solidification/stabilization have comparatively lower unit costs and are more commonly implemented.

13.11.5 Sediment Disposal

The term “disposal” refers to the placement of dredged or excavated material and process wastes into a temporary or permanent structure, site, or facility. The goal of disposal is generally to manage sediment and/or residual wastes to prevent contaminants associated with them from impacting human health and the environment. Disposal is typically a major cost and logistical component of any dredging or excavation alternative. The identification of disposal locations can often be the most controversial component of planning and implementing a dredging remedy and, therefore, should be considered very early in feasibility studies.

Historically, contaminated sediment from a remediation project has been typically managed in upland sanitary landfills, or hazardous or chemical waste landfills, and less frequently in CDFs. Contaminated sediment has also been managed in CAD sites. On-site disposal options (usually CDFs or CADs) can offer great cost advantage versus off-site disposal options (usually landfills) that may involve significant transportation costs and high tipping fees. Dredging remedies become more attractive when such lower disposal cost options are available. Also, the sediment may have a beneficial use in an environment other than the aquatic ecosystem from which it was removed (e.g., foundation material beneath a newly constructed brownfield site), especially if the sediment has undergone treatment. As noted below, all disposal options have the potential to create some risk. These risks may result from routine practices (i.e., worker exposure and physical risks and volatilization) while other risks may result from unintended events, such as transportation accidents and contaminant losses at the disposal site. All potential risks should be considered when comparing alternatives. The ARCS program's *Remediation Guidance Document* (USEPA, 1994) provides a discussion of the available disposal technologies for sediment, including an in-depth discussion of costs, design considerations and selection factors associated with each technology. USACE design guidance (USACE, in publication) provides additional discussion of disposal options and design considerations.

13.11.6 Sanitary/Hazardous Waste Landfills

Existing commercial, municipal or hazardous waste landfills are the most widely used option for disposal of dredged or excavated sediment and pretreatment/treatment residuals from environmental dredging and excavation. Landfills also are sometimes constructed onsite for a specific dredging or excavation project. Landfills can be categorized by the types of wastes they accept and the laws regulating their operation. Most solid waste landfills accept all types of waste (including hazardous substances) not regulated as Resource Conservation and Recovery Act (RCRA) hazardous waste or Toxic Substances Control Act (TSCA) toxic materials. Due to typical restrictions on liquids in landfills, most sediment should be dewatered and/or stabilized/solidified before disposal in a landfill. Temporary placement in a CDF or pretreatment using mechanical equipment may therefore be necessary.

13.11.7 Confined Disposal Facilities (CDFs)

CDFs are engineered structures enclosed by dikes and specifically designed to contain sediment. CDFs have been widely used for navigational dredging projects and some combined navigational/environmental dredging projects but are less common for environmental dredging sites, due in part to siting restrictions/considerations. However, they have been used to meet the needs of specific sites, as have other innovative in-water fill disposal options; for example, the filling of a previously used navigational waterway or slip to create new container terminal space (e.g., Hylebos Waterway cleanup and Sitcum Waterway cleanup in Tacoma, Washington). In some cases, new nearshore habitat has also been created as mitigation for the fill. Under normal operations of a CDF, water is discharged over a weir structure or allowed to migrate through the dike walls while solids are retained within the CDF. Typically effluent guidelines or discharge permits govern the monitoring requirements of the return water. For CDFs, contaminants may be lost via effluent during filling operations, surface runoff due to precipitation, seepage through the bottom and the dike wall, volatilization to the air, and uptake by plants and animals. The USACE has published a suite of testing protocols for evaluating each of these pathways in the CDF Testing Manual (USACE, 2003). Controls are available for each of the contaminant pathways to control contaminant exposure, including water treatment for effluents and runoff, and capping for volatilization, runoff and uptake by plants and animals. Details regarding the use and engineering design of CDFs are available in the USACE Engineer Manual *Dredging and Dredged Material Management* (USACE, in publication).

13.11.8 Contained Aquatic Disposal (CAD)

Contained aquatic disposal is a type of subaqueous capping in which the dredged sediment is placed into a natural or excavated depression elsewhere in the water body. The depression provides lateral containment of the contaminated material. The depression for the CAD cell may be excavated using conventional dredging equipment if natural or historically dredged depressions are not available for use. Uncontaminated material excavated from the depression may be subsequently used for the cap (USACE, in publication; Palermo et al., 1998b). A related form of disposal, known as level bottom capping, places the dredged sediment on a level bottom elsewhere in the water body, where it is capped. Level bottom capping, however, may require more maintenance and be less resistant to erosion than traditional CAD approaches.

CAD has been used for navigational dredging projects (e.g., Boston Harbor, Providence River) but has been rarely considered for environmental dredging projects. However, CAD has been selected as the disposal option for remediation projects at Bermerton, Washington, and New Bedford Harbor, Massachusetts. In instances when neither dredging with land disposal nor capping contaminated sediment *in situ* is feasible, and it may be appropriate to evaluate CAD as a disposal option.

Several potential contaminant release pathways exist with CAD cells. Contaminants may be released as a mud wave outside of the boundaries of the CAD, or to the water column or air during placement of the contaminated sediment. Expulsion of porewater may also occur during the initial consolidation of the sediment following placement. Other releases are common to *in situ* caps, such as through erosion of the cap or movement of contaminants through the cap. USACE and USEPA have developed testing and modeling procedures for evaluation of these processes (Palermo et al., 1998a, b; USACE, in publication; USEPA, 1991; USACE/USEPA, 1998).

13.12 CHAPTER HIGHLIGHTS

- Source control should be implemented prior to dredging when practical to prevent recontamination.
- Dredging can serve as a form of source control when the contaminated sediment in a management unit is physically unstable or poses much higher risk than the surrounding management units.
- Accurate site characterization is essential to a properly designed contaminated sediment dredging remedy.
- Dredging must be combined with residuals management to achieve reliable risk reduction.
- A dredging or excavation alternative should include details concerning all phases of the project, including sediment removal, staging, dewatering, water treatment, sediment transport and sediment treatment, reuse or disposal.
- Transport and disposal options may be complex and controversial; options should be investigated early and discussed with stakeholders.
- In predicting risk reduction effects of dredging or excavation of deeply buried contaminants, exposure and risk are related to contaminants that are accessible to biota. Contaminants that are deeply buried have no significant migration pathway to the surface, and are unlikely to be exposed in the future and may not need removal.
- Environmental dredging should take advantage of methods of operation, and in some cases specialized equipment, that minimize resuspension of sediment and transport of contaminants. The use of experienced operators and oversight personnel is very important to an effective cleanup.
- A site-specific assessment of anticipated sediment resuspension, contaminant release and transport, and its potential ecological impacts should be conducted prior to full-scale dredging.
- Realistic, site-specific predictions should be made of residual contamination based on pilot studies or data from comparable sites. Where residuals are a concern, thin layer placement/backfilling, MNR or capping may also be needed.

- Excavation (conducted after water diversion) often leads to lower levels of residual contamination than dredging (conducted under standing water).
- A dredging or excavation project should be monitored during implementation to assess resuspension and transport of contaminants, immediately after implementation to assess residuals and after implementation to measure long-term recovery of biota and to test for recontamination.
- The equipment and approaches used for removal of contaminated sediment by dredging or excavation must be compatible with the subsequent transportation, rehandling, treatment and ultimate disposal of the dredged sediments.
- Pretreatment to include dewatering is often necessary prior to final disposal, depending on the disposal options. Treatment of sediment solids to reduce toxicity or mobility of contaminants may be considered, but are not often used because of high cost and the requirements for permanent disposal of the treated sediment.
- Disposal options for dredged contaminated sediment from a remediation project include placement in sanitary landfills, hazardous or chemical waste landfills and less frequently in CDFs or CAD sites. Factors for evaluation of disposal options include availability of disposal sites, proximity to the dredging site, volumes to be managed, levels of contamination and many other regulatory and institutional factors.

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CHAPTER 14

MONITORING REMEDIAL EFFECTIVENESS

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14.1 INTRODUCTION

Contaminated sediment remediation is a long-term, often decadal, process from initial characterization to achieving remedial action objectives (RAOs). Monitoring remedial effectiveness is critically important in contaminated sediment management. It seeks to answer the fundamental question of "Were we successful?" As a result, it is also a topic of great sensitivity. From a pragmatic point of view, there are many disincentives to conducting remedy effectiveness monitoring. What happens if the remedy is not "successful" and hundreds of millions of private and public dollars have been spent over many years of cleanup, after years of investigation and negotiation? Do we start over again? Determine it cannot be done? While this concern is very real, it does not outweigh the statutory requirements, cost accountability, human and ecological risk implications, and the standards of good governance and environmental stewardship that mandate remedy effectiveness be tracked and verified.

It is our belief that a rigorous monitoring program will improve the effectiveness of sediment remediation, or, at a minimum, uncover its limits, thereby modifying our expectations. Monitoring, if done well, will tighten the relationships between contaminated water and sediment and the adverse human and ecological effects targeted for remediation. At the same time, robust monitoring tightens the cause-effect associations between remedial actions and environmental improvements. Without such monitoring, decisions on cleanup areas and techniques have far less basis and chance for success (e.g., NRC, 2007).

This chapter focuses on remedial goal (or remedy effectiveness) monitoring and we differentiate that activity from performance and construction monitoring. Remedial goal monitoring assesses whether risk reduction objectives were achieved. Construction and performance monitoring assess whether the remedy was constructed as designed and whether the specific remedial technology is performing as expected (e.g., whether monitored natural recovery [MNR] is occurring at the anticipated rate; caps maintain contaminant isolation, and dredging achieved contaminant cleanup levels in the dredge area). This chapter presents the elements necessary to monitor remedial effectiveness and provides guidelines for the design of monitoring plans. Lines of evidence to support remedial effectiveness evaluations are presented along with technologies and techniques used to develop those lines of evidence. Finally, Case Study examples are provided to describe how technologies are used to develop lines of evidence and how that information supports decision making.

Ultimately, we hope this chapter helps to clarify how to (1) develop a strong remedial goal monitoring plan using a project's RAOs and conceptual site model (CSM) and (2) develop and test hypotheses that serve to answer if, and why or why not, the remedy was effective.

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14.2 MONITORING PHASES AND TIMEFRAMES

U.S. Environmental Protection Agency's (USEPA's) *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* states that a successful sediment remedy is one where selected sediment chemical or biological cleanup levels have been met and maintained over time and risks are reduced to acceptable levels (USEPA, 2005, p. 8–1). That document highlights four key metrics for remedy effectiveness:

- Short- and long-term remedy performance (reduction and maintenance of sediment contaminant levels) and
- Short- and long-term risk reduction (e.g., decreases in fish tissue levels or benthic toxicity).

This is the essence of remedy effectiveness: *Has the remedy reduced exposures and risk in the short- and long-term?*

14.2.1 Monitoring Phases

Monitoring at contaminated sediment sites is conducted during different phases of the remedial action for different purposes. USEPA (2005) describes the purposes of monitoring before and during remedial action as "(1) assess compliance with design and performance standards; (2) assess short-term remedy performance and effectiveness in meeting sediment cleanup levels; and/or (3) evaluate long-term remedy effectiveness in achieving RAOs and in reducing human health and/or environmental risk."

A similar distinction is provided in the U.S. Navy's Guidance for long-term monitoring and implementation (Navy, 2010, p. 14) where four monitoring phases are described: baseline monitoring, construction monitoring, performance monitoring, and remedial goal monitoring. This partitioning is useful because the different phases have different purposes and parameters. Briefly,

1. *Baseline monitoring* establishes a pre-remediation basis for comparison during subsequent performance or remedial goal monitoring.
2. *Construction monitoring* evaluates parameters directly related to the construction. For example, whether dredge depth or cap thickness was achieved. Construction monitoring data are used to answer the question: Is the remedy constructed as designed?
3. *Performance monitoring* evaluates specifically whether the remedial technology is performing as designed; for example, did the cap effectively isolate contaminated sediments; are sediment contaminant concentrations addressed under MNR declining at an appropriate rate? Performance monitoring data are used to answer the question: Is the remedy mechanism performing as designed?
4. *Remedial goal monitoring* (remedial effectiveness monitoring) evaluates whether contaminant exposures and corresponding risk are reduced (the purpose of the remedy) to acceptable levels. Remedial goal monitoring data are used to answer the question: Is the remedy achieving anticipated risk reduction?

The phases are distinguished by the purpose, logistics, and the monitoring parameters. While the purposes are distinct, there can be overlap of parameters; for example, sediment chemistry will be monitored during baseline, performance, and remedial goal monitoring.

It is particularly important to note the distinction between performance and remedial goal monitoring. Performance monitoring evaluates whether the remedy itself is performing as designed (e.g., the cap continues to isolate contaminated sediment), remedial goal monitoring evaluates if the overall goal of the remedy is being achieved (e.g., fish tissue contaminant concentrations have been achieved). Again, in this chapter, we focus on remedial goal monitoring, supported by baseline monitoring. The emphasis is on the biological receptors commonly intended to be protected by remediation (e.g., benthos, fish, or consumers of aquatic organisms, including humans) and the contaminant exposures driving risk to those receptors.

14.2.2 Timeframes

USEPA's sediment management "Principles" (USEPA, 2002a) and Sediment Guidance (USEPA, 2005) recommend monitoring "*during and after* remedial action" (italics added for emphasis). The 2005 Guidance clarifies that "Baseline data needed for interpretation of the monitoring data should be collected. . ."

To appropriately assess remedy effectiveness, data from four timeframes are needed:

1. *Baseline, pre-remediation*: Establish pre-remedy conditions and trends for comparison to post-remediation conditions.
2. *During remediation*: Monitor exposures and risks to receptors during remedy implementation, particularly for remedies that may require years or decades to complete. Increases in exposure – transient or otherwise – are important to understanding the level of protection afforded by the remedy as well as trends in the post-remedy timeframe.
3. *Immediately following remediation*: Establish post-remedy conditions soon after remedy implementation so that long-term monitoring data points have appropriate context and can inform on mechanisms influencing remedy effectiveness, such as recontamination. Navy Guidance (Navy, 2010) includes this timepoint as "baseline monitoring" because it serves as a subsequent reference point; regardless of terminology, this "time = 0" timepoint is critical for understanding post-remediation trends and remedy effectiveness.
4. *Long-term*: Monitor in the post-remediation timeframe to establish whether performance standards and RAOs are achieved.

14.3 EFFECTIVE COMPARED TO WHAT?

Any statement regarding remedy effectiveness inherently contains a comparison: Has a performance standard been achieved? Do trends (e.g., a rate of decline in contaminant concentrations) indicate that a remedial goal can be achieved at a future timepoint? Are conditions better than they were? Are conditions now similar to an unimpacted reference area? To assess the effectiveness of a remedial action, there are three requirements. First, the objective of the remediation needs to be stated in terms that are measurable. Second, a pre-remediation baseline needs to be established for comparison to the post-remediation condition. Finally, the monitoring plan design needs to be capable of answering whether the objectives were achieved.

14.3.1 State Your Objective

The first step in monitoring for remedial effectiveness is to have clear RAOs linked to measurable performance standards. Typically, RAOs are narrative statements intended to provide a general description of what the cleanup is expected to accomplish (USEPA, 2005, pp. 2–15).

Cleanup levels[1,2] establish the contaminant concentrations in various environmental media to be achieved by the remediation. To best support remedy effectiveness monitoring, the RAOs should be supported by quantitative statements including cleanup levels that describe expectations of the remedy. Those statements should document the "what, where, and when" of the conditions that are to be altered by the remedy.[3] For example, the remedy is expected to reduce adult largemouth bass contaminant concentrations to 20 micrograms per kilogram (μg/kg) wet weight in [a specified area] within 10 years following implementation, or, post-cleanup, surface sediment samples (top 10 centimeters [cm]) within [a specified area] will achieve a surface-weighted average concentration of 50 μg/kg dry weight. The need for quantitative statements describing expectations of a remedy is expressed in the National Contingency Plan (NCP), the implementing regulations of the Superfund Program, where the Agency is directed to

> *Establish remedial action objectives specifying contaminants and media of concern, potential exposure pathways, and remediation goals…Remediation goals shall establish acceptable exposure levels that are protective of human health and the environment and shall be developed…40 CFR 300.430(e)(2)(i)*

Such quantitative statements provide a basis for evaluation and form the hypothesis that is tested via a structured monitoring program. The cleanup level may be risk-based; for instance, fish tissue contaminant levels derived from risk assessment procedures. Or, cleanup levels may be set at "background"contaminant concentrations. For sites where risk-based concentrations are achievable only in the long-term, then interim objectives may be appropriate. For example, the Hudson River Record of Decision (USEPA, 2002b) selected a risk-based concentration in fish tissue of 0.05 milligram per kilogram (mg/kg), but also included 0.4 and 0.2 mg/kg polychlorinated biphenyls (PCBs) as target concentrations with the intention that, if achieved, such levels could trigger relaxing of the fish tissue consumption advisory.

14.3.2 Establish a Baseline

An adequate pre-remediation baseline needs to be established to provide the basis for comparison to the post-remediation condition (USEPA, 2005). Once remediation begins, the capped or dredged areas cannot represent conditions in the absence of remediation. Baseline

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[1] In practice, there is great variety in the terminology (and nuance in meaning) associated with the contaminant concentrations that are to be achieved in various media by the remediation. Such terms include cleanup levels, cleanup goals, chemical and biological standards, remedial goals, cleanup criteria, target concentrations, performance goals, performance metrics, and performance standards. Federal Guidance (2005) does not precisely define the terms and their usage; that issue is still in flux (Ells, 2011).

[2] The term "cleanup level" is used here and is defined simply as the contaminant concentration (in whatever media is specified) that will achieve the risk reduction targeted by the remediation. The term "remedial goal" was not used because it typically specifies a "protective" concentration (see NCP quote in text), which may not be the target of a specific remedial action (e.g., if background or an interim concentration is to be achieved).

