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Technical Resource Document on Monitored Natural Recovery

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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TECHNICAL RESOURCE DOCUMENT
ON
MONITORED NATURAL RECOVERY

by

Battelle
Columbus, OH 43201

for

U.S. Environmental Protection Agency
National Risk Management Research Laboratory

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NOTICE

The U.S. Environmental Protection Agency (EPA), through its office of Research and Development (ORD), funded and managed the preparation of this document. This document is a technical resource primarily intended for federal project managers considering the use of monitored natural recovery (MNR) for remediating contaminated sediment sites under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), more commonly known as 'Superfund'. Many aspects of this document may also be useful to state and local government organizations, consultants, and other members of the environmental community and their technical advisors.

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and groundwater; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment, advancing scientific and engineering information to support regulatory and policy decisions, and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

Contaminated sediment sites pose significant risks throughout the United States to human health and ecological receptors/resources. Several approaches are available for remediating such sites and contributing to the recovery of the associated ecosystems. These approaches range from engineered solutions such as dredging and *in-situ* capping to reliance on natural physical, chemical, and biological processes to contain, destroy, and/or reduce the bioavailability and toxicity of contaminants in sediments. Reliance on natural recovery processes combined with a comprehensive monitoring program over time has become known as monitored natural recovery (MNR). This report was prepared as a technical resource document (TRD) on MNR to complement Agency guidance on MNR provided in a previous publication, *Contaminated Sediment Remedial Guidance for Hazardous Waste Sites*, Chapter 4, Monitored Natural Recovery (EPA, 2005a). EPA’s Office of Research and Development is making this report available to the user community as supplemental material to the above referenced guidance document.

Cynthia Sonich-Mullin, Director
National Risk Management Research Laboratory

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HIGHLIGHTS

ACRONYMS AND ABBREVIATIONS

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
ADP	acoustic Doppler profiler
AEP	available for equilibrium partitioning
AhR	aryl hydrocarbon receptor
AOM	amorphous organic matter
APHA	American Public Health Association
ASSET	Adjustable Shear Stress Erosion and Transport
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
AVS	acid volatile sulfide
BC	black carbon
BSAF	biota sediment accumulation factor
CB	chlorobiphenyl
CBR	critical body residue
CEC	cation exchange capacity
CSM	conceptual site model
CWA	Clean Water Act
CYP	cytochrome P450 mixed function oxygenase
DDT	dichlorodiphenyltrichloroethane
DET	diffusive equilibration in thin film
DGT	diffusive gradients in thin film
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
DRH	TPH-diesel range
EDTA	ethylene diamine tetraacetate
Eh	redox potential
EPA	U.S. Environmental Protection Agency
EqP	equilibrium partitioning
ESB	equilibrium partitioning sediment benchmark
EXAFS	extended X-ray absorption fine structure
FCV	final chronic value
FIAM	Free Ion Activity Model
FID	flame ionization detector
GC	gas chromatography
GRH	TPH-gasoline range
HOC	hydrophobic organic contaminant

ICP-AES	inductively-coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
I.D.	inner diameter
IOMD	intraorganic matter diffusion
IUPAC	International Union of Pure and Applied Chemistry
MDL	method detection limit
MeHg	monomethyl mercury
MFO	mixed function oxygenase
MGP	manufactured gas plant
MNR	monitored natural recovery
MS	mass spectrometry
NAPL	non-aqueous phase liquid
NOAA	National Oceanic and Atmospheric Administration
NOM	natural organic matter
NRC	National Research Council
NRMRL	National Risk Management Research Laboratory
NS&T	National Status and Trends
OCDD	octachlorodibenzodioxin
OSI	Organism-Sediment Index
PAH	polycyclic aromatic hydrocarbon
PCA	principal component analysis
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofurans
pH	hydrogen ion activity
pHpzc	pH at the point of zero charge
pKa	acid dissociation constant
POC	particulate organic carbon
ppm	parts per million
PSD	particle size distribution
PSEP	Puget Sound Estuary Program
PVA	polytopic vector analysis
QA	quality assurance
QC	quality control
RAO	remedial action objective
Redox	oxidation/reduction
RI	remedial investigation
ROD	Record of Decision
RRH	TPH-residual (crude and heavy fuel oil) range
RTM	reactive transport model
SEAWOLF	Sediment Erosion Actuated by Wave Oscillations and Linear Flow
SEM	simultaneously extracted metal
SIM	selected ion monitoring
SOM	soil organic matter

SPI	sediment profile imagery
SQT	Sediment Quality Triad
SRB	sulfate-reducing bacteria
SUDAS	Iowa Statewide Urban Design and Specifications
SVOC	semivolatile organic compound
TCDD	tetrachlorodibeno-*p*-dioxin
TCL	target contaminant list
TEA	terminal electron acceptor
TEF	toxicity equivalent factor
THC	total extractable hydrocarbon
TOC	total organic carbon
TPH	total petroleum hydrocarbon
TRD	technical resource document
UCM	unresolved complex mixture
UNEP	United Nations Environmental Programme
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
WHAM	Windermere Humic Aqueous Model
WHO	World Health Organization
XANES	X-ray absorption near edge structure
XAS	X-ray absorption
XRD	X-ray diffraction

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- Contract No. 68-C-00-185, Task Order 28
- Contract No. EP-C-05-057, Task Order 84
- Contract No. EP-W-09-024, Work Assignments 3-07 and 4-07

The scope of this TRD has changed several times during the conduct of this project to more fully and accurately represent a companion or complimentary report to EPA's guidance on MNR in Chapter 4 of the *Contaminated Sediment Remedial Guidance for Hazardous Waste Sites* published in 2005. Collaborative efforts between EPA and the project's prime contractor, Battelle (Columbus, OH), over several mid-course corrections have resulted in a TRD that reflects the Agency's goals of providing supportive information on methods for measuring and predicting MNR without infringing on the policy guidance and technical protocols established in the above-mentioned guidance document.

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ABSTRACT

In 2005, the United States Environmental Protection Agency (EPA) published a document entitled *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (EPA, 2005a), which provides technical and policy guidance for project managers and teams making risk management decisions for contaminated sediment sites. This EPA guidance document addresses both *in-situ* and *ex-situ* remedies for contaminated sediment sites, including, among others, dredging and excavation, *in-situ* capping, and monitored natural recovery (MNR).

This report is a Technical Resource Document (TRD) on MNR intended to function as a complement to Chapter 4 on MNR in the aforementioned EPA guidance document. As such, the purpose of this TRD is to provide detailed information on field-scale methodologies and approaches that can be used to measure and/or predict natural processes that contribute to the reduction of risks to human and ecological receptors at contaminated sediment sites. Although the document includes information that may be useful in developing a site-specific protocol, it is not a protocol or guidance document. The goals of this TRD are to: 1) identify and describe natural physical, chemical, and biological processes normally associated with recovery of contaminated sediments, and 2) discuss techniques and methods for quantifying and assessing the rates and extent of those recovery processes that may be occurring at a particular site. The number and types of measurement and analytical methodologies used for evaluating MNR at contaminated sediment sites will be influenced by the size and complexity of the site, project resources, available data, and the scope of decisions to be made.

This TRD consists of five technical sections that address different facets of MNR, including an introduction and overview of MNR (Section 1); a discussion on sedimentation and contaminant isolation (Section 2); consideration of the fate and transport of organic (Section 3) and inorganic (Section 4) contaminants in sediments; and a description of a six-point process for developing and implementing a long-term monitoring plan to evaluate and forecast MNR progress (Section 5). A comprehensive set of References for the five technical sections is provided (Section 6).

1.0 INTRODUCTION

1.1 Purpose and Objectives

In 2005, the United States Environmental Protection Agency (EPA) published its *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (EPA, 2005a), which provides technical and policy guidance for project managers and teams making risk management decisions for contaminated sediment sites. This EPA guidance document addresses both *in-situ* and *ex-situ* remedies for contaminated sediment, including dredging and excavation, *in-situ* capping, and monitored natural recovery (MNR).

This report is a Technical Resource Document (TRD) on MNR intended to function as a complement to Chapter 4 on MNR in the aforementioned EPA guidance document. As such, the purpose of this TRD is to provide information on field-scale methodologies or approaches that can be used to measure and/or predict natural processes that contribute to the reduction of risk to human health and ecological receptors/resources at contaminated sediment sites. Although it includes information that may be useful in developing a site-specific protocol, it is not in itself a protocol or guidance document. The goal of this document is to present natural physical, chemical, and biological processes that contribute to the recovery of contaminated sediments and to present methods that may be used to quantify and assess those processes at sites. The number and extent of technical tools that should be used for evaluating the appropriateness of MNR at contaminated sediment sites will be influenced by the size/magnitude and complexity of the site, project resources, available data, and the types and scopes of decisions to be made.

Resources used to develop this document include primarily published peer-reviewed literature, government literature, and the experience of the contributors to this TRD. Case studies are introduced as appropriate to illustrate various monitoring and assessment methods. Some examples are derived from the Lake Hartwell (Pickens County, SC) site, where, since 2000, EPA's National Risk Management Research Laboratory (NRMRL) and Region 4 staff have been investigating natural physical, chemical, and biological processes controlling the fate of polychlorinated biphenyl (PCB) contaminants in sediments. Additional case studies or examples are also used to illustrate or demonstrate specific processes or approaches.

This TRD includes the following sections:

1.0 *Introduction* provides an overview of MNR, introduces primary lines-of-evidence used in support of MNR and other MNR considerations, and discusses the role of conceptual site models (CSMs) in the site characterization and process of evaluating remedial alternatives.

2.0 *Sedimentation and Contaminant Isolation* describes methods to measure sediment deposition and contaminant burial processes. This section also focuses on methods to measure sediment shear strength and hydrodynamic forces to estimate the potential for contaminants to mobilize, thereby creating unacceptable risk.

3.0 *Fate of Common Organic Contaminants in Sediments* provides a broad discussion of the current understanding of the fate and transformation of three categories of persistent organic pollutants in sediments (*i.e.*, polycyclic aromatic hydrocarbons [PAHs], PCBs, and polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans [PCDDs/PCDFs]). This section includes techniques to evaluate bioavailability and chemical fingerprinting methods to identify weathering and transformation processes that can alter the mass, mobility, and relative toxicity of these contaminants.

4.0 *Fate of Inorganic Contaminants in Sediments* provides information concerning approaches to characterize the fate and transformation of inorganic contaminants. These include evaluations of geochemical changes in metal speciation as a result of oxidation/reduction (redox) processes that can affect solubility and bioavailability of metals.

5.0 *Long-Term Monitoring and Site Forecasting with Predictive Models* provides resources for development of a long-term monitoring program to support MNR. The long-term monitoring program may focus on surface sediments (establishing concentration reductions with time or evaluating and characterizing sediment erosion events), the recovery of biological/ecological receptors, or both.

6.0 *References* are provided in this section.

1.2 MNR Processes and Mechanisms

MNR is a remedy that uses ongoing, naturally-occurring processes to contain, destroy, or reduce the bioavailability or toxicity of contaminants in sediment (EPA, 2005a; National Research Council [NRC], 1997). MNR typically relies on decreases in contaminant bioavailability and toxicity in surface sediments. Throughout this document, “surface sediment” is defined as the site-specific biologically active benthic layer at the sediment-water interface. This layer typically is 5 to 10 cm thick in fresh water systems (EPA, 2005a) and can be as much as 1 m thick in estuarine and marine environments (Apitz *et al.*, 2002; Murdoch and Azcue, 1995). Bioavailability may be generally defined as the extent to which living organisms can uptake chemical contaminants by active (biological) or passive (physical or chemical) processes. Natural physical, chemical, and biological processes that contribute to natural recovery of contaminated sediments may include sediment burial, sediment erosion/dispersion, and contaminant sequestration/degradation (*e.g.*, precipitation, adsorption, and transformation). Each of these processes, discussed in greater detail below, can directly affect risk to site-specific receptors associated with site-specific contaminants, and consideration should, therefore, be given to understanding how each may apply to a given site and the ecological and human receptors associated with specific sites.

1.2.1 Natural Sediment, Physical, Chemical, and Biological Processes. Risk reduction and the recovery of ecosystem health or functionality depend on the following mechanisms that influence long-term contaminant and sediment transport:

- Control of primary and secondary sources to prevent ongoing chemical releases into surface sediments;
- Contaminant burial via sediment deposition and an assessment of whether burial is sufficient to limit contaminant mobility and transport;
- Sediment erosion potential and associated contaminant exposure under a range of reasonably expected flow events; and
- Contaminant sorption, solubility, chemical speciation, and transformation.

To the extent that physical, chemical, or biological processes reduce contaminant bioavailability and toxicity in surface sediments, these processes may contribute to the natural recovery of the biologically active zone of the sediment bed, and correspondingly to the recovery of ecological resources. All of the processes discussed will be present at every site to varying degrees, and the combination of these processes ultimately governs contaminant bioavailability and the associated site-specific risk.

1.2.1.1 Physical Processes. The dominant physical processes that affect the distribution of contaminants in sediment are transport, surface sediment mixing (which includes both bioturbation [Section 2.3.2.4] and hydrodynamic mixing), and pore water transport. Sediment transport includes erosion, deposition, and water column transport of uncontaminated and contaminated sediment particles and the potential for contaminant burial. Bioturbation and hydrodynamic mixing can result in and/or enhance surface sediment mixing, and benthic fauna can act as vectors for transporting contaminants into the food web. Bioturbation is often modeled as a physical process because the net result is the physical mixing of sediments and exchange of sediment pore waters with the overlying water column. Pore water transport includes diffusion from sediments and advection due to groundwater discharge. These physical processes play an integral role in the chemical and biological processes in the system.