[3] The application of "cleanup levels" can vary: at some sites, a cleanup level may be expected immediately post-remediation; another may have one cleanup level to be achieved immediately post-remediation and another to be achieved 10 years post-remediation. Some large sites with a patchwork of contamination may have higher cleanup levels set for certain areas that, when integrated across the entire site, achieve a lower site-wide cleanup level. Those variations are site-specific, and not central to the main point: cleanup levels need to be specified that clearly define the concentration, area, and time of anticipated attainment.

monitoring informs what would have happened absent remedial activities. Baseline conditions are used to develop the "no action" scenario, which is used when comparing the expected performance of remedial options in a feasibility study. Two options exist for establishing baseline: (1) pre-remediation trends in sediment and organism contaminant levels are monitored in the targeted remediation area, assuming that pre-remedy trends would continue in the absence of remediation and/or (2) an unremediated area with similar environmental and chemical characteristics is monitored. The latter option is rarely used, and emphasizes the importance of monitoring sufficient time points prior to remediation to establish trends. Establishing trends – in contrast to a single monitoring point – is necessary to capture any ongoing changes occurring in the absence of remediation (NRC, 2007; Bridges et al., 2010). Static conditions cannot be assumed. Still, a single year of baseline characterization to establish pre-remediation conditions is preferable to none for evaluating remedy effectiveness. Box 14.1 uses two Case Studies to emphasize the value of baseline in interpreting site monitoring data.

BOX 14.1 Long-Term Monitoring With and Without Baseline

Baseline data provide a critical context for assessing remedy effectiveness. Baseline is fundamental to evaluating whether the remediation has improved the condition (in contrast to whether a numerical objective has been achieved). Two site examples are provided here to highlight the importance and use of a robust baseline data set.

Tabbs Creek. Tabbs Creek (Figure 14.1) collected robust sample sizes of mummichogs annually for 7 years following remediation. The data set is quite useful for showing post-remediation concentration trends over time. However, a baseline remediation data set is not provided (Tetra Tech EC, 2009). The site's record of decision (USEPA, 1998a, Appendix A) does present a data point for "fish" at sampling stations, but no species or year are provided for context.

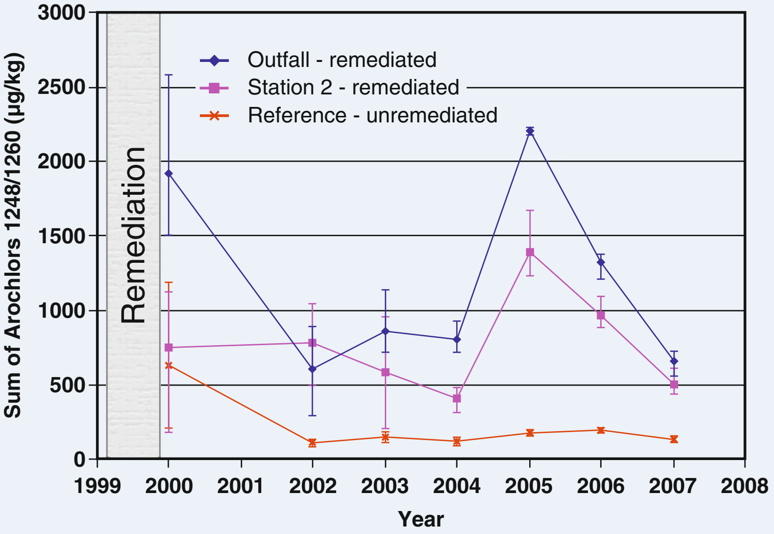

Figure 14.1. Post-remediation mummichog PCB concentrations at Tabbs Creek, Virginia. In 1999 and 2000, 12,371 t of sediment were dredged from the site and the dredged area was backfilled. The goal was to remove all sediments greater than 5 ppm of total PCBs and PCTs (polychlorinated terphenyls). Mummichog sampling consisted of three replicate, composite, whole body samples (20 individuals per composite) taken for 7 years post-remediation (data from Tetra Tech, 2009).

(continued)

BOX 14.1 (continued)

Without pre-remediation data, the effect of the remediation is unclear. Post-remediation monitoring data have no context for evaluating the effectiveness of the remedial operation. While the fish tissue contaminant levels could be compared to numeric cleanup levels (though none existed), the impact of the remediation cannot be ascertained.

Bryant Mill Pond. In contrast, the state of Michigan has monitored fish tissue contaminant concentrations in Portage Creek at the location of the (former) Bryant Mill Pond, which was remediated in 1999 (see Figure 14.2). Baseline fish tissue concentrations were collected at several time points prior to remediation and trend analysis was conducted to depict the expected trend in those concentrations into the future. That information was used to compare to post-remediation fish tissue contaminant concentrations. The analysis concluded that the removal action accelerated the rate of recovery in fish contaminant levels (CDM, 2009). Overall, the baseline data provide an appropriate context to evaluate the extent to which the remediation improved the primary indicator of health risk at the site.

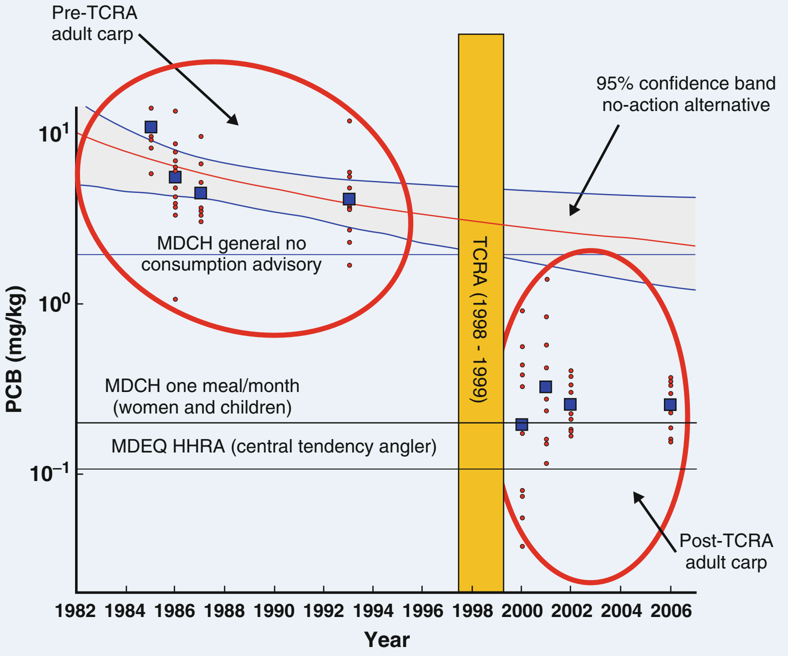

Figure 14.2. Baseline and post-remediation adult carp PCB concentrations in Bryant Mill Pond on Portage Creek, Michigan. In 1998 and 1999, Portage Creek was diverted and the pond area was dry excavated, removing 146,000 cubic yards to 1 ppm (cleanup level). Individual data for adult carp fillets analyzed for Aroclors are presented (CDM, 2009).

14.3.3 Develop a Plan

A monitoring plan needs to be structured to answer whether the RAOs and their related cleanup levels were achieved. Prior to remediation, monitoring endpoints and cleanup levels need to be established to determine whether the remedy was effective. Data collection has to be of sufficient spatial and temporal resolution to establish trends and rates of change, discern differences between sampling points, and confidently depict the levels that are being sought.

Consistency in sampling methods and parameters (e.g. season, locations and techniques) over time is critical; if these change, the ability to assess temporal differences (hence, remedial effectiveness) may be lost.

These concepts will be further addressed in the section on monitoring plan design and data quality objectives (DQOs), but their importance to remedy effectiveness monitoring warrants early, central emphasis. Monitoring plan elements should be developed as early in the process as possible – well before the remedy is implemented – and as early as it is understood which receptors are to be protected to what level. Implementation should also begin on a timely basis, prior to remedial action, in order to establish a baseline.

14.4 MONITORING TOOLS AND APPROACHES

There are a number of comprehensive resources that compile and describe technologies available for monitoring remedial effectiveness at sediment sites (Table 14.1). The choice of approaches or technologies for monitoring remedy effectiveness should be derived from RAOs and the CSM. The RAOs define the receptors of concern. The CSM represents the site's contaminant sources, transport pathways, exposure pathways, and receptors (USEPA, 2005) and guides the selection of the most important parameters to incorporate in the monitoring plan (See additional discussion in Section 14.5). This chapter does not seek to document all available approaches; rather it emphasizes those that have proven useful at sites.

Because contaminant exposures occur through various media and pathways to impact various receptors, monitoring plans frequently evaluate multiple parameters. Information derived from analyses or sampling technologies are commonly referred to as lines of evidence.[4] Rarely would a single endpoint or data source be sufficient to fully depict the risk to receptors at a site and the effect that remediation has had on the system. So, multiple lines of evidence are collected to depict contaminant exposures and effects. Table 14.2 presents commonly used lines of evidence, along with technologies for collecting those lines of evidence and their purpose in supporting remedy effectiveness evaluations. Section 14.8 provides Case Study examples of the uses of these lines of evidence to support site decision making.

Table 14.1. Technical Resources on Sediment Sampling Tools and Approaches

Document	References
A compendium of chemical, physical and biological methods for assessing and monitoring the remediation of contaminated sediment sites.	Battelle, 2003
A guidance manual to support the assessment of contaminated sediments in freshwater ecosystems. Volumes I–III.	MacDonald and Ingersoll, 2002
Long-term monitoring strategies for contaminated sediment management. Final guidance document.	Navy, 2010
Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: technical manual.	USEPA, 2001

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[4] See Magar et al. (2009) for a useful discussion on lines of evidence and their use to support decision making.

Table 14.2. Lines of Evidence for Supporting Remedy Effectiveness Evaluations

Line of Evidence	Example Technology or Technique	Purpose
Exposure pathways		
Sediment contaminant chemistry	Cores and grab samples	Document contaminant levels in sediments
Water column contaminant chemistry	Grab samples, composite samplers	Document contaminant levels in water column
Porewater contaminant chemistry	Grab samples, *in situ* or *ex situ* passive samplers	Document contaminant levels in porewater
Effects on receptors		
Benthic toxicity	Laboratory or *in situ* based organism toxicity tests (e.g., 28-day evaluations of mortality in the sediment-dwelling oligochaete *Lumbriculus variegatus*)	Document toxic effects of sediments to sediment-dwelling organisms
Contaminant bioaccumulation analyses	Laboratory or *in situ* monitoring of contaminant accumulation in benthic organisms accumulation (e.g., 28-day evaluations of contaminant accumulation in the sediment-dwelling *L. variegatus*)	Document uptake of contaminants into organisms from sediments
Contaminant concentrations in resident organisms	Monitoring of contaminants in electroshocked or trapped fish from the area of concern	Establish contaminant levels in organisms resident to the area of concern. The line of evidence serves as a proxy for potential effects to humans via consumption or directly to assess adverse effects to the organism (when toxicity data exist for comparison)
Benthic community indices	Monitoring benthic community diversity and/or pollution tolerance	Document health of benthic community structure and quantity

14.5 SELECTING RELEVANT INDICATORS OF EFFECTIVENESS

There are no requirements or guidance documents that direct the use of particular endpoints or technologies for documenting remedy effectiveness. USEPA's (2005) sediment remediation guidance states simply that:

> *Selection of endpoints depends on the requirements in the decision and/or enforcement documents, as well as more general considerations related to the cleanup methods selected and the phase of the operation…*

So, can direction be provided beyond "monitoring endpoints and approaches are site-specific"? Overall, monitoring is conducted to demonstrate that the objectives of the remediation are met; this entails directly monitoring the biologic receptors that are the Focus of the RAO[5] and the contaminant exposures driving risk to those receptors (i.e., it is not sufficient to simply monitor effects to the receptor to establish remedial effectiveness). See Box 14.2 for further discussion.

BOX 14.2 Monitoring Requirements: Regulatory and Scientific Perspective

At contaminated sediment sites, the question arises, "What do I need to monitor?" At least at the federal level, there are no specific requirements that define endpoints or media to be monitored. Indeed, a review of site experiences indicates wide variation in monitoring programs at remedial sites. Whereas some sites have used several inter-related lines of evidence capable of evaluating remedial effectiveness, others have collected only construction monitoring data (NRC, 2007).

Starting with the assumption that you need to monitor the target of your RAOs (e.g., fish contaminant levels or benthic toxicity), then what else is necessary? That is, if fish contaminant levels and/or benthic toxicity are being measured, is it necessary to also measure contaminant levels in water and sediments? These exposure data serve to verify the CSM; for example, if the biological monitoring data (e.g., fish tissue concentrations) are not improving, they can assist in evaluating why improvements did not occur. The reasons to not sample the environmental matrices presumed responsible for the adverse effects warranting remediation are expediency, cost, or avoidance of complications arising from the collected information. However, there is not a technical basis to eschew that sampling.

From a management or accountability viewpoint, contaminated sediment remediation is conducted (at substantial public and private cost) to eliminate or lessen contaminant exposures to receptors of concern from sediments. The effect of the remediation on targeted exposures needs to be evaluated to appropriately ascertain the effectiveness of the remediation.

RAOs document the purpose of the remedy and condition (or receptors) to be improved, and they "should reflect objectives that are achievable from the site cleanup" (USEPA, 2005). Presumably this means the RAOs and associated cleanup levels should be attainable; in turn, that attainment should be measurable. The CSM delineates the media and processes that drive risk to the relevant receptors. For example, RAOs at contaminated sediment sites commonly seek to protect benthic communities from exposure to harmful sediment contaminant concentrations or humans from exposure during consumption of fish (or shellfish) with elevated contaminant concentrations. In these instances, remedial goal monitoring would evaluate benthic toxicity and fish tissue contaminant levels, respectively. RAOs are the basis of endpoint selection and monitoring plan development. The CSM is used to identify monitoring parameters that document contaminant exposures that drive the unacceptable risk to receptors of concern. At sediment sites, these exposures will include sediment contaminants (as monitored by bulk sediment or sediment porewater chemistry), but may include other pathways such as soluble

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[5] In some instances, biologic receptors may not be specified, as the objective of the sediment remediation may be to reduce flux of contaminants from the remediated area. In this case, contaminant flux would be the primary determinant of remedial effectiveness.

contaminants in the water column. Monitoring contaminant exposure pathways (Table 14.2) serves overlapping roles. For performance monitoring, it verifies that the remediation had its intended operational effect. For remedial goal monitoring, it assesses whether the remedy reduced exposures as anticipated. The concordance of exposure and effects (or tissue residue) data is also used to verify (or modify) the CSM and assess whether remedy modifications are needed. For example, if, following successful remediation of sediment contaminant exposures, fish tissue contaminant levels do not decline, the CSM was not correct and further refinement is required.

Endpoints appropriate for remedial goal monitoring will also be influenced by the environmental setting. For example, at geographically large sites or sites that represent the primary source of contaminants to a water body, the remediation may be expected to decrease contaminant concentrations in site-wide populations of upper-trophic-level fish that are often targeted for consumption by humans. At smaller sites that lie within a water body impacted by a range of sources and areas, remedial goal monitoring may focus solely on local conditions by evaluating contaminant levels in benthos or fish with home ranges limited to the geographic areas of the site (in this instance, it would not be reasonable to anticipate decreases in tissue contaminant concentrations of wide-ranging fish). Alternatively, remediation at such a site may only be expected to reduce contaminant loading to the water body or food web (ostensibly, a source control effort). Here, contaminant flux from the area, sediment bioaccumulation or bioavailability assessments would be the primary endpoints to assess remedial effectiveness.

Ultimately, site managers are responsible for establishing the endpoints influenced by the remediation and the extent to which those endpoints are expected to be improved, and hence, risks reduced. These are the hypotheses the monitoring plan evaluates. The selected monitoring endpoints – whether they are wide-ranging upper-trophic-level fish or stationary benthos – are site-specific. Risk managers need to ensure they can be linked to the remediation and that they appropriately represent the RAOs of the project (NRC, 2007; Gustavson et al., 2008).

14.6 DEVELOPING A MONITORING PLAN: DATA QUALITY AND DATA MANAGEMENT

A monitoring plan establishes the monitoring objectives, and the monitoring parameters, locations, and frequency to meet the monitoring objectives. The monitoring plan should include documentation that ensures data quality and data management such that it complies with the Data Quality Act of 2001 (PL 106–554, Section 515). This legislation was passed by the U.S. Congress to ensure the “quality, objectivity, utility, and integrity of information, including statistical information” that may be used to support any federal agency’s position, decision, regulation, guidance, or dissemination of information.

Within the context of a monitoring plan, the RAOs should be specifically addressed through the development of monitoring DQOs. The DQO process helps to ensure that the proposed data collection and analysis is capable of answering the questions for which they were proposed. In the context of remedial effectiveness, this is whether the RAOs and associated cleanup levels have been achieved.

The USEPA’s Quality Program Procedures[6] contain numerous guidance documents including the use of DQOs, quality assurance project plans (QAPPs), and sampling designs – all of which are useful to ensuring the conduct of a technically- and legally-defensible

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[6] http://www.epa.gov/quality/qa_docs.html. Accessed July 31, 2012.

monitoring program. Additionally, more specific guidance on QAPPs for efforts that include geospatial data and modeling – which are common at sediment sites – are also provided. Database management is also important to establish early in the monitoring program, particularly because the monitoring program itself may last from years to decades whereas the parties and software may change over time.

14.7 ADAPTIVE MONITORING AND DECISION CRITERIA

The monitoring program for a site should be set up to be adaptive. Much has been written about the general practice and utilization of adaptive management (NRC, 2003, 2004), and this chapter will not reiterate those points. What adaptive monitoring means here is that as the data are collected and evaluated, changes or refinements to the monitoring plan (e.g., increase/decrease in sampling periodicity or sample sizes) can be made for many reasons. Technical examples informing such changes include: (1) a cleanup level, or RAO, or interim target or benchmark has been met; (2) a significant trend, expected trajectory, or percentage change in a line of evidence or monitoring endpoint has been (or not been) demonstrated by the data (e.g., slope of decline or percentage reduction of contaminant concentration in fish tissue); (3) the data have shown that the DQO for a monitoring endpoint cannot be adequately evaluated under the current sampling design; or (4) recovery of an ecological monitoring endpoint has been demonstrated (e.g., benthic community established and stable, reduction in toxicity). Cost considerations are also an important factor when establishing a monitoring plan, and they should be revisited throughout the program to additionally inform decisions on changes, additions, or refinements to the monitoring. The monitoring plan should be cost-effective and implementable.

The decision criteria that will be used as the basis for changes to the monitoring program should be developed prior to its onset, or as early as practicable. This is important given that for most contaminated sediment sites – especially those where the cleanup decisions were based on persistent organic contaminants like PCBs – the ultimate benefits of the remedy are not expected to be realized until decades into the future. This long-term expectation for achieving the RAOs poses challenges to the site technical team such that the monitoring program needs to be capable of: (1) demonstrating that a remedy is moving toward the RAOs in the short term (months to years), and (2) establishing a database that is adequate for evaluating whether the RAOs have been achieved over the long-term.