1.2.1.2 Chemical Processes. These processes are contaminant and site specific and define the mobility and fate of contaminants in the environment. Chemical processes include a range of reactions that govern the precipitation, adsorption, redox, transformation, and chemical speciation of a contaminant. These processes may be directly or indirectly influenced by microbiological and physical processes that control the flux of reactive chemical constituents entering and reacting with contaminants in sediments. These processes influence the partitioning of a chemical between solid and aqueous phases within the sediment bed and water column, thereby affecting the fate, transport, and bioavailability of the contaminant. For example, the fate of metals depends on environmental factors such as hydrogen ion activity (pH), redox characteristics, presence of sulfides, and organic carbon content. Likewise, the fate of organic contaminants may also be affected by abiotic chemical processes such as photocatalysis and sorption processes.

1.2.1.3 Biological Processes. According to the NRC (2001), “of the natural-attenuation processes, biodegradation is generally considered the most desirable because it can result in elimination of risk.” Additionally, macrobiological processes, such as benthic mixing and bioturbation, can contribute to the *in-situ* degradation or transformation of contaminants, which can affect mobility and, under certain conditions, toxicity. For hydrophobic organic contaminants, the time frame required for biodegradation can be greater than for risk reduction provided by burial and isolation processes, whereas biologically-mediated transformations may be more immediate for inorganic contaminants. While chemical transformation of inorganic contaminants is generally reversible, degradation of organic contaminants is typically irreversible. When modeling biotransformation processes, it is important to understand biotransformation kinetics, transformation products, changes in toxicity, and impacts on contaminant mobility.

1.2.2 Risk Reduction Processes. The interactions of the three processes outlined above determine the long-term risk trends at each site. Characterization of the influence of these processes on potential human and ecosystem exposure to contaminants provides the technical basis for evaluation of MNR. The primary risk reduction processes that are to be monitored to evaluate the success/failure of MNR to mitigate site-specific risks include:

- Contaminant isolation/burial;
- Contaminant dispersion;
- Contaminant sequestration; and
- Contaminant transformation.

1.2.2.1 Contaminant Isolation/Burial. Natural deposition of clean (or cleaner) sediment can reduce surface sediment contaminant concentrations with time. Burial occurs in depositional environments where the rate of sediment deposition exceeds the rate of erosion and transport. Contaminant burial results in compaction of underlying sediments, which typically reduces the vertical transport of water and dissolved components. Newly deposited sediments also provide additional reactive surface area for contaminant sequestration. Burial processes typically reduce water column and biota exposure to vertical diffusion and advection of contaminants from sediments and assist in physically isolating the contaminants from the biologically active zone. Isolation also reduces resuspension of contaminated sediments during high-flow events or storms. Finally, contaminant burial/isolation decreases the potential for contaminant transport into the food chain by reducing contaminant exposures at the sediment surface.

1.2.2.2 Contaminant Dispersion. Erosion and hydrodynamic dispersion of contaminated sediments can lead to localized contaminant concentration changes and, therefore, should be properly accounted for in the CSM. These processes result in mixing of clean and contaminated sediments, which can reduce the surface concentrations and potential bioavailability of the contaminants. However, reliance on dispersion for recovery of contaminated sediment sites is problematic because it may increase contaminant loading downgradient of the site. Furthermore, sediment erosion can expose buried sediment that often contains higher contaminant concentrations than those typically found in surface sediments. Project managers should carefully evaluate the effects of increased loading on receiving bodies where dispersion can result in unacceptable risks downgradient from primary areas of concern (EPA, 2005a).

1.2.2.3 Contaminant Sequestration. Sorption, precipitation, and other sequestering processes can reduce contaminant mobility and bioavailability. These processes may reduce the potential for vertical diffusive and advective pore water transport of buried contaminants, which helps to ensure that contaminants remain sequestered after burial. Sequestration is controlled by physical, chemical, and biological activity of the sediment and the contaminant.

1.2.2.4 Contaminant Transformation. To consider contaminant transformation an operative process for an MNR remedy, contaminants must not be converted to more toxic forms through biotic or abiotic mechanisms and more optimally be transformed to less toxic compounds. Abiotic transformation processes typical of sedimentary environments may include reduction, oxidation, mineralization, and hydrolysis. Biotic processes most commonly involve organisms using the contaminant as an electron donor or electron acceptor and converting the contaminant to a different chemical. The biotic transformation process is termed biodegradation. Abiotic transformation processes occur without enzymatic catalysis and include chemical reactions with reactive constituents in sediments (*e.g.*, complexation or redox reactions involving sediment minerals and/or pore-water reactants) or the overlying water column (*e.g.*, photochemical reactions). Common examples of abiotic processes include degradation of PAHs, partial dechlorination of PCBs, and precipitation of certain metals under reducing and sulfide-rich conditions. Chemical weathering to less toxic products or less bioavailable forms can provide long-term risk reduction. However, because weathering processes are often slow, reduction can require years or decades and may be incomplete and, in some cases such as inorganic contaminants, may be reversible. Biotic and abiotic processes often occur simultaneously and together may contribute to reduced risk to human and ecological receptors.

1.3 Assessing MNR

1.3.1 Source History and Control. Per EPA's *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (2005), the first principle for site management is *control sources early*:

> *"As early in the process as possible, site managers should try to identify all direct and indirect continuing sources of significant contamination to the sediments under investigation. These sources might include discharges from industries or wastewater treatment plants, spills, precipitation runoff, erosion of contaminated soil from stream banks or adjacent land, contaminated groundwater and non-aqueous phase liquid contributions, discharges from storm*

> *water and combined sewer outfalls, upstream contributions, and air deposition. In summary, source control should be implemented to prevent recontamination regardless of the selected remedial alternative"* (EPA, 2005a).

The first step in documenting source control is the determination of historical and current sources. Source control documentation relies primarily on historical records from prior remedial investigations and cleanup efforts and past disposal records, historic photos, etc. Sites also may have multiple point and non-point sources that can interfere with anticipated recovery. If evidence of source control is unavailable, it may be necessary to conduct a field investigation to demonstrate that source control has been achieved. Recognizing and unraveling multiple sources of contamination may require historical records, source tracking, working with local and state agencies, and advanced chemical forensics (EPA, 2004; Murphy and Morrison, 2007; Stout *et al.*, 2003; Van Metre *et al.*, 2000). Section 3.0 provides a detailed discussion of chemical fingerprinting for organic contaminants, which can be critical to an accurate understanding of contaminant sources.

Potential sources of sediment contamination at many sites are often numerous and complex, such as industrial discharges, urban runoff, combined sewer overflows, storm sewer systems, and others (EPA, 2001a; EPA, 2002a; EPA, 2004; EPA, 2005a) (Table 1-1). For example, non-point sources, such as urban runoff, can be a consistent and ongoing source of PAHs, PCBs, and metals and may negatively impact chemical concentrations in surface sediments, even after control of a major point source (Apitz *et al.*, 2002; Brenner *et al.*, 2001; Fletcher *et al.*, 2008). Due to the diversity of industrial marine operations and the ubiquitous nature of many anthropogenic contaminants, it can be difficult to ascertain the relative contributions from multiple sources (Stout *et al.*, 2003).

Table 1-1. Sources of Sediment Contamination

Discharges (direct or outfall) from industrial waste and wastewater treatment plants	Air emissions from power plants and incinerators into water bodies by precipitation or direct deposition	Disposal from docked or dry-docked ships
Chemical spills into water bodies	Seepage of contaminated groundwater into water body	Release of contaminants from ship maintenance facilities
Surface runoff from chemical storage facilities and mine waste piles and urban areas	Erosion from flood plains and agricultural areas	Infiltration from landfills

Adapted from EPA, 2005a.

In addition to identifying primary sources, it is often necessary to distinguish "external" upland/watershed secondary sources (*e.g.*, outfalls or non-point sources) from "internal" secondary sources associated with releases from legacy sediments (*e.g.*, resuspension of contamination from historical releases and migration through pore water transport). Internal contaminant sources, including high-risk sediment ("hot spots" - localized areas of high sediment contamination), can act as potential reservoirs that release contaminants into the aquatic system and slow recovery processes. Sediment and water column chemical concentrations also may be influenced by non-point sources that can be difficult to control, such as atmospheric deposition to the watershed. These distinctions may be particularly relevant if the boundaries of the site under consideration are not easily controlled.

The potential for sediment contamination as a result of groundwater discharge to surface water should be considered during evaluation of source control. Organisms that inhabit the transition zone between groundwater and surface water are at risk of exposure to contaminants that migrate through pore water or directly contaminate surface water (EPA, 2008). It is, therefore, important to understand the groundwater-surface water interactions that occur in streams, rivers, estuaries, lakes, and wetland settings.

1.3.2 Lines-of-Evidence. Since MNR relies on natural environmental processes to reduce the risk posed by contaminated sediments to the environment, it is important that MNR be thoroughly evaluated when it is being considered as a potential remedy. Systematically evaluating the feasibility of MNR as a component of the sediment remedy is best achieved through the development of a CSM that adequately captures the physical, chemical, and biological processes that control contaminant fate, transport, and bioavailability. The CSM will likely be derived from analysis of historical and contemporary site data and incorporate current and anticipated pathways of human and ecological exposure. The three main questions that an MNR evaluation is designed to address are:

1) Is there evidence that the system is recovering over time?
2) What processes are controlling system recovery?
3) Is system recovery occurring at a rate sufficient to meet remedial objectives, and is it sustainable?

These questions are answered using a multiple lines-of-evidence approach to evaluate the feasibility of using MNR as the remedial alternative at contaminated sediment sites. As stated in EPA guidance (EPA, 2005a), it is recommended that the following potential lines-of-evidence be evaluated:

- Long-term trend of contaminant levels in higher-trophic-level biota (*e.g.*, piscivorous fish);
- Long-term trend of water column contaminant concentrations evaluated over a typical low-flow period of high biological activity (*e.g.*, trend of summer low-flow concentrations);
- Sediment core data demonstrating trends in historical surface contaminant concentrations through time; and
- Long-term trends of surface sediment contaminant concentration, sediment toxicity, or contaminant mass within the sediment.

One line-of-evidence approach is the Sediment Quality Triad (SQT) developed to explore the relationship between contaminants in the sediment and the health of the supported biological community (Sorensen *et al.*, 2007). The SQT analysis is supported using multiple lines-of-evidence to explore the cause and effect of chemicals on ecological receptors. The lines-of-evidence included in the SQT are results of macrobenthic community, sediment toxicity, and sediment chemistry assessments. Sorenson *et al.* (2007) utilized the SQT approach on six sites in the Lower Hackensack River, NJ. In four of the six sites tested, they found that the macrobenthic community toxicity correlated with high contaminant concentrations. In some instances of extreme toxicity, the microbial community responsible for degrading the contaminants may be compromised and result in lower biodegradation rates. Using the SQT approach, they were also able to identify specific metals that had no effect on the benthic biota even though they were present at high concentrations. Sorensen *et al*. (2007) concluded that using multiple lines-of-evidence is very important and should be coupled to modeling and other known methods of evaluating toxicity. Long and Chapman (1995) used the SQT approach to measure sediment contamination and toxicity in Puget Sound. They compared the three components of the SQT and determined that chemical data alone were not reliable and stressed the importance of using multiple lines-of-evidence to determine if a cause-and-effect relationship exists.

1.3.3 Conceptual Site Model Development. The primary goals of site characterization are to:1) determine the nature and extent of contamination, and 2) evaluate the associated risk. The CSM is a primary tool for evaluating site-specific processes influencing contaminant fate and transport in sediment environments and estimating risk. EPA (2005) and the American Society for Testing and Materials (ASTM, 2003) provide guidance for the development of a CSM. The CSM should specify primary contaminant sources, primary release mechanisms, secondary sources, secondary release mechanisms, contaminated media, exposure routes, and receptors (Adriaens *et al*., 2004). The CSM's identification of the primary risk driver(s) at the site (*e.g.*, small surficial area with high concentrations and widespread low concentrations) ensures that remedies selected will appropriately address these risks. When evaluating MNR, the general CSM can be refined to better characterize primary and secondary release mechanisms and physical/chemical/biological processes that influence contaminant mobility and bioavailability over time.

1.3.4 CSM Structure and Relevant Processes. A general conceptual model framework for a site contaminated with organic compounds is presented in Figure 1-1. Potential contaminant pathways between surface and buried sediments, the sediment-water interface and the water column, and biota in the benthos and water column are illustrated in the figure (additional CSM examples, using different formats, are shown in the *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* [EPA, 2005a]). The figure illustrates how a conceptual model begins with an understanding of contaminant sources and pathways that are unique to individual sites. CSMs should be developed with an explicit directive towards mitigating the greatest risks at a site. For example, where remediation efforts are focused on reducing sediment toxicity to benthic organisms, measures must be taken to evaluate the evidence required to sufficiently mitigate the risk associated with benthic toxicity (*i.e.*, chemical data, toxicity studies, and benthic community profiles). However, where MNR is being used to mitigate risk to higher-trophic ecological receptors, such as piscivorous fish, birds, or humans, MNR needs to address contaminant availability and biomagnifications through the food chain.

The model shown in Figure 1-1 focuses on the physical movement of sediment-associated chemicals to and from the site, to and from the sediments, within the sediments, and to ecological receptors. Identified processes include surface water transport of dissolved and particle-bound contaminants; sediment suspension, settling, and burial; chemical partitioning; pore water transport; chemical transformation or decay; and air/water exchange. Potential contaminated media include sediments, pore water, surface water, air, and biota. At complex sites, contaminant transport processes may be portrayed in multiple CSMs that separately characterize sources, sediment and aquatic media, and chemical transport to human and ecological receptors.