On a site-specific basis, it is possible that more intense monitoring is needed in the short term (5–10 years) following implementation of a remedy. Once the immediate post-remedial conditions, including failure, are understood and/or the temporal and spatial trends of key lines of evidence (i.e., fish tissue, sediment concentrations) are established, the frequency and/or sample sizes of the monitoring can be reduced while ensuring that the expected trajectory of recovery is still accurate. Decision criteria for the shorter term evaluations of post-remedial conditions and trends should define a goal (e.g., an acceptable concentration or rate of decline in fish tissue concentrations), and then define the statistical tests that will be used to ascertain whether that goal was achieved. Those decision criteria should function to demonstrate the status of the remedy (i.e., approaching or achieving RAOs/targets/goals or failing to do so) and inform decisions on whether the monitoring plan needs to be changed, or whether another aspect of the remedy (e.g., scope of remedial action, project objectives) needs to be revised under adaptive site management. The application of statistical power analysis and determination of minimum significant differences that are achievable under various sampling design options is helpful to ensure that adequate sample sizes are collected (USEPA, 2008). Finally, the decision criteria should also be used for ending the monitoring program (i.e., exit criteria) when there is confidence that the cleanup levels and RAOs have been achieved. Those analyses would use the same technical and statistical bases as described above, but be specific to the RAOs.

14.8 CASE STUDIES: LINES OF EVIDENCE IN REMEDY EFFECTIVENESS MONITORING

In this section, Case Studies are outlined to provide a practical perspective on the implementation and use of the lines of evidence outlined in Table 14.2. Examples are not comprehensive reviews of site activities or sampling efforts, but are intended to present how a specific line of evidence was developed and used. Details are provided on the site, remediation, sampling, and use of the data to support decision-making for several Case Studies (Table 14.3). The reader is referred to site references for further detail.

14.8.1 Sediment Contaminant Chemistry, New Bedford Harbor, Massachusetts

Background. New Bedford Harbor was listed on the National Priorities List (NPL) in 1984 due to sediment contamination with PCBs and metals from historical industrial discharges (USEPA, 1998b). Several projects, including dredging, shoreline excavations, and a pilot-scale sediment cap, have occurred at the site since the early 1990s to address the contamination. The "North of Wood Street" area is the upstream area of the harbor, where the Acushnet River enters the harbor. In 2002–2003, earthen berms were constructed above and below the area, the river flow was diverted, and contaminated sediments between the berms were excavated in the dry. Shoreline areas were excavated and replaced with clean fill (Tetra Tech FW, 2005).

Sampling Description. Samples were collected following remediation to determine whether cleanup goals had been achieved; 61 samples were taken throughout the 3.8 acre sediment bed remediation area. The data showed an average concentration of 7.0 parts per million (ppm) in the remediation area (Tetra Tech FW, 2005), which was below the 10 ppm "cleanup criteria" for sub-tidal sediments. Post-remediation, monitoring of PCBs in the top 6 inches (in.) of sediments was conducted to assess recontamination of the excavation area and was planned to include 20% of the original sample locations (Tetra Tech FW, 2005). Post-remediation sampling has been conducted multiple times since 2004; several locations have been consistently sampled over that period. Figure 14.3 (from Battelle, 2009) shows data from the repeat sampling locations between 2003 and 2008.

Table 14.3. Case Study Examples of Lines of Evidence Used in Decision Making at Contaminated Sediment Sites

Line of Evidence	Site
Sediment contaminant chemistry	New Bedford Harbor North of Wood Street Remediation, Massachusetts
Water column contaminant chemistry	Hudson River Implementation Monitoring, New York
Porewater contaminant chemistry	Grasse River Activated Carbon Pilot, New York
Benthic toxicity	Ward Cove, Ketchikan, Alaska
Contaminant bioaccumulation analyses	Grasse River Activated Carbon Pilot, New York
Contaminant concentrations in resident organisms	Cumberland Bay, Lake Champlain, New York

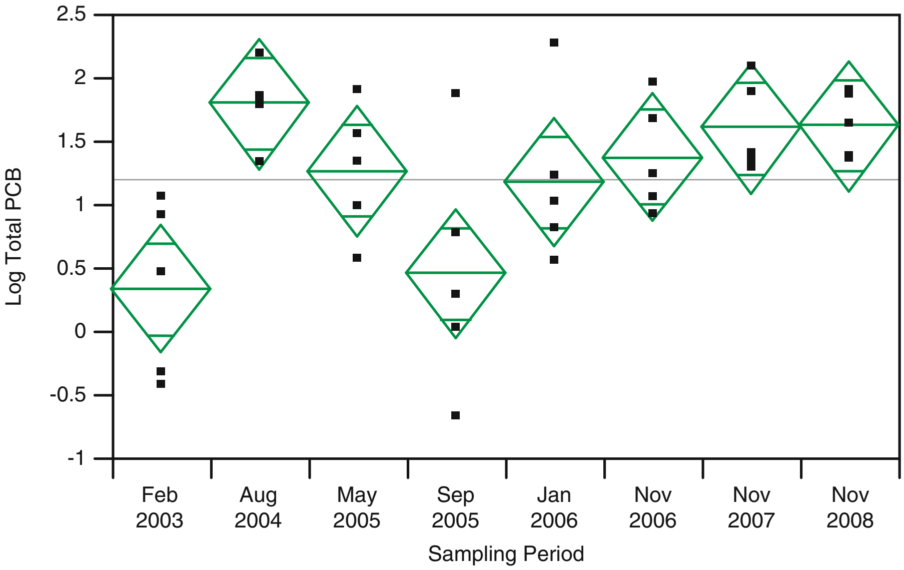


Figure 14.3. Temporal trends in total PCB (log scale) in river sediment at sampling stations North of Wood Street (2003–2008). *Squares* represent individual points; *top* and *bottom* of the *diamonds* are the 95% confidence interval of the mean (excerpted from Battelle, 2009).

Use of Data. The objective of the post-remediation sediment contaminant monitoring was to assess the effectiveness of prior remediation and potential recontamination of this area due to sediment transport from unremediated areas of the Harbor (Battelle, 2009). The lowest sediment PCB concentrations were seen just after remediation. A post-remediation increase was observed in 2004 and recent years remain elevated compared to 2003 (Figure 14.1). These data provide empirical evidence on sediment movement and recontamination. Annual sediment monitoring is slated to continue at the North of Wood Street area to assess recontamination from adjacent unremediated harbor areas (Battelle, 2009).

14.8.2 Water Column Contaminant Concentrations, Hudson River, New York

Background. Sediments in the Hudson River, New York, are contaminated by PCBs associated with manufacturing processes and waste discharges to the river. Following an interim No Action decision in 1984, the 2002 Record of Decision called for dredging of areas within a 40-mile stretch of the river between Hudson Falls, New York, and the Federal Dam at Troy, New York (USEPA, 2002b). Phase 1 dredging began in 2009, using a number of barge-mounted mechanical excavators with sediments transported by scow to a shore-based off-loading facility. During dredging activities, the water column was sampled to assess releases of PCBs to the water column (Louis Berger Group, 2010).

Sampling Description. As part of the site's Engineering Performance Standards, sampling for PCBs in the water column was conducted at several locations downstream of active dredging operations (Malcolm Pirnie Inc. and TAMS Consultants, 2004). Thompson Island Dam, the closest downstream sampling station, was located approximately 2–5 miles downstream from where dredging occurred. Sampling was taken daily from fixed sampling inlets as a 24-hour composite at transects across the river. Unfiltered (whole) samples were analyzed for "tri + PCBs" (PCB congeners with three or greater chlorine atoms) (Anchor QEA, 2009).

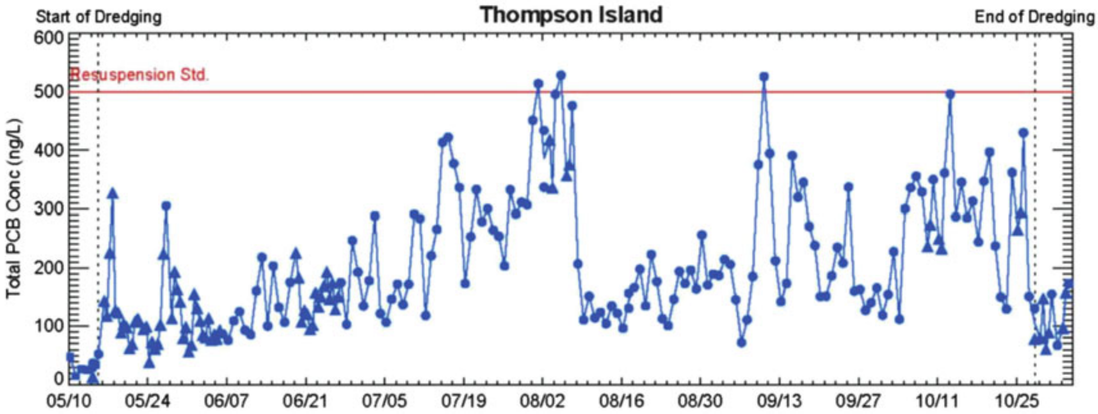


Figure 14.4. Tri+total PCB concentrations in Hudson River whole water samples taken at Thompson Island, downstream of 2009 dredging activities (excerpted from Anchor QEA, 2009).

Use of Data. The primary objectives of the water column monitoring were to evaluate conformance with USEPA's Safe Drinking Water Act Maximum Contaminant Level (MCL) (500 nanograms per liter [ng/L] parts per trillion [ppt]) and to minimize the release of PCBs to downstream areas (Louis Berger Group, 2010). Data indicate that Phase 1 dredging activities increased water column concentrations of PCBs that were available for downstream transport, including three exceedances of the MCL (Figure 14.4). These data were used directly to trigger shutdown of the Phase 1 dredging operations when the MCL was exceeded. In addition, the data have been used to: (1) estimate the amount of contaminants released and transported by dredging activities; (2) provide insight on aqueous exposure concentrations to fish in the study area; and (3) inform improvements to the project design and operation to minimize such increases in water column PCBs during Phase 2 dredging that began in 2011.

14.8.3 Contaminant Concentrations in Porewater, Grasse River, New York, Activated Carbon Pilot

Background. Sediments at the Grasse River site near Massena, New York, are contaminated with PCBs released during historical waste discharges. To support the development of remedial alternatives within the feasibility study for the site, several pilot studies have been conducted to evaluate capping, dredging, addition of activated carbon, and MNR as remedial options for PCB-contaminated sediment (Alcoa, 2010). The Activated Carbon Pilot Study (ACPS) was initiated in 2006 to evaluate whether granular activated carbon placed in sediments reduces the bioavailability of PCBs in sediments. The ACPS evaluated different placement and mixing techniques in a 0.5-acre test area of the river bed; results were compared to an untreated background area within the site. To date, post-remediation monitoring was conducted over three consecutive years (2007–2009).

Sampling Description. Amongst other parameters, porewater contaminant chemistry has been monitored to evaluate changes in PCB bioavailability since the addition of carbon to the sediments. Two methods have been used: (1) laboratory batch equilibrium testing and (2) *in situ* passive sampling with polyoxymethylene (POM). Passive samplers, such as POM, accumulate only the freely-dissolved contaminants, which can be quantified and used to estimate the freely-dissolved concentration in the porewater. Three to six replicate sediment samples were taken for the batch testing in the treatment and reference areas (Alcoa, 2010). Batch equilibrium testing involves equilibrating sediment samples with overlying water during mixing and analyzing the aqueous phase for contaminant concentrations after suspended particulates are

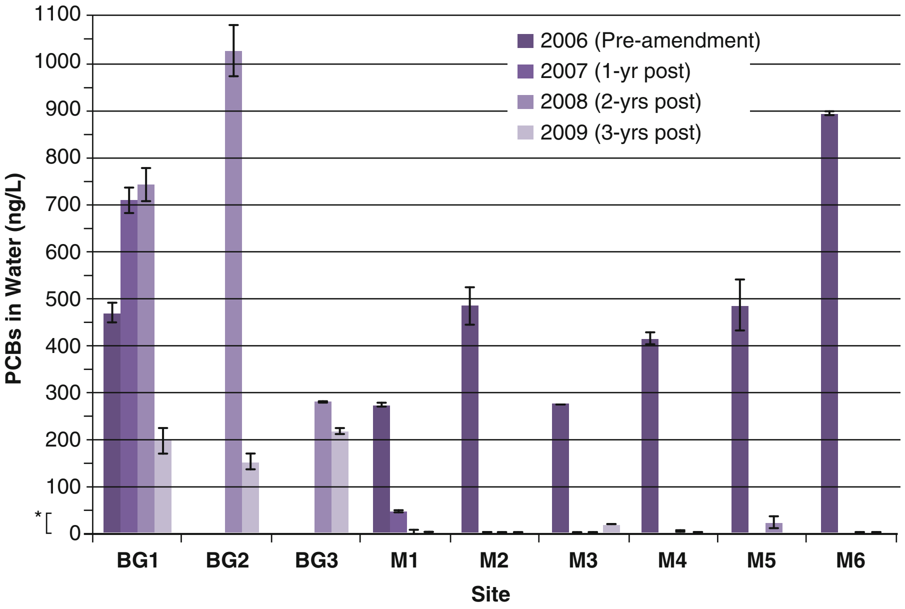


Figure 14.5. Aqueous equilibrium PCB concentrations in sediment porewater for background and activated carbon treatment area based on batch equilibrium measurements. BG – background; M 1–6 are locations within the treatment area (excerpted from Alcoa, 2010).

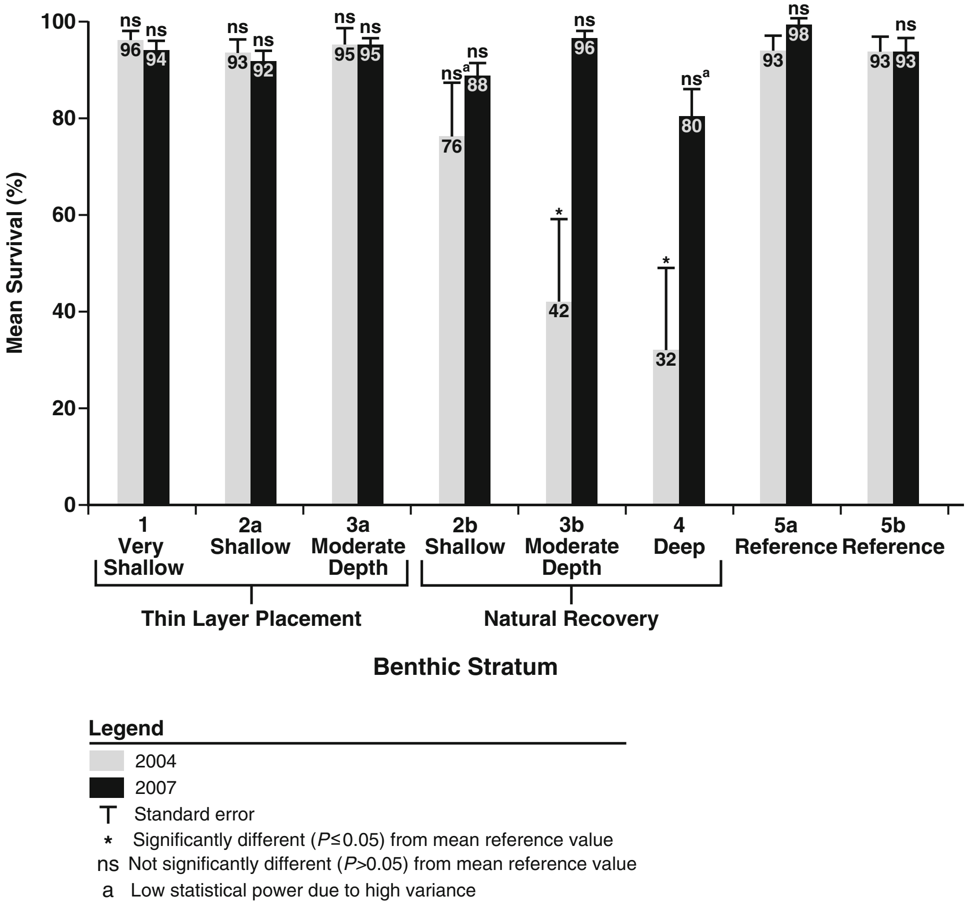
removed by flocculating with alum (Alcoa, 2006). *In situ* POM exposures were tested initially on a trial basis in 2006 and 2007, with more sites added in 2008 and 2009. Porewater results indicating the effectiveness of the carbon amendment for reducing porewater PCB concentrations are shown in Figure 14.5.

Use of Data. These data indicate that the treatment with activated carbon substantially decreased concentrations of PCBs in interstitial porewater, which indicates reduced bioavailability of the contaminants (Alcoa, 2010). This information indicates the potential for integrating activated carbon placement into the site remedy during the remedial design phase.

14.8.4 Benthic Toxicity, Ward Cove, Ketchikan, Alaska

Background. Sediments in Ward Cove, Ketchikan, Alaska, were contaminated from historical releases of large quantities of organic material as byproducts from wood pulping. Cleanup targeted ecological risks associated with the benthic toxicity of three contaminants of concern (ammonia, 4-methlyphenol, and sulfide) in sediments (USEPA, 2000). Remediation took place from 2000 to 2001, over 80 acres. The selected remedy included areas of MNR, placement of 6–12 in. of sand ("thin layer placement"), or dredging (USEPA, 2010). The RAOs at the site were to reduce toxicity of surface sediments and enhance recolonization of surface sediments to support healthy marine benthic macroinvertebrate communities (USEPA, 2000).

Sampling Description. Sediment sampling was specified to occur in July every third year after completion of the remedial activities (e.g., 2004 and 2007) until RAOs were achieved (Integral, 2009). Toxicity testing was one line of evidence used to evaluate attainment of the RAOs. Toxicity of the surface sediments was tested using the 10-day amphipod acute toxicity test based on *Eohaustorius estuarius*. Two reference areas were also designated within the cove, based on water depth and distance from known sources of chemical contamination. Comparisons were made by statistically comparing the mean conditions in each area of concern with conditions in the corresponding reference area.



Note: Value of mean amphipod survival is noted at top of each bar

Figure 14.6. Amphipod acute toxicity results at various stations (based on depth and remedial activity) in Ward Cove during 2004 and 2007 (excerpted from Integral, 2009).