Figure 1-2 presents a general conceptual model framework for a site contaminated with an inorganic contaminant. The figure uses mercury as an example to show sources of mercury contamination including municipal/industrial waste, mine drainage, and deposition. The fate of inorganic contaminants is partly determined by the change in chemical speciation of the contaminant in the sediments. Speciation of an inorganic contaminant also influences its toxicity, mobility, and bioconcentration/biomagnification as well as other properties. Partitioning of inorganic contaminants in sediments depends on the solid phases present or those being formed within the sediment. This topic is discussed in further detail in Section 4 of this document. The risk receptors associated with metals contamination in surface sediments, surface water, and groundwater are also illustrated in Figure 1-2.

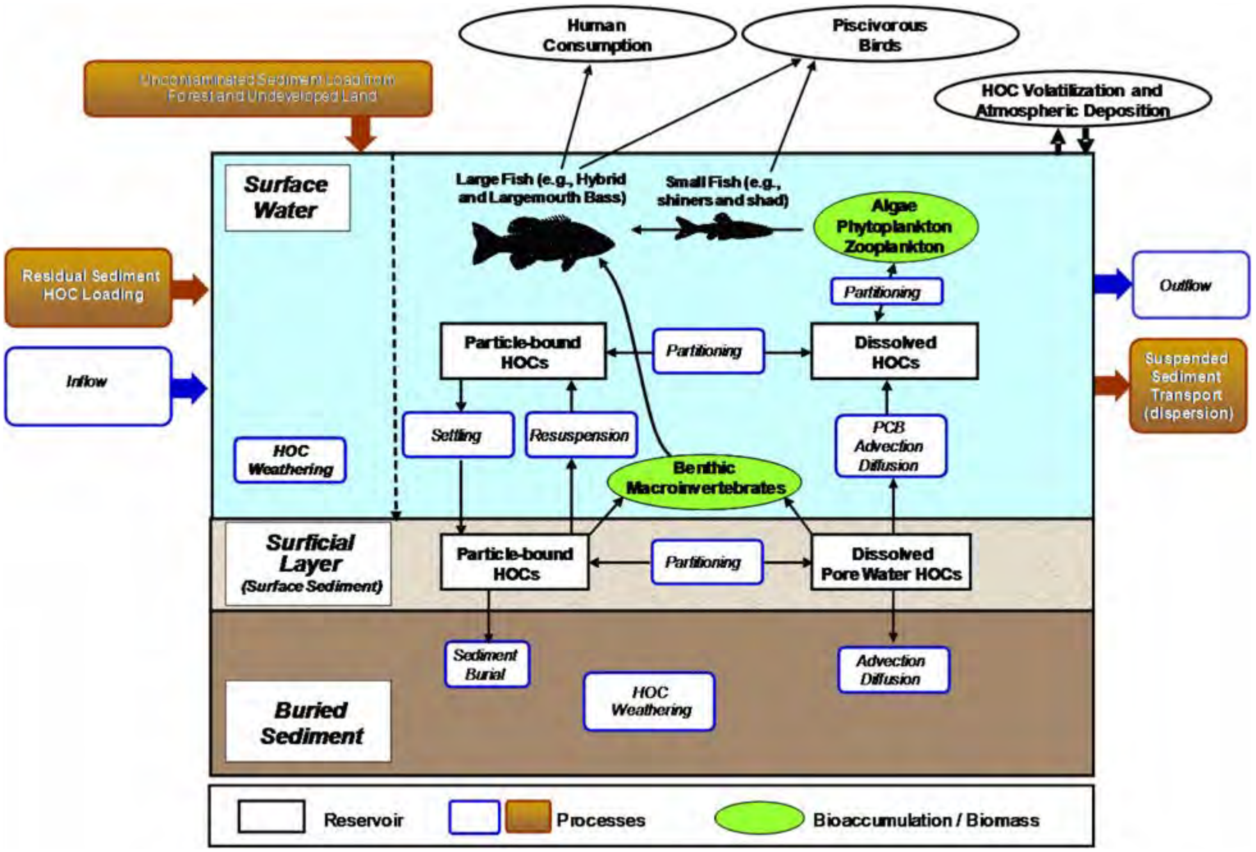


Figure 1-1. Conceptual Site Model Development – Hydrophobic Organic Contaminants (HOCs) (adapted from Adriaens *et al*., 2004)

When depicting the fate and transport of metals in the CSM, metals speciation must be considered together with the types of inorganic and organic solid-phase components present in the sediment that influence the toxicity, bioconcentration/biomagnifications, and partitioning of inorganic contaminants in sediment. In the aqueous phase, the distribution and concentration of metals is determined by ionic strength, specific inorganic co-contaminants, alkalinity, pH, and dissolved organic carbon (DOC). The presence of organic carbon is important both in the aqueous and solid phases because contaminant metals tend to form complexes with organic species. This complexation is at times irreversible, decreasing the bioavailability of the metal contamination. Co-precipitation of toxic metals with sulfide species occurs during diagenesis, reducing their bioavailability. In general, metals speciation promotes partitioning to sediment when the pH and Eh of the surface water are high and a high concentration of organic matter is present. However, when the pH, Eh, and organic matter concentration are low, the metal may change speciation such that it partitions to the liquid phase and into the surface water.

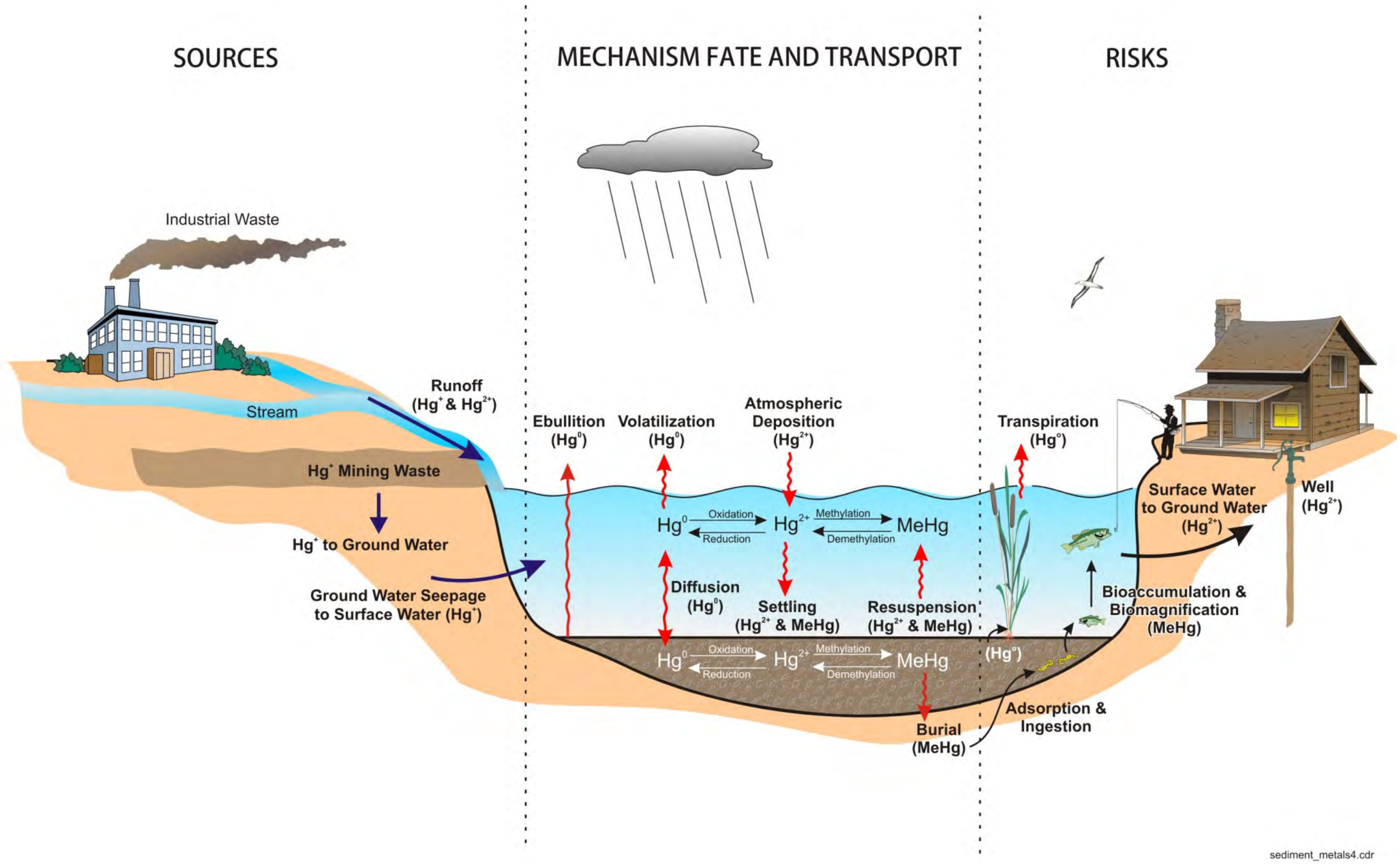


Figure 1-2. Conceptual Site Model Development - Inorganic Contaminants

1.3.5 Management of Risk. The goal of selecting and implementing any remedial alternative is to reduce risks to human health and/or ecological receptors/resources. Identified advantages of MNR include its noninvasive nature (as compared to sediment removal by dredging or sediment burial by capping), which may benefit ecological communities that are sensitive to disturbance, and comparatively low implementation cost (EPA, 2005a). Disadvantages of MNR include longer times to achieve risk reduction to acceptable levels and the lack of active controls to minimize potential future exposures of contaminants left in place (EPA, 2005a). MNR should be considered when it would meet remedial objectives in a reasonable time frame as compared to realistic estimates of the time to design, implement, and complete a dredging or capping remedy (EPA, 2005a). The time frame to achieve risk reduction is site specific and should be explicitly stated and understood. For each site, the time frame is based on a decision rule (*i.e.*, a specific cleanup level at which the contaminant is no longer considered a risk).

***1.3.5.1 Risk of Remedy*.** Because all sediment remedial alternatives have advantages, disadvantages, uncertainties, and risks when applied at a particular contaminated sediment site, management decisions should be based on the relative net risks of each remedial alternative (EPA, 2005a). It is critical for effective risk management that these uncertainties and risks be identified individually and comprehensively for each site. Risks considered should include those risks introduced by implementing the remedial alternatives as well as residual risks (EPA, 2005a) associated with any contaminated sediments left in place (intentionally or unintentionally) after the remedial alternative has been completed. This information on the risks of the remedial alternatives can then be used in comparing net risk reduction among alternatives as part of the decision-making process for remedy selection (EPA, 2005a).

1.3.5.2 Adaptive Management. At many sites, and especially at complex sediment sites, an adaptive management approach, whereby site assumptions are tested and re-evaluated as new information is gathered, should be considered (EPA, 2005a). Whether an adaptive management approach is cost effective is a site-specific decision (EPA, 2005a). Resources on adaptive management at sediment sites include the NRC report *Environmental Cleanup at Navy Facilities* (NRC, 2003) and *Adaptive Management as a Measured Response to the Uncertainty Problem: Addressing Uncertainty and Managing Risk at Contaminated Sediment Sites* (Connolly and Logan, 2004).

2.0 SEDIMENTATION AND CONTAMINANT ISOLATION

Natural sediment deposition can contribute to MNR through the gradual burial of contaminated sediments (Brenner *et al.*, 2004; Delaune and Gambrell, 1996; EPA, 2005a; Magar, 2001; Voskov *et al.*, 1991). However, because depositional environments are repositories for contaminated sediment particles, source control is an integral component of MNR. Once the contaminant source is controlled, natural contaminant weathering and sediment transport processes, including deposition of cleaner sediments, can result in the burial and isolation of the contaminated sediment, resulting in a decrease in surface sediment concentrations over time. This reduction in surface sediment concentrations should result in reduced risk from the contaminated sediment.

This section presents:

- Effects of erosion and deposition on the MNR of contaminated sediments;
- Dynamics of sediment transport;
- Measurement of surface sediment concentrations with time;
- Uncertainties in determining surface sediment concentrations with time; and
- Case studies where MNR of contaminated sediments successfully reduced contaminant concentrations.

2.1 Contaminant Burial and Isolation

One of the primary processes responsible for successful remediation by MNR is the deposition of cleaner sediments to effectively bury and isolate the contaminated sediments. With successful source control, the deposition of cleaner sediments commonly results in lower surface sediment contaminant concentrations over time. The depth of the surface sediments of interest must be determined on a site-specific basis and will generally depend on both physical and biological processes acting on the sediments and contaminants of interest. These processes are commonly dominated by:

- Physical and Chemical Processes – Sediment transport (erosion, deposition, and physical mixing), diffusion, advection due to tidal pumping or groundwater, and chemical reactions/transformations including gas migration; and

- Biological Processes– Benthic organism interaction with contaminants and sediments through physical mixing of particles, pore water irrigation, and uptake.

The depth of this active upper region can vary significantly as a result of these processes. The top 5 to 50 cm of sediment can be considered surface sediment depending on the dominant processes at a particular site (Fletcher *et al.*, 2008).

Surface sediments are mainly composed of partly decomposed organic material, deposited soil and sediment, and weathered bedrock. Surface sediments may be rich in organic matter and, therefore, possess a high capacity for contaminant adsorption to the sediment surface. Though sediment particle sizes are controlled by flow conditions, morphology and biological processing, and upstream mineralogy, surface sediments at typical contaminated sites are generally less than 2 mm in diameter (SPAWAR Systems Center, 2003). Contaminants in surface sediments often pose the greatest risk of chemical exposure to benthic and higher trophic ecological receptors and to humans through ingestion of contaminated fish or direct contact with contaminated sediments. Thus, recovery of surface sediments in the form of lowered contaminant concentrations and/or reduced chemical bioavailability is often the immediate goal of sediment remediation processes.