Use of data. The RAO for the reduction of surface sediment toxicity was considered achieved when organism survival exceeded 75%. In 2009, all locations exceeded that criterion, indicating that the RAO based on sediment toxicity has been achieved throughout the area of concern (Integral Consulting, 2009) (Figure 14.6). Based on toxicity and other lines of evidence (e.g., benthic community metrics), USEPA determined that the RAOs for the Marine Operable Unit have been achieved and that no further sediment monitoring would be performed (USEPA, 2010).

14.8.5 Contaminant Bioaccumulation Analyses, Grasse River, New York, Activated Carbon Pilot

Background. As described above, several pilot studies were conducted in Grasse River, New York, to evaluate remedial options for PCB contaminated sediments, including evaluating the effect of activated carbon additions on PCB bioavailability (Alcoa, 2010). The effect of the carbon treatment on PCB bioaccumulation in the sediment-dwelling oligochaete *Lumbriculus variegatus* was the key biological line of evidence used to evaluate whether carbon treatment reduced the bioavailability and organism uptake of PCBs.

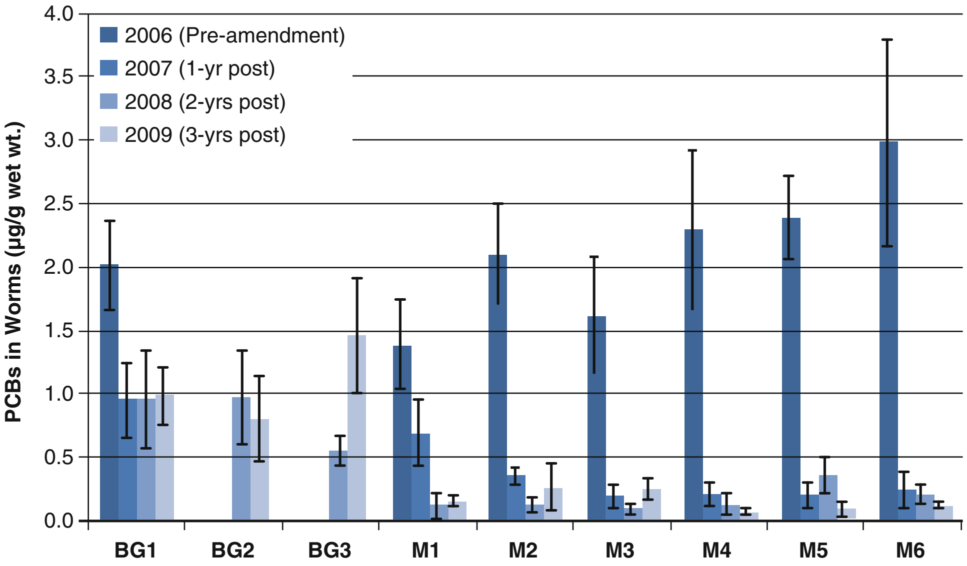


Figure 14.7. Average total PCB concentration in *Lumbriculus variegatus* from before and for 3 years after activated carbon treatment of sediments. Bioaccumulation tests were conducted *in situ* at background and activated carbon treatment sites. BG – background; M 1–6 are locations within the treatment area (excerpted from Alcoa, 2010).

Sampling Description. *L. variegatus* were exposed *in situ* and *ex situ* to Grasse River sediments. *In situ* sampling was accomplished by placing organisms in cages on the sediment bed (Alcoa, 2006; methods adapted from Burton et al., 2005). Briefly, site sediments were placed in replicate exposure chambers along with *L. variegatus*. These chambers were placed on a rack, lowered to the sediment surface, and left in the river for 14 days. *Ex situ*, or laboratory, exposures were conducted by collecting river sediments and shipping them for testing. At the Grasse River, *L. variegatus* were exposed in 150 milliliters (mL) of sediment for 14 days. In both cases, PCB concentrations in *L. variegatus* were measured by congener analysis. Further details on the sampling and monitoring results are available in Beckingham and Ghosh (2010, 2011).

Use of Data. PCB uptake by sediment-dwelling organisms is a direct measure of the bioavailability of contaminants in sediments. *L. variegatus* assays are widely used as standardized measures of bioaccumulation of contaminants from sediments. One advantage is that in contrast to, for example, resident fish, the exposure history of the organisms is fully understood. Contaminant uptake only stems from the collected sample so uncertainty exists as to whether results are representative of the entire site (an issue addressed through collection of multiple locations and replicates at individual locations). The reduction in PCB bioaccumulation following activated carbon treatment was apparent over 3 years in both *in situ* and *ex situ* evaluations (Figure 14.7 [*in situ*]). The reduction in tissue concentrations mirrors the reduction in porewater concentrations shown in Figure 14.5.

14.8.6 Contaminant Concentrations in Resident Organisms, Cumberland Bay, Lake Champlain, New York

Background. Cumberland Bay, located on Lake Champlain at Plattsburgh, New York, was contaminated with PCBs from industrial discharges, including from paper recycling activities. Sediment PCB contamination in the bay was greatest within a sludge bed of wood and paper pulp, wood debris, and waste paper that encompassed approximately 50 acres (NYSDEC, 2001).

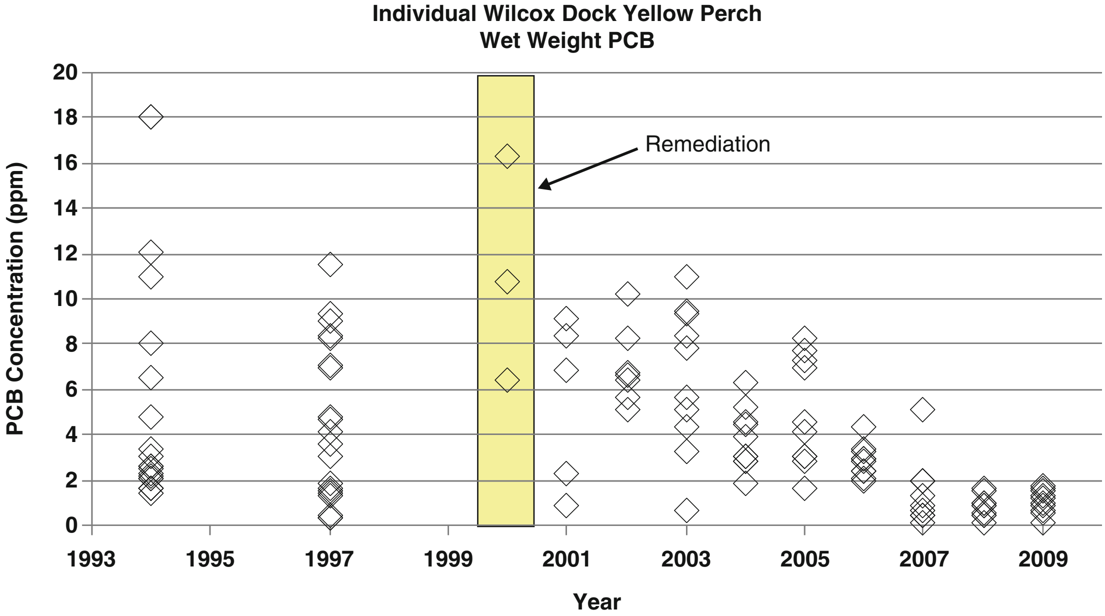


Figure 14.8. Fish tissue PCB concentrations (total PCB as Aroclors) over time in yellow perch sampled in the fall in Lake Champlain, New York, at Cumberland Bay (Wilcox Dock) (adapted from figure provided by Michael Kane, New York State Department of Environmental Conservation, April 2010).

Dredging occurred at the site between 1999 and 2000, with the objective of removing the entirety of the contaminated sludge bed. Residual contamination remained following dredging, owing to challenges presented by debris and heterogeneity of bottom conditions (NYSDEC, 2001; NRC, 2007).

Sampling Description. Fish tissue monitoring at the site includes a variety of species, such as rock bass, perch, and American eel. These have been collected by the state of New York since the 1980s and have been used to support fish consumption advisories, which are in place for Cumberland Bay for American eel, brown bullhead, and yellow perch (NYSDOH, 2010). The site is notable for the relatively long time since remediation and the consistent collection of resident fish for contaminant monitoring during that timeframe. Fish sampling had previously occurred during the spring and fall, but has shifted to the fall timeframe when levels of PCBs are higher and believed to be more representative of resident fish (Myers, 2007). The long-term data set for yellow perch collected during the fall at Wilcox Dock (within the cleanup area) has 12 time points, typically consisting of ten perch from each period (a notable exception: the "during dredging time frame, in 2000 only has three fish").

Use of Data. The primary purpose of these data is to evaluate whether fish consumption advisories are warranted for Cumberland Bay on Lake Champlain. However because of their consistent collection before, during, and after remediation, they also can be used to evaluate the influence of the remedial dredging on fish tissue contaminant concentrations. The data demonstrate substantial inter-individual variability in contaminant concentrations with some animals above 10 ppm prior to and immediately after remediation (Figure 14.8). Since then, average concentrations have declined and the variability has lessened; however, fish are currently still at levels that necessitate fish consumption advisories (NYSDOH, 2010).

14.9 SUMMARY

Contaminant cleanup at sediment sites is a long-term process from initial characterization to achieving RAOs. Along with statutory requirements, the human and ecological risk implications of the cleanups, the large private and public expenditures associated with operations, and the generally public ownership of remediated waterways mandates that remedy effectiveness is tracked and verified. Planning is needed as early in the process as possible to set the stage for monitoring the progress toward and attainment of RAOs. Active remediation at sites is a complex undertaking with monitoring occurring to establish risk, verify "as-built" conditions, satisfy permit (or their substantive) requirements, and monitor whether risk reduction objectives were met. Thus, a framework of remediation phases and timeframes has been presented to place site activities and their associated monitoring into context.

Remedy effectiveness monitoring includes a number of fundamental components. First, clear objectives of the remediation need to be stated in terms of the media or receptors to be improved, contaminant levels to be achieved, and the associated timeframe. An adequate database of baseline conditions is required so that environmental improvement and remedy effectiveness can be quantitatively evaluated. Finally, a monitoring plan needs to be developed that includes indicators and analyses capable of establishing whether remediation has achieved the RAOs of the project. A range of chemical and biological lines of evidence can be used to document that contaminant exposures have been lessened and that resulting risk to (or from) biological receptors has been reduced to acceptable levels. Lines of evidence supporting remedy effectiveness evaluations are drawn from the RAOs that define the receptors of concern and the CSM that defines the environmental media driving risk to those receptors. The usefulness in decision-making of several of these lines of evidence has been borne out in applications at contaminated sediment sites.

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CHAPTER 15

CONTAMINATED SEDIMENT RESEARCH AND DEVELOPMENT NEEDS

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15.1 INTRODUCTION

The complexity of contaminated sediment sites and the potentially enormous costs if remedies are not implemented effectively and efficiently drives a need for continued research and continuous improvement of technologies and practices for design, implementation and monitoring. The costs at contaminated sediment sites are largely driven by their size (both in terms of area of potentially impacted sediments and the volume of soil and water diluents) and the difficulties of working in the water environment. Research into methods to optimize removal technologies can provide incremental benefits by reducing the volume of the contaminated sediments that must be treated or disposed of. Research that can minimize the managed volume by accurate assessment of areas likely to exhibit significant risk can be extremely effective at containing costs. In addition, any methods that can lead to management of sediments *in situ* without the costs and complexity of removal and the incumbent onshore processing of sediments also provide effective cost containment. Finally, technologies that can aid assessment of the risks posed by contaminated sediments and aid prioritization of areas by risk can help contain costs at sediment sites. Moreover, these assessment technologies can also help assess the performance of remedies, demonstrating the successful achievement of remedial objectives and allowing closure of the remedial efforts.

Ongoing research is largely focused in these areas and has led to an expansion of the types and variety of assessment and remedial technologies. Increasingly, measuring and reducing bioavailability rather than contaminant mass is the focus of assessment and remedial activities, a reflection of our improved understanding of contaminant processes in sediments and the cost-effectiveness of this approach. In addition, *in situ* management approaches have become more and more understood and available and consideration of these approaches is a routine part of the remedy evaluation at all contaminated sediment sites. These trends are expected to continue as research continues in the assessment and management of contaminated sediments. This chapter will identify some of the key areas of uncertainty as well as trends in technologies and approaches that will guide research efforts in the coming years.

15.2 FRAMEWORK FOR SEDIMENTS RESEARCH

Research in technology and approaches for effectively managing contaminated sediments has been conducted for more than 20 years by federal, academic and private partners. The U.S. Environmental Protection Agency (USEPA) and the academic Hazardous Substance Research Centers led early research into contaminated sediment remediation building upon a longer record of contaminant assessment efforts by both federal and academic organizations.

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Over the past decade the Strategic Environmental Research and Development Program/ Environmental Security Technology Certification Program (SERDP/ESTCP), the facilitator of the current volume, has funded research to address specific areas of uncertainty in contaminated sediment assessment and remediation.

Increasingly, however, private concerns are conducting the research necessary to continue to improve technologies and practices for managing contaminated sediments. This is particularly true with large scale demonstration efforts that allow evaluation and testing of specific technologies at particular sites. In order to continue to build on the research of the past and continue to improve contaminated sediment assessment and management it is critical that funding for such work be continued and that regulatory agencies remain open to innovation and testing at sites for which they are responsible. We believe that research along the lines outlined below could be especially effective in improving sediment management practices if innovative approaches can be implemented, tested and, ultimately, gain acceptance.

15.3 RESEARCH NEEDS

15.3.1 Contaminant Sources, Behavior and Fate

Understanding the sources, behavior and fate of contaminants in sediments is critical to the ability to manage them effectively. The development and application of a conceptual site model (CSM) is extremely important for contaminated sediment sites, in part because the recovery of all contaminated sediment sites relies to some extent on natural attenuation processes. Understanding the sources and processes that lead to exposure and risk and their attenuation by ongoing system dynamics is important to understanding where natural attenuation may be relied upon to achieve risk reduction goals and how to select and implement active remedies that complement natural attenuation. Complex contaminated soil and groundwater sites may also require a solid conceptual site model but rarely is it as complex or the success of the remedy as dependent upon its understanding as it is with contaminated sediments.

Contaminant behavior can be impacted by numerous processes which vary based on the type of site (marine and estuarine bays, harbors, lakes, wetlands, and rivers). Spatial and temporal heterogeneity throughout a contaminated site further complicate efforts. Robust and cost-effective methods are needed to assess and quantify whether contaminants remain in place, are buried over time, or move through the aquatic system and into ecological and human receptors. It is not possible to define these conditions without site specific measurements and that has placed a premium on technologies and techniques for measurements of these processes.

The causes of uncertainty in our understanding of contaminated sediment sites relative to contaminant fate and behavior include:

1. Uncertainty in how well our simplified approximations of complex processes and site conditions represent the actual processes and conditions;
2. Uncertainty in how the site conditions and characteristic conditions vary across a site, given the typically sparse dataset available and inadequate monitoring tools for some processes; and
3. Uncertainties in how site conditions and processes will change over time (e.g., future hydrologic and meteorologic conditions, changes in land use), making extrapolation from current conditions difficult.

Resolution of these uncertainties is to a large degree dependent upon the intensity and reliability of the site and contaminant assessment effort. Uncertainties stem from inadequate characterization of contaminant sources, processes, spatial heterogeneity and system dynamics and specific challenges in each of these areas are described below.

15.3.1.1 Source Identification and Reduction

At many field sites, there is more than one source of contamination and early and accurate incorporation of the influence of such sources on the CSM model is critical. If management efforts target one source but neglect to address others, success in reaching cleanup goals will be elusive. Tools to identify sources as well as assess their significance and impact on proposed remedies are needed. Coordinated efforts among the responsible parties are critical, and research and assessment efforts should identify reasonably achievable targets in the face of limited or incomplete reduction of contributing sources. Ongoing sources have been a serious challenge in remediating contaminated sediments (Nadeau and Skaggs, 2007) and will continue to be unless techniques are developed to routinely identify and quantify ongoing sources.

Specific challenges include identification of the relative importance of upland contaminant sources. This would include both point sources and non-point sources with the latter being particularly difficult to quantify if the contaminant of concern is distributed throughout a watershed. Combined sewer overflows are a particular concern in large cities and in historically contaminated water bodies (e.g., Shear et al., 1996). Irvine et al. (2005) emphasize the need for a watershed approach in evaluating the contribution from combined sewer overflows and identify some of the challenges in sampling and quantifying their contribution. The highly variable nature of the source and the diverse nature of the upland sources all make quantification exceedingly difficult.

15.3.1.2 Transport Processes and Properties

Although the basic transport characteristics of contaminated sediments are largely understood, it remains difficult to predict cohesive sediment erosion, aggregation and deposition at a particular site. Chapter 3 focuses on sediment erodability and sediment resuspension but the contribution of these processes to the sediments themselves is more a function of deposition and contaminant release. These processes are modeled by relatively crude relationships that define the mass deposition rate (Einstein and Krone, 1962). The process of recontamination of sediment, however involves not only deposition but the aggregation and development of a cohesive sediment layer that consolidates and strengthens over time (Hanzawa and Kishida, 1981). While these processes are occurring, the bed's stability and resistance to erosion and resuspension is varying. Thus the stability of sediment deposits are a strong function of the recent stress history around the site. Significant progress in the description of these processes requires advances in sediment aggregation and cohesion and finally consolidation and strengthening.

Although uncertainty in the sediment response to flow events may control sediment transport uncertainty, it is equally difficult to predict future design storm events, i.e. the conditions that might lead to sediment and contaminant transport. The uncertainty in sediment properties is largely driven by spatial variability and the typically sparse dataset employed to test and calibrate models. Greater resolution in that dataset can resolve or help resolve this problem. Our knowledge of low frequency storm events, however, is not easily improved. It is based upon a relatively short historical record and the past does not predict a future that may be influenced by climate change and unprecedented anthropogenic forcing. Precipitation extremes and presumably, therefore, extremes in watershed and river flows are among events that have been most closely linked to global climate change (Coumou and Rahmstoft, 2012).

A quantitative understanding of what may be considered design storm events would improve system modeling in support of remedy selection, design, and implementation but general acceptance of the conditions of such a storm may be increasingly difficult to achieve.

There are other processes and site influences that may be difficult to characterize. As an example, the direct measurement of groundwater upwelling flux is difficult due to limited sensitivity of measuring equipment and the large variability in groundwater upwelling in some heterogeneous environments (Burnett et al., 2006). Groundwater upwelling is the most important factor in evaluating the potential impacts of buried hydrophobic contaminants in a non-eroding sediment environment. It is generally the only mechanism that can lead to exposure and risk of such contaminants. It also directly indicates the viability of *in situ* management of contaminated sediments or dredging residuals. Continued improvement and increased availability of effective techniques will be important for improving our ability to develop accurate conceptual site models and appropriately evaluate remedies for contaminated sediments.