In depositional environments, natural sedimentation can result in contaminant burial and reduced surface sediment concentrations over time. Areas prone to sedimentation and sediment accretion generally lie downstream of areas that are frequently eroded or receive soil and sediment particles from natural processes, agricultural erosion, urban runoff, and oceanic or riverine sediments. Once deposited, the sediment particles may remain in place and become covered by subsequent sediment deposition. The gross rate at which the particles accrete and deposit in a sediment column is controlled by local variables such as flow conditions, water chemistry, mineralogy, effective settling rates of particles and flocs, bed slopes, and bed armoring/roughness (Elimelech *et al*., 1998; Lick, 2010-; Rose and Appleby, 2005). During periodic events (*e.g.*, high river flow or storm waves), sediments may become resuspended and transported off site. The effects of the processes must be determined in order to affirm potential MNR sites are net depositional.

Following source control, reductions in surface sediment concentrations tend to be gradual depending on the net sediment deposition rate, hydrodynamic and bioturbation mixing rates in surface sediments, and the contribution of upstream contaminant flux into the watershed. Thus, even after source control, the following factors may affect spatial and temporal changes in chemical distributions in surface sediments:

- The presence of *residual contamination* can require decades to move through a watershed. This contamination may re-contaminate areas that were previously remediated or contaminate clean sediments that were deposited after the contaminated sediments.
- *Bioturbation* and *hydrodynamic mixing* can change a contaminant's distribution in surface sediment. Bioturbation refers to the agitation of surface sediments by benthic organisms that process the surface sediments to live or search for food. The top layer of the surface sediment inhabited by aquatic organisms is the biologically active zone. The population and density of these organisms will be dependent on the local environment, but may include sedentary burrowing organisms such as polychaetes, crustaceans, and cephalopods. Additionally, hydrodynamic mixing occurs when regular currents cause the surface sediments to resuspend and temporarily suspend in the water column (*e.g.*, tidal environments). These two processes affect contaminant concentration by mixing older, deeper (potentially more contaminated) sediments into the surface layer, thereby slowing contaminant burial and isolation.
- *Extreme events* that occur on an infrequent basis may be responsible for the net erosion of previously buried contaminated sediments. The eroded sediments could recontaminate local surface sediments or be transported off site.

2.2 Potential for Contaminant Mobilization

Typically, MNR is considered at sites that demonstrate a degree of inherent sediment bed stability, which is why the sediment deposits formed and persisted historically. In conducting an MNR assessment, the principal questions are: can sediment bed stability be expected to persist long term under normal conditions, and can future extreme events cause unacceptable exposure and risk? To answer these questions, sediment erosion potential should be evaluated under normal- to high-energy events such as flood flows, extreme tidal fluctuations, wind-induced waves and currents, and ice scour. Man-made sources of erosion such as propeller wash from passing vessels can also create elevated bottom shear stresses leading to localized erosion (see Section 2.4.3.1f). Benthic organisms also contribute to localized erosion as they burrow and process sediment, which may cause sediments to become resuspended or change overall sediment stability. The resuspension of contaminated sediment may result in unacceptable exposure levels and harm to ecological receptors or human health. Therefore, erosion potential and long-term sediment accretion processes must be understood and quantified to provide a basis for the selection of MNR as a remedy.

Sediment accretion is a naturally occurring process that results in the deposition, incorporation, and accumulation of suspended sediment particles into the surface sediment in a water body. This process is dependent on the physical and chemical properties of the suspended sediments and the overlying current velocities. More information will be provided later on how these and other factors affect sediment accretion rates.

The terms *sediment scour* and *erosion* describe the detachment and removal of sediment particles from the sediment bed via hydrological shear stress imposed on the sediment bed. The bottom shear stress responsible for removal of sediment particles from the sediment bed is caused by water moving over the sediment bed due to currents or wave action (see Blake *et al.*, 2007; Van Rijn, 1993; Yang *et al*., 1996). Events of concern in evaluating erosion potential include high flow or flood events, extreme tidal conditions, and high winds that may result in large waves and currents. Resuspension processes may result in net erosion when the combination of resuspension, transport, and deposition results in a loss of sediment from the area of interest. Scouring is generally associated with localized high-water velocities, whereas erosion is typically used to denote net effects over a large area. Scouring tends to leave a hole or impression in the area where it occurs, but erosion occurs more evenly across a broader area.

2.3 Contaminant Transport via Sediment Transport Processes

At many contaminated sediment sites, contaminants are strongly sorbed to sediment particles (an exception would be contaminant movement into sediment by a contaminated groundwater plume), and, therefore, the physical and chemical processes that affect sediment particles have an influence on contaminant fate and transport. As stated in the previous sections, the key to understanding sediment transport is the characterization of the dominant processes involved in moving sediments. These processes are sediment erosion, transport of sediments in the water column, and sediment deposition. Other secondary processes can affect sediment transport (*e.g.*, landslides and earthquakes), but these basic processes govern the long-term sediment transport at a given site. The following sections briefly outline these key processes (Figure 2-1) (Adriaens *et al.*, 2004; Lick, 2010; Ziegler, 2002).

2.3.1 Sediment Transport Processes

2.3.1.1 Sediment Erosion. Sediment erosion and resuspension are the movement of particles from the sediment bed into the overlying water column. Sediment erosion is initiated by mobilization and subsequent transport of particles away from the localized area. Erosion can result in unacceptable increases in risks to ecological receptors and/or humans by exposing buried sediments with substantially higher contaminant concentrations and suspending contaminated particles in the water column.

Erosion is initiated by shear stress (τ_o) at the sediment-water interface exceeding a critical value that results in a sediment particle being lifted from the sediment bed. Shear stress, or bed shear stress, is produced by the friction of water and suspended sediment flowing over the sediment bed. Resting sediment particles are in constant equilibrium between these drag forces from fluid shear, the lift forces from flow over the particles, and the gravitational and cohesive forces that work to bind the particles to the sediment bed. At a critical velocity, the combined drag and lift forces on the uppermost particles of the sediment bed are greater than the gravitational and cohesive forces that bind surface