Chemical property uncertainty also contributes to overall uncertainty. Key areas of uncertainty include the behavior of mixtures of contaminants, in particular the ongoing evolution of complex mixtures, and the impact of spatial heterogeneity on the distribution of fate of contaminants. As an example, chemical analysis of polychlorinated biphenyls (PCBs) is often done on the basis of arochlors, mixtures characterized by the percentage of chlorine in the mixture. Analysis is relatively inexpensive and regulations of the amount of PCBs in sediments are typically done on the basis of total PCBs, both of which encourage the continued use of arochlor concentrations as a measure of PCBs. Unfortunately, the fact that it is a mixture means that its physical and chemical properties cannot be accurately characterized by single "mixture" properties and components of the mixture will migrate and degrade at different rates and cause different effects. This problem can be reduced by characterizing PCBs by homolog group (i.e., by the different numbers of chlorines on particular isomers). Homologs exhibit similar chemical and physical characteristics although even this is not very useful to characterize toxic effects which are a strong function of the PCB structure (NRC, 2001). Most useful is individual congener analysis of PCBs although this may make data difficult to compare to past data that was collected on an arochlor basis. Even the physical and chemical characteristics of individual congeners, however, are subject to some uncertainty (Li et al., 2003). Sources of physical and chemical property data may also not be consistent (e.g., octanol-water partition coefficients of PCBs may vary by 0.1–0.3 log units). Correlations predicting other physical properties should thus always identify the source of the correlating factor. Lu et al. (2011), for example, showed that correlations of sorbent-water partition coefficients in solid phase microextraction should employ a consistent set of octanol-water partition coefficients to minimize uncertainty.

15.3.1.3 Spatial Heterogeneity

Spatial heterogeneity means that interpolating sparse data leads to significant uncertainty. A large contaminated sediment site may be limited to acre size spatial resolution for processing intensive samples such as sediment cores. For example, the lower Fox River in Wisconsin is 39 miles long and has an average width of around 1,000 feet (ft) (with the exception of Little Lake Butte des Morts). Collection of even 10,000 sediment cores in a river this large would result in one core per half acre of sediment bottom on average. While generally more than adequate to describe the general physical characteristics of the sediment, greater resolution would be desirable for defining chemical distribution and to design an effective remedy. Better tools for *in situ* screening, rapid characterization and remote sensing are needed to generate higher resolution spatially distributed data.

Field screening or rapid sediment characterization technologies are needed to provide measurements of chemical, biological, or physical parameters on a real-time or near real-time basis. A variety of rapid sediment characterization tools have been tested and demonstrated in sediments (Kirtay, 2008). These tools have historically included chemical screening tools such as x-ray fluorescence, ultra-violet fluorescence and immunoassays for various chemicals, as well as physical screening tools including particle scattering for grain size analysis and infrared moisture analysis. Additional tools are needed to characterize other physical and chemical properties of the sediment and to provide more defensible data for decision support.

Remote sensing and geophysical approaches also have the potential to improve our ability to characterize spatial heterogeneity. Multibeam acoustic (sonar) monitoring has the most potential to characterize large areas of sediments quickly. These techniques are underutilized or underanalyzed. Kostylev et al. (2001) has employed multibeam sonar to evaluate water depth, sediment type and bed geomorphology. Their particular application was to characterize benthic habitat. This information could also be invaluable in developing and testing conceptual site models. Airborne remote sensing can also be useful to evaluate zones of groundwater discharge (Wilson and Rocha, 2012), but also suspended sediment concentration, flows and recharge (Pavelsky and Smith, 2009).

15.3.1.4 Temporal Effects

Temporal events such as turbulent perturbations of sediments also introduce uncertainty in contaminant fate and transport. In the face of uncertainty, current approaches use a conservative “threshold of resuspension” criteria to evaluate the potential for sediment erosion. A better approach would be to assess the rate and extent of erosion and/or deposition associated with a particular event. The effect of unsteady flows on sediment dynamics have been studied (e.g., Admiraal et al., 2000) but the resulting contaminant release has not. For example, modest erosion in a low frequency event may not be a significant source of contaminant release or significantly influence the performance of a remedy. Also, there is a need to improve understanding of contaminant release as sediment is resuspended. Instead we tend to track particles and not the contaminants that should be our true concern.

The impacts of prop wash dynamics and navigation also remains poorly characterized (Rodriquez et al., 2002). Moreover, approaches that have been developed tend to focus on whether prop wash exceeds the threshold of sediment resuspension (e.g., Beachler and Hill, 2003) rather than the rate and extent of sediment resuspension or contaminant release. Efforts to address these impacts by sediment type and contaminant characteristics are needed.

Temporal effects also include medium term concerns such as the dynamics associated with flow events (hours to days) and seasonal dynamics (weeks to months). In addition, long term dynamics associated with changes in waterway uses or watershed land use, climate change and long-term management of point and non-point sources can all have substantial impacts on a sediment remedy and its effectiveness yet it has proven difficult to incorporate these effects in planning and evaluation.

15.3.2 Risk Characterization and Monitoring

Risk characterization and monitoring is fundamental to meeting our goal of risk reduction. Risk assessment and characterization is needed from the selection, design, and implementation of an approach to assessing its effectiveness over the long term. Even earlier in the process, site characterization and monitoring is used to establish conceptual site models, background and cleanup levels and to assess relevant sources and stressors. Enabling technologies include modeling and measurement tools. While historically contaminated sediment sites were assessed by measuring contaminant concentrations in sediments, a significant body of research has shown that total concentrations are poorly correlated with toxic impacts. Development of tools to assess the bioavailability of contaminants is under way, but further work is needed in this area to support and demonstrate appropriate risk-based approaches.

15.3.2.1 Bioavailability Controls

A major impediment to the use of bulk solid measures of contaminant concentration is that it does not directly relate to risks and effects. The bioavailability of contaminants is affected by physical, chemical, and biological controls in the subsurface environment. Kraaij et al. (2003), You et al. (2009), and van der War et al. (2004) have found porewater concentrations as measured by passive samplers to be a good indicator of hydrophobic organic contaminant (HOC) bioaccumulation in soil and sediment organisms. More recently, Lu et al. (2011) and Gschwend et al. (2011) showed that lipid normalized bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) and PCBs in freshwater and marine benthic organisms could be related to HOC porewater concentrations with an effective bioaccumulation factor given by the octanol-water partition coefficient. These studies do not suggest that the route of exposure to the organisms studied is the porewater concentration but only that the porewater concentration provides a useful indicator of bioavailability. Similarly, porewater related measures of metals such the acid volatile sulfides/simultaneously extracted metal (AVS/SEM) paradigm (USEPA, 2005; see Chapter 7) provide an excellent first order indicator of benthic toxicity to metals. Porewater concentrations do not describe toxicity or bioaccumulation in all cases and research is needed to identify under what conditions these measures may or may not be good indicators of bioavailability.

Ultimately the controls on bioavailability are site-specific and a framework for evaluating multiple lines of evidence for assessing bioavailability is needed. Maruya et al. (2010) summarizes the manner in which bioavailability can be incorporated into conventional sediment quality assessment frameworks. Research needs identified in this framework includes advancing passive sampling devices such as those discussed above and in Chapter 7. Identifying critical body residues and biomimetic extractions to relate to those residues would also be useful to complement the use of direct porewater concentration measurements. Maruya et al. also identify the need to understand the effects of contaminant mixtures and spatial and temporal changes in contaminants *in situ*, particularly metals. Robust and cost-effective tools for assessing bioavailability are needed and field demonstration and validation are necessary for their acceptance. Work has progressed on the use of passive sampling and the *in situ* measurement of porewater contaminants but additional work, particularly on the limitations of such approaches, is needed before these approaches are fully accepted.

Much of the work above is focused on benthic organisms which intimately interact with the sediments, often achieving near chemical equilibrium with porewater and sediment conditions. A more difficult challenge is tying sediment concentrations and bioavailability to concentrations in fish or establishing the link to higher organisms and human health. These links are made more difficult by the inherent disequilibrium or mass transfer resistances between sediment and receptor and the potential for multiple routes and sources of exposure.

Porewater concentrations have proven to be very useful indicators of availability (e.g., as discussed in this volume) but further work is needed to identify the applicability and/or limitations of approaches such as these. Similarly, other indicators, such as direct biological indicators in sentinel species to specific bioassays, need evaluation of their representativeness, reproducibility and accuracy. Biological assays are inherently difficult due to differences between organisms and the inherent variability of biological processes but are often more easily accepted by site regulators and the public than chemical tests. Chapter 6 of this volume details the state of the art in biological testing and identifies some of the limitations of such tests.

15.3.2.2 Multi-stressor Systems

In addition to multiple sources, there may be multiple stressors involved at contaminated sediment sites. Failure to cast the risk posed by contaminated sediments in light of these other stressors, which may be of greater ecological significance, can impact success in reaching risk-based cleanup goals. Other stressors that should be explored include other contaminants but nutrient levels, habitat quality, flow, solids, and invasive species. Technologies that can target multiple stressors and identify dominant stressors should be identified and developed.

McCauley et al. (2000) identified a variety of approaches to assess sediment quality in the face of multiple stressor concerns. Conventional biological testing such as sediment toxicity testing can identify whether a sediment poses substantial risk but is largely powerless to determine the source of that risk. Toxicity identification evaluation (TIE) is one of the few approaches that can be used to identify the source of toxicity in sediments. These procedures are designed to identify toxicity by physical and chemical manipulation of the sediments to separate various sources of toxicity. At this time, however, the effect of the extraction and separation procedures on the sediment and porewater are not well understood and that complicates the interpretation of the results. These approaches have historically used water column organisms in testing, weakening the interpretation of the results for benthic and sediment interacting organisms. More research to refine these methods and establish their applicability to a wide range of sediment contaminants and conditions is needed.

15.3.2.3 Measurement Tools

Tools for the *in situ* assessment of risk in complex sediments environments are lacking or often too expensive to deploy broadly. The inability to capture real-time high-density risk measurements in sediment systems is a gap that impacts modeling efforts, risk assessment, site management, and monitoring. Efforts are needed to develop measurement tools that can be deployed with lower cost and with greater spatial resolution. These tools need not provide a complete picture, but they do need to reduce uncertainty to a level deemed acceptable by the regulatory community and site managers and a cost commensurate with their effectiveness. Real-time, non-invasive characterization tools would be particularly advantageous. Passive sampling porewater measurements are an example of such a tool but further work is needed to identify the limitations of such approaches and the tool is still largely a research technique that has not found routine availability in commercial firms or laboratories.

15.3.2.4 Risk-Based Cleanup Goals

In setting cleanup goals for contaminated sediment sites, understanding background levels of contamination is an important first step. Research is needed to determine how to set background levels and use them in defining risk-based cleanup goals. Further, research is needed to support cleanup goals that more effectively support desired risk reduction than bulk solid concentration, the universal regulatory standard currently applied. Over time, it is hoped that increasingly alternative, more relevant cleanup indicators and goals can be identified, applied and tested.

A major challenge is the fact that cleanup goals that are easily measured and evaluated are perhaps least likely to be related to risk goals. For example, it is easy to measure the volume of sediments that are disposed of but difficult to identify the risk reduction that resulted. The NRC (2007) observed that it was not possible to "establish whether dredging alone is capable of achieving long-term risk reduction" due to inadequacies in monitoring, application of multiple remedies and the use of non-risk based cleanup goals.

In general the most direct measures of risk fail in providing real-time feedback to remedy performance. A remedy is often used in an attempt to reduce risk in complex organisms such as humans, other mammals, or other predators at the top of the food chain. These organisms are not closely linked with sediments and respond far more slowly to remedies, regardless of the effectiveness of that remedy. Effective remedy adaptation, however, requires near real-time feedback and thus we often rely upon operational measures such as depth or volume of dredging or thickness, or cap area and thickness. Intermediate between direct measures of risk reduction and these operational measures are the chemical cleanup goals. Due to issues such as multiple stressors, inadequate source control and bioavailability, however, these are also generally inadequately linked to long-term risk reduction. The only way to establish such a link is through a thorough understanding of the processes and conditions operative at a sediment site, i.e. an accurate and complete CSM, and use of that CSM to define risk-based cleanup goals that will ultimately lead to the desired long-term risk reduction. Thus the need for development of appropriate risk-based cleanup goals is essentially a need to develop the characterization and assessment tools that inform an accurate and dynamic CSM.

15.3.2.5 Modeling

Mathematical models are the quantitative embodiment of the CSM. Accurate mathematical models and the CSM on which they are based can provide a holistic picture of a contaminated site – historic, present, and future – that helps inform management decisions. Models that can account for the complex integrated multimedia processes encountered at field sites are needed. Models are expected to improve with increasing numbers of sites that have high quality and high resolution data available.

Modeling a complex site typically involves hydraulic processes, sediment transport, chemical fate and transport, and food chain transfer of contaminants from directly exposed organisms, i.e. the benthic community, to the higher level organisms that are typically of interest. Our knowledge and understanding of these models decreases as we move through this process with the result that uncertainty increases at each stage. Again, development and refinement of models is dependent upon the site characterization and understanding that leads to an accurate conceptual site model and accurate parameterization of the key processes in each modeling stage.

There are extensive data requirements to fully calibrate and validate each stage of the models. Calibration and validation data is often more limited as we move from hydraulic models to sediment transport models to chemical fate and transport and tropic transfer models. This is the primary reason why the uncertainty in the latter models exceeds that of the former. Moreover, while collection of the necessary data is appropriate for large, complex contaminated sites, it may not be appropriate or cost-effective to collect that data for smaller simpler sites. It is hoped that model development and refinement at complex sites will help provide useful modeling tools that have adequate parameterizations that are applicable at smaller, simpler sites without substantial calibration. Regardless, it is important to develop an understanding of when a sophisticated, complex model is needed and useful and when it will not substantially assist in remedy selection, implementation and evaluation.

15.3.3 Remediation and Management

Several *in situ* technologies for managing contaminated sediment sites have been developed as alternatives to *ex situ* approaches that are costly and potentially damaging to the environment. These technologies include:

- *In Situ* Capping – subaqueous caps with sequestering amendments and various design and implementation options.
- *In Situ* Remediation – bioremediation and other methods to sequester contaminants.
- Monitored Natural Recovery (MNR) – assessment tools and methodologies to predict and monitor natural recovery.

Dredging, however, remains an important option for managing many field sites. A consistent approach is needed to compare various technologies, including dredging, and better understand conditions that encourage or discourage their use.

For some of these technologies, there are technology-specific research needs to address. More broadly though, efforts should address the long-term effectiveness of management, i.e., its permanence and ability to achieve desired goals. Bridges et al. (2011a) describe a framework for selecting and implementing remedies at contaminated sediment sites that is designed to accelerate the pace of achievement of remedy goals. This framework encourages early definition of explicit goals and objectives and metrics to monitor success relatives to those goals and objectives, full engagement of stakeholders, and optimization approaches as more is learned about a site. They also encourage seeing sediment management as a collaborative process and the need to incentivize progress toward the ultimate goal of risk reduction. Adaptive management approaches were also embraced by NRC (2003) which provides a number of examples of how adaptive management has been applied in various remedial efforts.

Research has the potential to substantially improve the selection, design and implementation of remedies at contaminated sediment sites. A variety of questions need to be addressed. Are efforts achieving and maintaining the desired goals? What ultimately is achievable considering sites with multiple sources and stressors? How is management success best defined at field sites? Long-term data is needed to address these questions effectively. To obtain this data, monitoring tools capable of capturing high-density data cost-effectively must be developed and this data must be appropriately linked to long-term risk reduction at a site.

Some concerns and challenges of individual technologies for contaminate sediment remediation are summarized below.

15.3.3.1 Monitored Natural Recovery

Efforts are needed to quantify and predict the processes that lead to recovery and support the selection of MNR as a remedy. Continuous review and improvement in approaches is needed to couple the evaluation of MNR with developing monitoring and characterization tools. Many of the needs to support MNR decisions are similar to that to support site characterization and conceptual site model development. A major limitation is the difficulty of predicting forward in time based upon measurements but that is a critical requirement for the selection of MNR. Magar et al., 2009 provide a description of how MNR is assessed, selected and monitored. Many of the tools available and potentially available are alluded to in that report. Chapter 9 in this volume also provides an overview of the state of the art in MNR. As identified therein, MNR requires multiple lines of evidence and strong evidence that recovery as indicated by observations will continue into the future. Natural recovery is often the result of burial for persistent, strongly solid associated contaminants but may also be the result of contaminant fate and/or transport processes. The methods to demonstrate the appropriateness of MNR are as varied as the mechanisms by which recovery may occur. Research to support the development of improved CSMs and improve site risk assessment are, in general, the same tools that could be used to support MNR.

15.3.3.2 *In Situ* Treatment and Capping

Conventional capping of contaminated sediments with sand or dredged material is well established and is supported by guidance (Palermo et al., 1998). More recently, however, a variety of amendments have been proposed to enhance the treatment or containment properties of the approaches. These amendments range from established materials such as activated carbon and organophilic clays to more exotic materials that have only been prepared and tested in the laboratory. The critical need for both *in situ* treatment and capping is evaluation and, ultimately, prediction of long-term performance of these amendments. Laboratory and short-term field data show that some amendments have great promise (e.g., activated carbon for dissolved HOC and organophilic clay for separate phase nonaqueous phase liquid [NAPL]) (Rakowska et al., 2012; Ghosh et al., 2011; Cetco, 2007). There exists no information, however, on the long-term effectiveness of amendments on time-scales of order of the design lifetime of sediment caps or *in situ* treatment remedies. Preliminary studies have shown promise for amendments such as activated carbon and organophilic clays but the field demonstrations using such materials are of the order of 5–10 years old, much shorter than the expected design life of a cap. Activated carbon, for example, is subject to fouling and the result is reduced adsorption and more limited capacity (McDonough et al., 2007). The amount of a particular amendment needed to achieve desired results and how fouling of an amendment over time might increase the required amount is an area for further study.

For both *in situ* treatment and capping technologies, engineering issues remain with regard to optimizing mixing, delivery, and placement of materials. In general, intensive mixing and delivery of treatment amendments can give rise to many of the same resuspension concerns as dredging. Recent advances such as the use of Sedimite™ (Ghosh et al., 2011) may resolve these problems by allowing low density amendments such as activated carbon to be placed without significant disturbance of the underlying sediments although questions arise as to the stability and effectiveness of the amendments placed in this manner. Ghosh et al. (2011) also describes techniques used to place and physically mix activated carbon into sediments.

Research is also needed to understand the geotechnical response of the underlying sediment to address issues related to slope stability and bearing capacity. Many of the most difficult contaminated sediments are extremely soft and exhibit little strength. While there has been success in placement over such materials, the delivery rates and control necessary to ensure success may dramatically increase costs of *in situ* management of the contaminated sediments.

There remain questions about the long-term integrity of even an armored, engineered, cap. The design basis for cap armoring remains focused on the threshold of resuspension rather than setting a design that might allow some erosion but would remain largely in place and protective under the strongest and longest duration storm event that is expected to be encountered. In addition, the development of cap protection criteria tends to focus on natural hydraulic stresses as opposed to those that might result from short-term navigation effects. The technological basis for design based upon transient navigation and propwash effects is only partially developed (e.g., Beachler and Hill, 2003). Research is needed into the stresses expected from a wide range of recreational and commercial navigation activities and the required armoring necessary to limit erosion to management levels.

Engineering and assessment tools are also needed to address thin finite cap layers, both their placement and effectiveness. Lampert et al. (2011) suggests that a thin layer cap can be effective as long as its thickness exceeds the depth over which active bioturbation will occur. Even this result, however, presumes that groundwater upwelling is negligible and when upwelling is significant there is great uncertainty whether a thin layer cap or dredging residual backfill will provide effective long term containment of contaminants.

Research is also needed to understand the geotechnical response and chemical migration of the underlying sediment and contaminants in the face of gas or NAPL contaminated sediments. Field observations have noted problems associated with gas ebullition including gas uplift of impermeable layers (Reible et al., 2006) and facilitated transport of NAPL due to gas migration (McLinn and Stolzenburg, 2009). Measurement of groundwater upwelling flux is difficult but measurement of gas flux is even more difficult due to its strongly heterogeneous nature and sensitivity to boundary manipulations (e.g., placement of gas flux chamber). Gas ebullition may be a short term phenomena in some sites in that a cap or source control efforts may reduce the deposition of fresh labile organic matter on contaminated sediments, effectively eliminating gas ebullition through the contaminated layer in a relatively short time. Gas ebullition associated with degradation of a large pool of contaminants, however, may continue indefinitely and lead to needs for special design considerations for capping or other remedial approach. Currently site specific studies are necessary but over time, experience and testing could allow more accurate a priori design.

It would be highly desirable to avoid long-term contaminant migration through *in situ* degradation and detoxification processes. Unfortunately many sediment contaminants are refractory and conditions within sediments (highly reduced) discourage rapid degradation of most contaminants. Moreover, great uncertainty exists in how to encourage bioremediation of sediment contaminants either in the sediment layer or in a cap layer separating sediment contaminants from the overlying water. Traditional approaches such as nutrient or microbe addition may be short-lived and delivery approaches may encourage sediment resuspension and release. Sediment capping provides an opportunity to provide amendments that may stimulate degradation but regular amendment addition may be required to sustain activity. Chapter 10 discusses microbial degradation and identifies both opportunities and barriers for advancing degradation as a viable component of sediment *in situ* treatment or capping. Chapter 10 specifically identifies the challenges of migrating successes in the laboratory to the field, a necessary step to achieve the potential of *in situ* management by degradative processes.

A novel means of achieving and maintaining appropriate conditions for degradation of sediment contaminants is through the use of a continuous application of electricity via electrodes (Sun et al., 2010; Zhang et al., 2010; Yan and Reible, 2012). The energy requirements are modest to enhance degradation processes and could be sustainably supplied via wind or solar electricity production. In some cases, placement in sediments is envisioned to directly degrade sediment contaminants. Challenges for this application include maintaining electrode integrity and ensuring areal uniformity in degradation. Placement in caps provides easier placement and construction but also leads to challenges in electrode integrity and limits the enhanced degradation to contaminants that may migrate through a cap.

It is important to recognize that transformation processes do not always lead to reductions in risk and improvements in sediment quality. Partial dechlorination products of chlorinated organic contaminants are generally more mobile and sometimes more toxic than the parent compound (NRC, 2001). Mercury contamination is rarely a direct concern except to the extent that methyl mercury is formed within the sediments. The presence of a cap may actually increase methylation in the surficial sediments although generally a cap is expected to reduce methyl mercury mobility and availability (Johnson et al., 2010). The bioavailability of mercury and the rate and extent of methyl mercury formation are complex topics that continue to require research to fully understand and successfully manage.

15.3.3.3 Dredging

Dredging remains one of the most common and often preferred form of sediment remediation. Despite its long history, the long-term effectiveness of dredging is not well understood as pointed out by NRC (2007). Dredging has not evolved significantly in the past few decades with observed improvements largely associated with increased knowledge and control over dredge positioning. This has led to an improved efficiency in dredging and potential reductions in the need for overdredging and redredging. The fundamental problems of dredging, resuspension and residuals, remain as significant issues, particularly in sites with debris, hardpan or bedrock, or soft easily mobilized sediments. Due to the site and operation specific nature of these problems, it is often difficult to predict their significance a priori or effectively monitor and manage their influence during a dredging operation. Some guidance does exist for the estimation of sediment resuspension and residuals (Patmont and Palermo, 2007), but how this may translate to contaminant release and exposure is less well understood. Bridges et al. (2011b) describe the "4 Rs of Environmental Dredging", resuspension, release, residuals and risk, and recognize that understanding all four is required to adequately assess the potential risks of dredging. Post-dredging data sets from past projects are unlikely to address remaining uncertainty regarding short- and long-term effects (NRC, 2007). Instead, it is more likely that improved monitoring of ongoing and future dredging operations will reduce uncertainty in these processes.

In addition, the impact of the 4Rs may differ substantially in large long-running dredging projects (e.g., miles of river and years of implementation) compared to small, short term efforts (e.g., one season of less of dredging). What is the ecological significance of one resuspension event or dredging over a single season to dredging over 10–15 years?

15.3.3.4 Combined Remedies

The complexity of contaminated sediment sites suggest that essentially all remedies will actually be combined remedies. All remedies rely to some extent on natural attenuation. Most dredging remedies require backfill or cover to reduce the risks of residuals. It has long been recognized that effective sediment remedies may involve combinations of dredging, capping, *in situ* treatment and MNR. Further work is needed to assess the benefits of using combined remedies for contaminated sediment sites and to be able to identify the risk reduction associated with individual components of the remedy to aid future planning and planning at other sites.

Often combined remedies are the result of an adaptive process. In general, implementation of a remedy that does not achieve desired goals can lead to updating and improving the CSM and allow optimization of a remedy or refinement of an implementation that may achieve the desired goals. Often viewed negatively as "the try it and see" approach to remediation, in reality testing and updating the CSM and optimizing and refining a model based upon site specific results, has been an important tool in soil and groundwater remediation and should also be part of sediment remediation.

15.3.4 Technology Transfer and Education

Removal of contaminated sediments has long been the preferred remedy for handling contamination; however, there are cost and ecological considerations associated with removal as well as a significant body of research indicating that *in situ* treatment can be as effective at reducing risk, with lower costs and minimal ecological damage. Efforts are needed to further educate the regulatory community and public on this issue.

Similarly, education is critical to raising awareness of the impacts of multiple sources and stressors at contaminated sediment sites. Managing contamination from one source without addressing other sources or stressors is unlikely to achieve success. Overall, a system level perspective by all stakeholders involved is needed. This is challenging, however, given the nature of current regulations with distinct elements.

Uncertainty remains a core point of discussion in decisions regarding remedy selection, design, implementation, and monitoring. Considering the uncertainty along the full spectrum of processes involved, it is important to establish bounds on the ability to model or predict an event 5–10 years in the future and explain to stakeholders what is and isn't well known. Framing the discussion in terms of risk reduction can be useful.

The USEPA increasingly is opening existing Records of Decision (RODs) when monitoring data indicate that site conditions have changed from when the ROD was signed. This could indicate insufficient understanding of relevant processes at the time the management approach was implemented. Building performance-based goals into the ROD and recognizing the important role of adaptive management in contaminated sediment sites could help to address this issue.

Related to innovative technologies, more guidance is needed on how best to transition technologies from their development to the field. There is a gap between how well a process can be understood and then transferred to field application. At what point in the development process can outyear predictions be relied upon for management purposes? Are there intermediate steps (e.g., mesoscale) that may be important to understand biological effects, engineering, and large-scale performance at field sites? Large-scale demonstrations also may be useful in framing issues at the system level.

Engaging the regulatory community is also essential to transitioning these technologies to field use. Efforts are needed to explore which mechanisms for doing so are most effective, e.g., presentations, training, and workshops as well as web and visualization tools. The U.S. Navy and USEPA Superfund Center models should be reviewed. Beyond tool development, personal contacts and relationships are important.

15.3.5 Summary

The goal of the research that might be conducted to address the identified gaps is the identification, design and implementation of remedies that are both more effective and more rapidly achievable. Much of this will be through experience gained at contaminated sediment sites as we select and implement remedies at more and more sites. Absolutely critical, however, is effective monitoring of these remedies and continuously asking the questions:

- Did the remedy perform as expected?
- Did the remedy meet risk reduction goals?
- Could a remedy have been implemented more rapidly and more effectively at less cost?

By continuing to ask these questions, the uncomfortable truths that may be found in the answers will ultimately lead to remedies that are more effective and efficient. Ultimately the goal is the implementation of a combination of remedy and/or restoration that achieves the long-term goals for the waterway. Understanding and gaining broad acceptance of those goals and understanding how the processes and conditions at a site may limit or constrain what and how tools may be employed is critical to moving forward in effectively managing contaminated sediments. Similarly, we must ask if any proposed research will help us move toward a goal of efficient, effective remedies at one or more sites. If such a link can be identified, then the research should be undertaken.

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APPENDIX A
LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

°C	Degree(s) Celsius
µg/g	Microgram(s) per gram
µg/kg	Microgram(s) per kilogram
µm	Micrometer(s)
2-NA	2-naphthoic acid
AC	Activated carbon
ACPS	Activated Carbon Pilot Study
ANOSIM	Analysis of similarity
ANOVA	Analysis of variance
ARAR	Applicable or relevant and appropriate requirement
ARCS	Assessment and Remediation of Contaminated Sediments
AUC	Area under the curve
AVS	Acid-volatile sulfide
BACI	Before-After, Control-Impact
BaP	Benzo[*a*]pyrene
BAZ	Biologically-active zone
BC	Black carbon
BCF	Bioconcentration factor
BLM	Biotic Ligand Model
bph	Biphenyl upper
BphA	Biphenyl 2,3-dioxygenases
BphB	*cis*-2,3-dihydro-2,3-dihydroxybiphenyl dehydrogenases
BSAF	Biota-sediment accumulation factor
CAD	Contained aquatic disposal
CCA	Canonical Correspondence Analysis
***cis*-DCE**	*cis*-1,2-dichloroethene
CDF	Confined disposal facility
CEC	Cationic exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm	Centimeter(s)
cm/d	Centimeter(s) per day
cm/hr	Centimeter(s) per hour
cm/s	Centimeter(s) per second
cm/yr	Centimeter(s) per year
cm^2/s	Square centimeter(s) per second
COC	Contaminant of concern
COPC	Contaminant of potential concern
CSM	Conceptual site model
CT	Computerized tomography
CUL	Cleanup level
DCB	Dichlorobenzene
DCE	Dichloroethene
DDT	Dichloro-diphenyl-trichloroethane
DGT	Diffusive gradient in thin film
Dhc	*Dehalococcoides*
DIFS	DGT-induced fluxes in soil and sediment
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DQO	Data quality objective
dw	Dry weight
EaCoMT	Coenzyme M transferase
EISB	Enhanced *in situ* bioremediation/ biotransformation
EMNR	Enhanced monitored natural recover
EqP	Equilibrium partitioning
ERA	Environmental risk assessment
ERM	Effects range median
EROD	Ethoxyresorufin-O-deethylase
ESB	Equilibrium partitioning sediment benchmark
ETM	Estuarine turbidity maximum
FIAM	Free Metal Ion Activity Model
FPR	False positive rate

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FS	Feasibility study
ft	Foot/feet
ft^2	Square foot/feet
g/L	Gram(s) per liter
g/mL	Gram(s) per milliliter
GAC	Granular activated carbon
GIS	Geographic information system
gm/cm^3	Gram(s) per cubic centimeter
GSD	Grain size distribution
GST	Glutathione S-transferase
HI	Hazard index
HMW	High molecular weight
HOC	Hydrophobic organic compound
HOPDA	2-hydroxy-6-phenyl-6-oxohexa-2, 4-dieneoate
IAR	Inverse aspect ratio
in.	Inch(es)
kg/m^3	Kilogram(s) per cubic meter
K_{OW}	Octanol-water partition coefficient
kPa	Kilopascal
L	Length
lb	Pound(s)
lb/ft	Pound(s) per foot
lb/ft^2	Pound(s) per square foot
L/g	Liter(s) per gram
L/kg	Liter(s) per kilogram
LEFM	Linear elastic fracture mechanics
LMW	Low molecular weight
LoE	Lines of evidence
LOE	Level of effort
LRM	Logistic regression modeling
m	Meter(s)
m/s	Meter(s) per second
m^2	Square meter(s)
MCB	Monochlorobenzene
MCL	Maximum Contaminant Level
MDA	Malondialdehyde
MDS	Multidimensional Scaling
MeHg	Methylmercury
mer	Mercury resistance
mg/kg	Milligram(s) per kilogram
MGP	Manufactured gas plant
mm	Millimeter(s)
mm^3	Cubic millimeter
MMO	Methane monooxygenase
MNR	Monitored natural recovery
NAPL	Nonaqueous phase liquid
NCP	National Contingency Plan
NDO	Naphthalene dioxygenase
NEBA	Net Environmental Benefits Analysis
ng/L	Nanograms(s) per liter
NOAA	National Oceanic and Atmospheric Administration
NOM	Natural organic matter
NRC	National Research Council
O&M	Operation and maintenance
OD	Oxidative demethylation
OM	Organic matter
ORP	Oxidation reduction potential
OU	Operable Unit
Pa	Pascal(s)
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PCE	Perchloroethene
PCR	Polymerase chain reaction
PDMS	Polydimethylsiloxane
PE	Polyethylene
PICT	Pollution-Induced Community Tolerance
POC	Particulate organic carbon
POM	Polyoxymethylene
ppm	Part(s) per million
PRC	Performance reference compound
PRG	Preliminary remedial goal
PSB	Permeable sorptive barrier
psu	Practical salinity unit
QAPP	Quality assurance project plan
RAO	Remedial action objectives
RDase	Reductive dehalogenase
REBE	Relative Environmental Benefits Evaluation
RfD	Reference dose
RG	Remediation goal
RI	Remedial investigation
RMO	Remedial action objective
ROC	Receiver Operating Characteristic
RPM	Remedial project manager
S-BLM	Sediment biotic ligand model
SEDTA	Sediment Transport Assessment
SEM	Simultaneously extracted metal
SOM	Sediment organic matter
SPI	Sediment profile imaging
SPMD	Semi-permeable membrane device
SPME	Solid-phase microextraction
SQG	Sediment Quality Guideline
SRB	Sulfate reducing bacteria
SSC	Suspended solids concentration
SWI	Sediment-water interface
T-BLM	Terrestrial Biotic Ligand Model

TCA	Tricarboxylic acid cycle
TCB	Trichlorobenzene
TCE	Trichloroethene
TEAP	Terminal electron acceptor
TBP	Theoretical Bioaccumulation Potential
TIE	Toxicity identification evaluation
TPR	True positive rate
TRA	Tissue residue-effects approach
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	Vinyl chloride
VOI	Value of information
VSWCB	Virginia State Water Control Board
WoE	Weight of evidence
WRD	Water Resources Division
wt%	Weight percent
yr	Year

APPENDIX B
GLOSSARY

[1]**100-year (yr) flood** - Hydrodynamic flow event with an expected occurrence frequency of 1 % in any given year.

Abiotic - Occurring without the direct involvement of organisms.

Absorption - The uptake of water, other fluids or dissolved chemicals by a porous material, a cell or an organism.

Activated carbon - A highly adsorbent form of carbon used to remove odors and/or toxic substances from liquid or gaseous emissions.

Adsorption - A process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate).

Advection - Transport of a substance by a fluid (e.g., groundwater) through the fluid's bulk motion in a particular direction (i.e., convection).

Aerobic - Environmental conditions where oxygen is present. Aerobic respiration by living organisms requires oxygen to generate energy.

Aggradation - Process by which the bottoms of water bodies are raised due to deposition of sediment.

Aliphatic compounds - Any chemical compound belonging to the organic class in which the atoms are not linked together to form a benzene ring.

Anaerobic - Environmental conditions where oxygen is absent. In water, a dissolved oxygen concentration below 1.0 milligram per liter (mg/L) is generally considered anaerobic. Anaerobic respiration is a means for a living organism to generate energy in the absence of oxygen.

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[1] This glossary is a compilation of definitions of terms synthesized by the volume editors and chapter authors from a variety of published and unpublished sources, including previous volumes in the SERDP/ESTCP Remediation Technology Monograph Series.

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Analytical model - A mathematical model, often based on simplifying assumptions, that has a closed form solution (i.e., the solution can be expressed in terms of known functions).

Anion - A negatively charged ion.

Anoxic - "Without oxygen." Anoxic refers specifically to conditions of no dissolved oxygen but possibly with nitrate present.

Aquifer - An underground geological formation that stores and conducts water in significant amounts and can supply the water for wells, springs, etc.

Armoring - The process of coarsening of a riverbed as fine-grained sediments are preferentially eroded. Also refers to the placement of coarse materials specifically to reduce further erosion of sediment bed.

Attenuation - Reduction of contaminant concentrations over space or time. Includes both destructive (e.g., biodegradation, hydrolysis) and non-destructive (e.g., volatilization, sorption) removal processes.

Bacterium - A single-celled organism of microscopic size (generally 0.3–2.0 micrometers [µm] in diameter). As opposed to fungi and higher plants and animals (*eukaryotes*), bacteria are *prokaryotes* (characterized by the absence of a distinct, membrane-bound nucleus or membrane-bound organelles and by deoxyribonucleic acid [DNA] that is not organized into chromosomes).

Baseflow - The portion of a stream's flow from groundwater exchange rather than from overland runoff

Bathymetry - Georeferenced water depths relative to a fixed water datum.

Baseline - A set of data representing ambient conditions that are collected before remediation is implemented. Compared with post-treatment data to evaluate the effectiveness of remediation.

Bedload - Sediment movement on top of or near a channel bed by rolling, sliding and saltating, i.e., jumping.

Bedrock - The solid or fractured rock underlying surface solids and other unconsolidated material or overburden.

Bed shear strength - A direct measure of a sediment bed's resistance to a flow-induced shear stress at the surface of the bed. Also called the **critical shear stress for erosion**. Bed shear stress is a force per unit area of the bed surface that acts parallel to the surface of the sediment bed and is generated by a current flowing over a sediment bed.

Benthic - Of or pertaining to the sediment-water interface (e.g., benthic organisms or benthic boundary layer).

Bentonite - An expandable clay mineral, subject to swelling when wet and shrinking when dry. Can be formed by chemical alteration of volcanic ash.

Bioassay - A bioassay is a test using a biological system. It involves exposing an organism to a test material and determining a response. Or to measure bioaccumulation.

Bioaugmentation - Addition of microbes to the subsurface to improve the biodegradation of target contaminants. Microbes may be "seeded" from populations already present at a site or from specially cultivated strains or mixtures of microorganisms.

Bioavailability - The degree to which a compound is available for uptake or transformation by an organism.

Biobarrier - A remediation technology designed to intercept and biologically degrade a contaminant as it passes through the permeable surface sediments.

Biochemical - Produced by or involving chemical reactions of living organisms.

Biodegradation - Biologically mediated conversion of one compound to non-toxic, mineralized end products.

Biomarker - Physiological, biochemical or histological changes that serve as indicators of exposure or effects usually at the suborganismal level.

Biomass - The total quantity or weight of an organism or organisms in a given area or volume.

Bioremediation - Use of microorganisms to control and destroy contaminants.

Biotransformation - General term for the biologically catalyzed conversion of a chemical to another product, not necessarily resulting in detoxification.

Bioturbation - The normal life cycle activities of organisms that live at the sediment-water interface, including burrowing, foraging and sediment ingestion, that lead to movement and mixing of sediments and associated contaminants.

Black carbon - Carbon phases found in sediments that appear to absorb hydrophobic organic contaminants more strongly than suggested by the organic carbon-based partition coefficient, i.e., that the effective organic carbon-based partition coefficient is much greater than is observed due to sorption onto carbons such as natural vegetative organic matter. This increased sorption is typically associated with condensed or "hard" carbon phases such as soot and it results in equilibrium partitioning theory and equilibrium partitioning sediment benchmarks that typically over-predict the porewater concentration and biological effects of a given concentration of contaminants in the sediment.

Breakthrough curve - The evolution of solute concentration measured at a fixed location such as in a column or a well.

Buffering capacity - A measure of a solution's ability to resist changes in pH upon the addition of an acid or base.

Capping - The placement of a layer of clean sediment or sand over contaminated sediments to eliminate or reduce their erosion, physically isolate them from benthic organisms or reduce the contaminant flux to the overlying water. The cap may be composed of an inert material such as sand or amended with sorptive or reactive components.

Carboxylic acid - An organic acid characterized by one or more carboxyl groups (-COOH).

Catalyst - A substance that promotes a chemical reaction but does not itself enter into the reaction.

Cation - A positively charged ion.

Chemical equilibrium - In a closed system, the net reaction rate is zero the forward and backward rates are equal and opposite such that the concentrations of the reacting substances do not change with time.

Chlorinated solvent - A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compound's structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning and other operations. Examples include trichloroethene (TCE), perchloroethene (PCE) and trichloroethane (TCA).

Clays - Silicate minerals formed by rock weathering containing trace metal oxides and organic matter and characterized by individual grain sizes of less than 2 µm. Clays are an important component of cohesive sediments and often contain a substantial fraction of the contaminants in sediments.

Cleanup level - Used to describe the degree of remediation required with respect to achieving a certain concentration of contaminants of concern (COCs) in soil, groundwater or other media at a given site or within a particular target treatment zone (TTZ). Cleanup levels are commonly specified by regulatory authorities and programs and can include numeric values for specific media. Under some regulatory programs, cleanup levels may be used as remediation goals.

Cohesive sediments - Sediments composed of fine particles such as clays and silts whose behavior is controlled by surface electrical forces that increase interparticle attraction. Particles smaller than 60 µm in diameter (defined either by actual dimension or the dimension of a spherical particle of equivalent settling velocity) are generally considered cohesive.

Colloidal matter - Substance such as organic matter <1 µm in diameter microscopically dispersed throughout surface or interstitial water.

Cometabolism - The metabolism of two compounds by an organism in which the degradation of the second compound (the secondary substrate) depends on the transformation of the first compound (the primary substrate). For example, in the process of oxidizing methane, some bacteria can fortuitously degrade chlorinated solvents that they would otherwise be unable to attack.

Combined remedies - A term used to describe the proactive combination of two or more remediation approaches or technologies.

Conceptual site model (CSM) - A hypothesis about how contaminant releases occurred and are occurring at a site, the current state of the contaminant source and transport/fate pathways to receptors.

Consolidation - Self-weight compaction of sediments with deposition of new material. The accumulating weight of a sediment will cause the porewater, held between sediment grains, to be expelled, creating a decrease in porosity with depth and time.

Contaminant of concern (COC) - One or more contaminants present at a site that contribute to the risk and impact the nature and extent of remediation. They may be selected as the targets to be destroyed or otherwise removed during remediation.

Contaminant rebound - An increase in concentration over the course of a post-treatment monitoring period following an initial decrease in contaminant concentration (typically aqueous concentration) immediately after site remediation.

Continuous-flow stirred-tank reactor (CSTR) - A perfectly mixed reactor that achieves compositional uniformity throughout its volume.

Critical body residue - A theory of toxic effects associated with a threshold accumulation of contaminants in the body of an organism.

Damkohler number (Da) - A dimensionless number that relates the chemical reaction time scale to the time scale of a relevant transport or mass transfer time scale. (The characteristic time is inverse to the rate.) In transport in porous media, the Damkohler number is typically the transport time scale divided by the reaction time scale.

Darcy scale - A scale that averages over volumes and areas that contain many pores, enough so that Darcy's law holds. Smaller than the field scale.

Darcy's Law - The relationship discovered by Henri Darcy that states the average flow rate defined by the specific discharge in a porous medium is proportional to the negative hydraulic-head gradient.

Darcy velocity - The Darcy velocity is the specific discharge (discharge through an area divided by the total area, both pores and solids) used in modeling at the Darcy scale.

Dechlorination - A reaction involving the removal of one or more chlorine atoms from a chlorinated organic compound.

Degradation - The transformation of a compound through biological or abiotic reactions. Also, the process by which the bottom of a water body is lowered due to erosion of bed sediment.

Dehalogenation - Removal of one or more halogen atoms (e.g., chlorine, fluorine or bromine) from an organic compound.

Dehalorespiration - Energy-yielding respiratory metabolism that encompasses the reductive removal of halogen atoms from a halogenated compound, such as chlorinated or brominated ethenes.

Deposition - Process of suspended sediment settling and coming to rest on the bed/bottom of the water body.

Desorption - Opposite of sorption the release of chemicals from solid surfaces.

Diagenesis - Chemical, physical and biological changes in sediments, particularly in the near surface environment where the changes are referred to as early diagenesis.

Dichloroethene (DCE) - An ethene containing two chlorine atoms that may be used as a degreaser a dechlorination break-down product of PCE and TCE.

Diffusion (molecular diffusion) - The flux of solute from areas of higher concentration to areas of lower concentration due to random molecular motion.

Dilution - The increase in volume that a given amount of solute occupies. Dilution tends to decrease solute concentration.

Dispersion - The spreading of a stream or discrete volume (plume) of solute in a flow field. Also known as hydrodynamic dispersion. Dispersion is typically considered in terms of mechanical dispersion and molecular diffusion.

Dispersion coefficient - Parameter in the advection-dispersion equation (ADE) that characterizes the rate of dispersion. Possible types include: effective, ensemble, local, macro and mechanical. Units are length squared over time $[L^2T^{-1}]$.

Dispersivity - A parameter in advection-dispersion transport models. Originally assumed to be a characteristic property of the porous medium, but has been shown to vary with the scale of the problem. Multiplied by the average linear velocity to yield the mechanical dispersion coefficient when using the linear parameterization of dispersion. Units are length [L].

Dredging - The process of removal of sediments in the wet, that is, without draining a contaminated sediment site. Dredging can be conducted by both mechanical (e.g., clamshell bucket) or hydraulic (e.g., cutterhead suction dredge) means.

Dredging prism - The volume of sediments defined by area and thickness proposed for removal by dredging.

Ebullition - The process of gas migration to the surface as a bubble, typically after the accumulation of a gas such as methane during methanogenesis. Gas ebullition can disturb and transport sediments and carry volatile, dissolved and surface active contaminants to the surface.

Electrical conductivity - See "Specific conductance."

Electron - A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions (e.g., oxidation-reduction reactions). Every atom contains electrons and protons (positively charged particles).

Electron acceptor - Substance that receives electrons (and therefore is reduced) in an oxidation-reduction reaction, which may be abiotic or biotic. Common electron acceptors in the subsurface are oxygen, nitrate, sulfate, ferric iron and carbon dioxide. Chlorinated solvents (e.g., TCE) can serve as electron acceptors under anaerobic conditions.

Electron donor - Substance that donates electrons (and therefore is oxidized) in an oxidation-reduction reaction, which may be abiotic or biotic.

Enhanced *in situ* bioremediation (EISB) - See "*In situ* bioremediation."

Environmental dredging - The removal of contaminated sediments from a water body for purposes of sediment remediation.

Enzyme - A protein created by living organisms to use in transforming a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.

Equilibrium partitioning (EqP) theory - The theory of a quasi-static relationship between solid and adjacent water or porewater concentration of a contaminant. For hydrophobic organic compounds, this relationship is normally assumed to be given by $W_s = K_{oc}f_{oc}\,C_w$, where W_s is the solid phase concentration, K_{oc} is the organic carbon-based partition coefficient of the compound, f_{oc} is the fraction organic carbon of the sediment and C_w is the adjacent water or porewater concentration. The equilibrium partitioning theory often overestimates the water or porewater concentration in sediments due to the presence of strongly sorbing "black" carbon phases on the solid.

Equilibrium partitioning sediment benchmarks (ESB) - The estimation of a screening level solid concentration on the basis of prediction of a solid concentration based upon a water or porewater concentration that is toxic, and the use of equilibrium partitioning theory. The equilibrium partitioning sediment benchmarks are typically conservative in that the benchmark solid concentration is typically greater than predicted from a porewater concentration by equilibrium partitioning theory due to the presence of strongly sorbing "black" carbon phases on the solid.

Erodibility - A measure of a sediment bed's propensity to lose sediment particles due to the action of currents and/or waves.

Erosion - The removal or wearing away of soil particles from the bottom or sides, i.e., wetted perimeter, of a water body through the action of moving water, i.e., currents and/or waves.

Estuarine turbidity maximum (ETM) zone - The mixing zone between upland fresh water and sea water. Also known as the tidal mixing zone and estuarial mixing zone.

Ex situ - Latin term referring to the removal of a substance from its natural or original position, such as the treatment of dredged material after removal from a sediment environment.

Fermentation - Oxidation or reduction of an organic compound occurring without the uses of an external electron acceptor.

Fick's Law - A mathematical equation that quantifies the diffusive mass flux as proportional to the negative concentration gradient.

Flocculation - Coagulation and growth of suspended cohesive sediment particles.

Fluvial - Of, relating to, or happening in a river.

Full scale - Implementation of a remediation technology at a scale that is intended to represent what would be deployed to treat the entirety of a target treatment zone.

Generated residuals - Contaminated post-dredge surface sediments that are dislodged or suspended by the dredging operation and are subsequently redeposited on the bottom of the water body.

Geochemical - Produced by or involving non-biochemical reactions.

Geochronology - Analysis of sediment history (e.g., sedimentation rates) using depth profiles of radioisotope measurements to date layers in the core.

Geomorphology - The study of the characteristics, configuration and factors influencing the long-term evolution of the sediment bed and surrounding landforms.

Grain-size distribution (GSD) - The fraction of particles within each size interval.

Growth substrate - An organic or inorganic compound used as an electron donor and upon which bacteria can obtain energy for growth.

Half-life - Time required to reduce the concentration of a constituent to half of its initial value.

Henry's Law - The assumption of linear partitioning of contaminants between water and air, typically valid for low solubility contaminants. In combination with the sediment-water partition coefficient, this parameter largely defines equilibrium partitioning in the environment. The Henry's Law constant is typically proportional to compound vapor pressure and inversely proportional to water solubility.

Heterogeneity - The occurrence of variability of properties in space.

Hydraulic conductivity - A measure of the ability of a porous medium to transmit a liquid (typically water) when subjected to a difference in hydraulic head. Has units of length over time

[LT^{-1}] (e.g., meters/day). It depends on the permeability of the porous medium and the viscosity of the fluid.

Hydraulic gradient - Change in hydraulic head per unit distance a vector that points in the direction of maximum increase of the head.

Hydrocarbons - Chemical compounds that consist entirely of carbon and hydrogen.

Hydrodynamics - The movement of water when external forces, such as wind and gravity, act on a water body.

Hydrophobic - "Water-fearing." Hydrophobic compounds, such as oils and chlorinated solvents, have low solubilities in water and tend to form a separate nonaqueous phase.

Hydroxyl (^{-}OH) - A chemical group that consists of one atom of hydrogen and one of oxygen and is neutral or negatively charged.

Hyporheic exchange - Exchange of water between groundwaters and surface waters at a site. This exchange can occur via a variety of mechanisms without direct groundwater movement to surface water.

Immiscibility - The inability of two or more substances or liquids to readily dissolve into one another, such as oil and water.

Impermeable - Not easily penetrated. The property of a porous media or soil that does not allow, or allows only with great difficulty, the movement or passage of water.

Implementation monitoring - Monitoring conducted during the application of a remedy to evaluate construction performance.

In situ - Latin term meaning "in place." In the natural or original position, such as the treatment of sediments in-place.

***In situ* bioremediation** - The use of microorganisms to degrade contaminants in place with the goal of obtaining harmless chemicals as end products. Generally, *in situ* bioremediation is applied to the degradation of contaminants in saturated soils and groundwater, although bioremediation in the unsaturated zone can occur.

***In situ* remediation** - Remedial approaches that leave the sediment in place such as *in situ* capping and *in situ* treatment through the addition of sequestering amendments. *In situ* bioremediation is the use of microorganisms to degrade contaminants in place with the goal of producing harmless chemicals as end products.

***In situ* toxicity tests** - In-place biological assays evaluating toxic effects on organisms in sediments or water. That is, not conducted in the laboratory after removal of the sediments. Organisms are typically caged to control their exposure to the area of concern.

Inorganic compound - A chemical that does not contain a reduced form of carbon, that is, a carbon atom with a valence state $< +4$.

Interstitial water - Water in the pore space between sediment particles. The equivalent of groundwater in an aquifer.

Intrinsic bioremediation - A type of intrinsic remediation that uses the innate capabilities of naturally occurring microbes to degrade contaminants without requiring engineering steps to enhance the process.

Isolation cap - An engineered sediment cap involving the placement of clean sediment or dredged material with or without amendments to contain contaminants and separate the biologically active zone from underlying contaminated sediments.

Isotope - Any of two or more species of an element in the periodic table with the same number of protons. Isotopes have nearly identical chemical properties but different atomic masses and physical properties. For example, the isotopes chlorine 37 (^{37}Cl) and chlorine 35 (^{35}Cl) both have 17 protons, but ^{37}Cl has two extra neutrons and thus a greater mass.

Isotope fractionation - Selective degradation of one isotopic form of a compound over another isotopic form. For example, microorganisms can transform the ^{35}Cl isotopes of perchlorate more rapidly than the ^{37}Cl isotopes.

Kinetics - The study of rates in chemical kinetics it is the study of the rate of a chemical process.

Lactate - A salt or ester of lactic acid.

Log K_{ow}. - Logarithmic expression of the octanol-water partition coefficient (K_{ow}) a measure of the equilibrium concentration of a compound between octanol and water.

Long-term monitoring (LTM) - Monitoring conducted after a remedial measure achieves its construction and implementation objectives, to ensure continued protection and performance and to document risk reduction.

Longitudinal dispersion - Dispersion in the direction of bulk flow.

Macroscopic - Large enough to “homogenize” or “average over” smaller-scale processes. For example, the Darcy scale is macroscopic in relation to the pore scale.

Mass balance - An accounting of the total inputs and outputs to a system. For dissolved plumes, it refers to a quantitative estimation of the mass loading to a dissolved plume and the mass attenuation capacity within the affected subsurface environment.

Mass transfer - The general term for the physical processes involving molecular and advective transport of atoms and molecules within physical systems. In this context, the term refers to the movement of solute mass between different locations such as occurs in absorption, evaporation, precipitation and distillation. Here, a location usually means a stream, phase, domain, fraction or component.

Maximum Contaminant Level (MCL) - Standards set by the U.S. Environmental Protection Agency (USEPA) or state equivalent for drinking water quality that provide for a legal threshold limit on the amount of a hazardous substance that is allowed in drinking water under the Safe Drinking Water Act. The limit is usually expressed as a concentration in milligrams or micrograms per liter of water.

Mechanical dispersion - Transport phenomena due to the variations in local velocity, both in magnitude and direction along the tortuous flow paths and between adjacent flow paths as a result of the velocity distribution, that causes a solute (tracer) mass to spread and occupy an ever-increasing volume of the porous media.

Media - Groundwater, porous media, soil, air, surface water or other parts of an environmental system that can contain contaminants and be the subject of regulatory concern and remediation activities.

Metabolism - The chemical reactions in living cells that are necessary to maintain life, including reproduction and the conversion of food sources to energy and new cell mass.

Metabolite - The intermediates and products of metabolism.

Methanogen (methanogenic archaea) - A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Some methanogens use carbon dioxide as an electron acceptor to produce methane while others obtain energy by splitting acetate into carbon dioxide and methane.

Methanogenesis - Process of producing methane during biological metabolism.

Methanotroph (methanotrophic bacteria) - A microorganism that is able to oxidize methane for energy.

Micelle - An aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic “head” regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle center.

Microcosm - A laboratory vessel established to resemble the conditions of a natural environment. A microcosm is typically an effort to reproduce a single key feature of the natural system.

Mesocosm - A laboratory or controlled field environment established to resemble the conditions of a natural environment. A mesocosm is typically an effort to reproduce the multiple features or all features of a natural environment in a controlled manner.

Microorganism (microbe) - An organism of microscopic or submicroscopic size, e.g., bacteria.

Mineral - A naturally occurring solid formed through geological processes that has a characteristic chemical composition, a highly ordered atomic structure and specific physical properties. A rock, by comparison, is an aggregate of minerals and/or mineraloids and need not have a specific chemical composition.

Mineralization - The complete degradation of an organic chemical to carbon dioxide, water and possibly other inorganic compounds or elements.

Miscible - Two or more liquids that can be mixed and will remain mixed under normal conditions.

Mixing - A process by which two or more substances are joined together such as occurs with cap material during placement onto soft sediments.

Model calibration - Using site-specific information from a historical period of time to adjust model parameters in the governing equations to obtain an optimal agreement between a measured data set and model calculations for the simulated state variables.

Model validation - Demonstrating that a calibrated model accurately reproduces known conditions. Model validation is inherently limited to the range of data employed in the calibration and validation data sets. Since future conditions are not "known," a "validated" model may not have the ability to predict future conditions.

Mole fraction - The number of moles of a component of a solution divided by the total number of moles of all components.

Molecular diffusion - See "Diffusion."

Monitored natural recovery (MNR) - A remedial approach that relies on natural physical, chemical and biological processes to isolate, destroy or otherwise reduce the bioavailability or toxicity of contaminants.

Monte Carlo simulation - A problem-solving technique used to approximate the probability of certain outcomes by running multiple trial runs, called simulations, using random variables. Monte Carlo methods allow evaluation of complex situations involving random behavior, such as games of chance, and can help reduce uncertainty in estimating future outcomes in areas such as risk assessment or actuarial analyses.

Mudstones - A fine-grained sedimentary rock whose original constituents were clays or muds. Hardened mud a mix of silt and clay-sized particles.

Nanoscale - Generally deals with structures of the size 100 nanometers (nm) or smaller. For example, reactive iron produced in this size range is referred to as nanoscale iron.

Natural recovery - Reduction in the mass, toxicity, mobility, volume or concentration of contaminants in sediment caused by natural processes that act without human intervention. These *in situ* processes include chemical transformation, reduction in contaminant mobility or bioavailability, physical isolation and/or dispersion.

Natural organic matter (NOM) - A form of naturally occurring organic matter that has been broken down to some base-level compounds (such as cellulose, chitin, protein, lipids, etc.). NOM provides nutrients to insects, bacteria, fungi, fish and other organisms at the base of the food chain.

Nonaqueous phase liquid (NAPL) - An organic liquid that does not mix easily with water and thus maintains itself as a separate phase from water.

Numerical model - A mathematical model that uses a numerical time-stepping procedure to estimate behavior of a system over time (as opposed to an analytical model). The mathematical solution is represented by a generated table and/or graph. Numerical models require greater computing power, but they can allow more realistic simulations of complex systems.

Octanol-water partition coefficient (K_{ow}) - Ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. Octanol with the chemical formula $CH_3(CH_2)_6CHOH$ is an organic solvent used as a surrogate for NOM. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment. Inversely related to aqueous solubility (a high K_{ow} indicates a compound will preferentially partition into an organic phase rather than into water).

Operation and maintenance (O&M) - Activities conducted at a site to ensure a technology or approach is effective and operating properly. The term O&M covers a wide range of activities, from overseeing the proper functioning of a system to conducting monitoring to evaluate the effectiveness of an action.

Organic - Referring to or derived from living organisms. In chemistry, organic compounds contain reduced forms of carbon in combination with hydrogen and other elements.

Organophilic clay - A manufactured clay in which minerals (typically sodium) have been cation exchanged with organic substituents to render the clay more sorbing of organic material, including NAPL.

Oxic - Containing oxygen or having been oxygenated. Often used to describe an environment, a condition or a habitat in which oxygen is present.

Oxidation - Transfer (loss) of electrons from a substance, such as an organic contaminant. Oxidation of compounds can supply energy that microorganisms use for growth and reproduction. Often, but not always, oxidation results in the addition of an oxygen atom and/ or the loss of a hydrogen atom.

Oxidation-reduction potential (ORP) - The tendency of a solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (to be reduced by oxidizing the new species) a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (to be oxidized by reducing the new species). A positive ORP indicates the solution is oxidizing, while a negative ORP indicates reducing conditions are dominant.

Partition coefficient (K_d) - Ratio of the concentrations of a substance in a liquid phase in contact with a solid phase. Measure of the sorption potential whereby a contaminant is distributed between the solid and water phase. With the Henry's Law constant, the partition coefficient defines the equilibrium distribution of a hydrophobic organic compound between air, water and sediment.

Passivation - Process of making a material "passive" in relation to another material. Often used to refer to the formation of a hard, non-reactive surface film on many reactive or corrosive materials (such as aluminum, iron, zinc, magnesium, copper, stainless steel, titanium and silicon) that inhibits further reactivity.

Pathogen - Microorganisms (e.g., bacteria, viruses or parasites) that can cause disease in humans, animals and plants.

Peclet number (Pe) - A dimensionless quantity that expresses the relative importance of advection and diffusion or dispersion of solutes.

Permeability - A measure of the ability of a material, such as soil or aquifer porous media, to transmit fluids such as water. It is the measure of the relative ease of fluid flow under unequal pressure. Units of measurement are length squared [L^2].

Permeable sorptive barrier (PSB) - A permeable wall or layer containing sorptive media that retards the motion of contaminants from underlying sediments or a source area. Because the sorptive layer will exhibit finite capacity, the use of a PSB is normally coupled with source control to reduce the mass or volume of contaminant to be sorbed.

pH - Equals the negative logarithm of the hydrogen ion molar concentration, and used to express the intensity of the basic or acid condition of a liquid generally ranges from 0 to 14, where 0 is the most acidic and 7 is neutral. Natural waters usually have a pH between 6.5 and 7.5.

Phytoremediation - The use of plants and in some cases the associated rhizosphere (root zone) microorganisms for *in situ* remediation of contaminants.

Pilot-scale - A scale of demonstration, testing or evaluation under laboratory or field conditions that can incorporate certain features and processes that are representative of a full-scale system. A pilot-scale study is often used to investigate the design and performance of a full-scale system. See "Full-scale" and "Pilot test".

Pilot test - A trial run of a remediation technology implemented at the field scale. Performed to assess the feasibility of the remediation technology and/or to collect field-scale data on which to base full-scale design. Generally conducted at a smaller scale than full-scale treatment.

Polychlorinated biphenyls (PCBs) - Organic compounds composed of 1–10 chlorine atoms attached to two joined benzene rings (biphenyls) and formerly used in a wide variety of applications, such as electrical transformers and capacitors for insulating purposes and in gas pipeline systems as lubricant. The sale and new use of these chemicals were banned by U.S. law in 1979.

Polycyclic aromatic hydrocarbon (PAH) - Chemical compound that consists of fused aromatic rings and does not contain heteroatoms or carry substituents. PAHs occur in oil, coal and tar deposits and are produced as byproducts of fuel burning (whether fossil fuel or biomass). As a pollutant, they are of concern because they are toxic to aquatic life, and some PAH compounds have been identified as carcinogenic, mutagenic and teratogenic.

Polymerase chain reaction (PCR) - Technique to amplify a single or few copies of a specific DNA sequence by several orders of magnitude. Allows detection of a target gene or parts of a gene, even when present at low concentrations in soil, sediments or groundwater, for example. PCR relies on thermal cycling, consisting of cycles of repeated heating and cooling of the reaction for DNA melting and enzymatic replication.

Porewater - The water within the interstitial space between sediment grains. Also known as interstitial water.

Porosity - The fraction of the subsurface volume filled with pores or cavities through which water or air can move.

Practical salinity units (PSU) - The ratio of the conductivity of seawater to the conductivity of a standard solution of potassium chloride. Standard seawater has a PSU of 35.

Precipitate - The formation of a solid from a solution or suspension by chemical or physical change.

Pyrite - An iron sulfide mineral with the formula FeS_2. The most common of the sulfide minerals. Also called fool's gold.

Radioactive decay - The process by which an atomic nucleus of an unstable atom decays to form other atoms and in the process yields energy.

Rebound - See "Contaminant rebound."

Recharge - Process by which water is added to a zone of saturation, usually by percolation from the ground surface (e.g., the recharge of an aquifer via precipitation and infiltration). Also, the amount of water added.

Redox reactions - Reduction/oxidation reactions are those in which atoms have their oxidation number changed. For example, carbon may be oxidized by oxygen to yield carbon dioxide or reduced by hydrogen to yield methane. The redox potential (ORP) reflects the tendency of a chemical species to acquire electrons and thereby be reduced. In a redox reaction, one chemical species—the reductant or reducing agent—loses electrons and is oxidized, and the other—the oxidant or oxidizing agent—gains electrons and is reduced.

Reducing - Environmental conditions that favor a decrease in the oxidation state of reactive chemical species (e.g., reduction of sulfates to sulfides).

Reduction - Transfer of electrons to a substance such as oxygen occurs when another substance is oxidized.

Reductive dechlorination - Reaction involving removal of one or more chlorine atoms from an organic compound and their replacement with hydrogen atoms. A subset of reductive dehalogenation. Key reaction for anaerobic degradation of chlorinated hydrocarbons.

Reductive dehalogenation - The process by which a halogen atom (e.g., chlorine or bromine) is replaced on an organic compound with a hydrogen atom.

Remedial action - The actual construction or implementation phase of a contaminated site cleanup following remedial design.

Remediation - Cleanup technology or approach used to remove or contain contamination.

Remediation goal - Defines what the remedial actions are intended to achieve or accomplish. Goals can be general for the overall remediation system (or treatment train) or they may be specific to one of the technologies in the treatment train (see "Treatment Goals" below). Under CERCLA, goals are often numeric levels. For example, during the Feasibility Study process under CERCLA, preliminary remedial goals (PRGs) are the concentrations used to define the area to be remediated and to what level. PRGs become remedial goals (RGs) once a Record of Decision (ROD) specifies the selected remedy and modifies the PRGs.

Reynolds number (Re) - A dimensionless quantity that expresses the relative importance of inertial forces compared to viscous forces in a flow system. A small Reynolds number is associated with laminar flow a large Reynolds number is associated with turbulent flow.

Residence time (retention time) - The average amount of time that a particle spends in a particular system.

Residual sediment - Sediment and associated contaminants left after a dredging operation. A combination of undredged inventory (either planned or unplanned) and sediment resuspended, lost and redeposited by dredging.

Resuspension - The erosion of deposited sediment and movement of sediment particles into the water column. The resuspension rate is a function of the flow-induced bed shear stress and the shear strength of the deposited sediment. Also used to refer to sediment and contaminant losses due to movement of sediment into the water column through losses during dredging operations.

Retardation - Slowing of the movement of substances through a porous media relative to the advective velocity. For example, a contaminant exhibiting a retardation factor of 5 moves one-fifth as fast as the water itself or a non-reactive tracer such as chloride, which has a retardation factor near 1.0.

Risk - The probability of an undesirable outcome or consequence, e.g., the probability of adverse health effects due to contaminants.

Risk analysis - The techniques, methods and approaches for developing an understanding of the processes shaping the scope and magnitude of risks.

Risk communication - The exchange of information that supports making informed judgments about risk and risk management.

Risk management - The structured process through which actions for reducing risks are identified, evaluated, selected and implemented.

Salinity - Percentage of salt in water.

Saturation - The fraction of porous media pore space that contains fluid (e.g., water or NAPL). If no fluid is specified, it is generally taken to refer to water saturation.

Second-order reaction - A chemical reaction with a rate proportional to the concentration of the square of a single reactant or the product of the concentration of two reactants: rate = $k[A][B]$ or $k[A]^2$.

Sediment stability - Refers to the ability of a sediment layer to resist erosional forces acting on the bed surface due to the action of currents and/or waves and remain largely intact and undisturbed over time.

Sediments - Soil, sand and minerals carried from land into water bodies and suspended or deposited by flowing water. The physical movement of sediment particles are due to the action of moving water and gravity.

Sedimentation - The process of deposition of sediment. Often refers to total deposition over a specified time period (e.g., a storm event or a single year).

Shear stress - That component of stress that acts tangential to a plane through any given point in a body.

Silts - Sediments exhibiting a grain size intermediate between that of clays and non-cohesive sands, typically between 2 and 60 μm in diameter.

Site characterization - The collection of environmental data that are used to describe the conditions at a property and delineate the nature and extent of a site's contamination.

Soil or sediment mixing - An approach used to deliver and distribute remedial amendments to contaminated soil or sediments.

Sediment organic matter (SOM) - Organic constituents in the sediment, including undecayed plant and animal tissues, their partial decomposition products and the soil biomass. SOM includes high molecular-weight organic materials (such as polysaccharides and proteins), simpler substances (such as sugars, amino acids and other small molecules) and humic substances. Often characterized by the fraction organic carbon in a sediment.

Solubility - Ability of a substance to dissolve (or solubilize). The solubility of a specific solute is its maximum concentration in a given solvent at a reference temperature.

Solute - A substance dissolved in another substance. A relevant example is a contaminant dissolved in sediment porewater.

Solvent - A substance, usually a liquid, capable of dissolving another substance.

Sorb - To take up and hold by either adsorption or absorption.

Sorption - Collection of a substance on or within a solid and held by physical or chemical attraction. Can refer to either absorption (in which one substance permeates another) or adsorption (surface retention of solid, liquid or gas molecules, atoms or ions).

Source strength - The mass discharge from a source zone. Represents the mass loading to a plume per unit time (e.g., grams TCE released per day).

Source zone - A zone that serves as a reservoir of contaminants that sustains contaminant concentrations in the system. This may be an upland source of contaminated solids, contaminated groundwater or surface water or the sediments themselves. The nature of the source may be contaminants dissolved, sorbed to solids or a separate NAPL.

Specific conductance (electrical conductivity) - Rapid method of estimating the dissolved solid content (total dissolved solids) of a water by testing its capacity to carry an electrical current.

Stabilization/solidification - Remediation technique in which contaminants are physically bound or enclosed within a stabilized mass (solidification) or their mobility is reduced due to chemical reactions induced between a stabilizing agent and the contaminants (stabilization).

Stakeholder - A person (often considered to be other than regulators, owners or technical personnel) who has a legitimate interest in a contaminated site.

Steady-state - A condition of a physical system or device that does not change over time or in which any one change is continually balanced by another, such as the stable condition of a system in equilibrium.

Stoichiometry - The quantitative (measurable) relationships between the reactants and products in a balanced chemical equation.

Streamline (flow line) - A line that is everywhere tangent to the flow velocity vector. Shows the direction a fluid element will travel in at any point in time.

Stratum (strata) - A layer of subsurface media with internally consistent characteristics that distinguishes it from contiguous layers. Each layer is generally one of a number of parallel layers that lie one upon another, laid down by natural forces. Typically seen as sands of different colored or differently structured material exposed in cliffs, road cuts, quarries and river banks.

Substrate - The reactant that is consumed during a catalytic or enzymatic reaction.

Sulfate-reducing bacteria (SRB, sulfate reducer) - Bacteria that convert sulfate to hydrogen sulfide. Often play important roles in the oxygen-limited subsurface.

Surfactant - A material that can greatly reduce the surface tension of water when used in very low concentrations. Primary ingredient of many soaps and detergents.

Suspended load - The amount of sediment that is supported by the upward components of turbulence in a channel and that stays in suspension for an appreciable length of time.

Thermodynamics - The study of the conversion of energy into work and heat and its relation to macroscopic variables, such as temperature and pressure.

Thin layer placement - The placement of a thin (typically 6 in. or less) layer of sediment, sand or amendments to reduce exposure to underlying sediments. Also referred to as thin layer capping.

Tortuosity - A parameter used in some models. It represents the actual length of a fluid flow path in porous media, which is sinuous in form, divided by the straight-line distance between the ends of the flow path.

Total concentration - Typically used to refer to concentrations in water and is the sum of the concentration in all phases that make up the water, e.g., truly dissolved contaminants, colloidally bound contaminants and particulate bound contaminants if referring to an unfiltered sample.

Total organic carbon (TOC) - A measure of the mass of carbon bound in organic compounds in a substance (e.g., soils, sediments and water).

Toxicity - The degree to which a substance or mixture of substances can cause harm to organisms. Acute toxicity involves harmful effects in an organism through a single or short-term exposure. Chronic toxicity is the ability of a substance or mixture of substances to cause harmful effects over an extended period.

Toxicity test - An experimental procedure used to evaluate the degree to which a substance or mixture of substances can cause harm to organisms.

Tracer test - Used to "trace" the path of a migrating fluid. For groundwater applications, tracer tests are commonly conducted by dissolving a tracer chemical into groundwater at concentrations that do not significantly change the aqueous density. These might be used to trace groundwater migration rates into and through sediments.

Transport - The processes of moving sediment particles or solutes (in fluid), namely, advection, diffusion and dispersion.

Treatability test - A means of evaluating the suitability of treatment technologies or processes prior to their implementation. Treatability tests are commonly carried out under laboratory conditions.

Treatment goal - Specific criteria by which the successful completion of an activity can be determined.

Treatment performance monitoring - Monitoring to obtain data concerning the effectiveness of a technology or approach and achievement of treatment goals.

Transient - A condition of a physical system or device that is time-dependent.

Turbulence (turbulent flow) - A flow regime characterized by chaotic property changes. This includes low momentum diffusion, high momentum convection and rapid variation of pressure and velocity in space and time.

Undisturbed residuals - Contaminated sediments found at the post-dredge sediment surface that have been uncovered by dredging but not fully removed. Also called undredged inventory.

Vapor pressure - A measure of a substance's propensity to evaporate. The force per unit area exerted by vapor in an equilibrium state with surroundings at a given pressure. Increases exponentially with an increase in temperature. A relative measure of chemical volatility, vapor pressure is used to calculate water partition coefficients and in the determination of volatilization rate.

Viscosity - The molecular friction within a fluid that produces flow resistance. Describes the resistance of a fluid that is being deformed by shear stress.

Volatile - Evaporates readily at normal temperatures and pressures.

Volatile organic compound (VOC) - Any organic compound that has a high enough vapor pressure under normal conditions to significantly vaporize and transfer from a liquid to a gas phase.

Volatilization - Transfer of a chemical from the liquid to the gas phase (as in evaporation).

Xenobiotic - A substance that is not normally found in organisms.

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