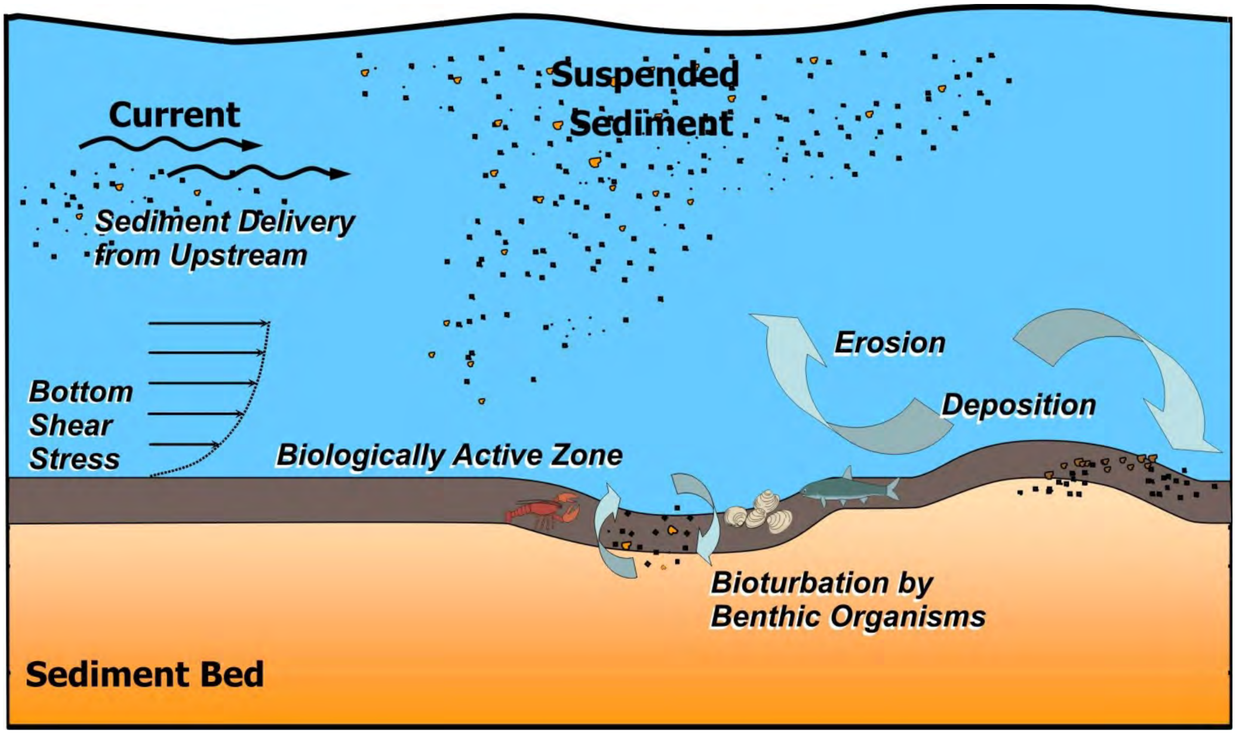


Figure 2-1. Simplified Diagram of Major Sediment Transport Processes

sediments to the bed, dislodging them from their equilibrium positions. This velocity is related to the *critical shear stress* for erosion (τ_{ce}), which is defined as the shear stress at which a small but accurately measurable rate of erosion occurs. Initially, sediment erosion tends to occur in a few isolated locations. However, as shear stress increases with increasing flow velocity, the movement of particles becomes more sustained, causing a net erosive flux from the sediment bed (Roberts *et al.*, 1998; Van Rijn, 1993; Yang *et al.*, 1996).

Shear stress is denoted as force per unit area (*e.g.*, N/m^2) and can be estimated based on bottom-current velocities. It has been studied in detail for currents and waves and can be defined and quantified mathematically given sufficient information regarding the hydrodynamics of the system (Schlicting, 2000; Van Rijn, 1993; Ziegler, 2002).

Resuspension can also be caused by bioturbation, *i.e.*, the disturbance of sediments by benthic flora and fauna (Clarke *et al.*, 2001). Benthic organisms utilize surface sediments as their habitat. These organisms can process sediment during activities such as burrowing, feeding, and ventilating. The activities of organisms and plant roots in the surface sediments lead to a vertical redistribution of sediment particles. During biological processing of the bulk sediment, deeper sediments are transported to the surface while surface sediments become buried or suspended in the water column. As the organisms burrow, eat, and excrete the sediments, they may cause instability in sediments contributing to erosion. Benthic organisms also can cause the sediment to become more cohesive through excretion of biopolymers that bind the sediment. A further discussion of bioturbation is found in Section 2.3.2.4.

2.3.1.2 Sediment Transport. Once dislodged from their equilibrium position in the sediment bed, sediment particles can be transported in the water column (either short or long distances) prior to deposition. Two modes of transport are *bedload* transport and *suspended load* transport. Bedload involves the transport of particles that move along the bed (*i.e.*, rolling in contact with the bed) and saltating (*i.e.*, bouncing) in a thin layer (Yang *et al.*, 1996; Van Rijn, 1993). Suspended load transport involves the suspension of particles into the water column and subsequent transport with the current. The mode of transport for a given particle is largely affected by sediment properties and flow regime.

Bedload transport often dominates sediment transport in rivers with coarse-grained beds and coastal regions where the current has insufficient energy to suspend the particles from the sediment bed. It tends to be of less importance for fine-grained sediments; however, aggregates (*i.e.*, clumps) of fine-grained particles can move as bedload. Aggregates can also disaggregate into smaller particles; this process increases the potential for suspended load transport.

Sediment particles transported as suspended loads move close to the velocity of the water. At steady state, upward transport of sediment particles is balanced by gravitational particle settling and deposition, which can result in sustained sediment suspension. From steady-state conditions, increasing flow velocities will generally result in net sediment erosion once the critical shear stress has been reached, whereas decreasing velocities will result in net sediment deposition. Vertical profiles of suspended, non-cohesive sediment concentrations can be calculated based on particle size, a reference concentration, and fluid velocity (Rouse, 1938; Van Rijn, 1993). Sediment transport can be coupled with hydrodynamics and modeled to provide information on the deposition of various sediment classes to determine the evolution of sediment layers and benthic habitat. Many such models are in use at contaminated sites. EPA (2005) provides guidance for selecting and applying coupled hydrodynamic and sediment transport models.

2.3.1.3 Sediment Deposition. Deposition is the process by which sediment particles settle out of the water column and onto the sediment bed, causing net accretion of particles and subsequent burial of older sediment. Suspended sediment in the water column will begin to settle when the settling velocities exceed the forces that are maintaining the particle in suspension. These forces are a balance of gravitational pull, fluid velocities, and fluid drag and are controlled by the physical and chemical nature of the fluid (water) and the particles (size, shape, density, propensity to aggregate, surface charges of particles, etc.). Once the settling velocities are sufficient to deposit the particles on the bed surface, the particles will either be incorporated into the sediment bed or transported back into the water column. At sufficiently low bed shear stresses, particles begin to accrete and remain with the sediment bed. As bed shear stress decreases, the probability of settled particles remaining a part of the sediment bed increases. This probability approaches 100% as the bed shear stress approaches zero. Deposition can happen at either low or high water velocities depending on the characteristics of the suspended sediment particles. For example, during flood events where the high suspended sediment concentration exceeds the carrying capacity of the water, deposition can occur at velocities exceeding normal deposition thresholds.

As fine-grained particles interact in the water column, they may aggregate or flocculate, especially at high suspended sediment concentrations. Flocculation tends to enhance sediment deposition by increasing particle mass. This process depends on sediment type and surface charge, sediment concentration, fluid velocity and shear, and water chemistry. In general, as sediments flocculate, they form larger particles that settle and deposit faster than smaller individual particles. Techniques that have been developed to predict flocculation and determine aggregate particle sizes are reported in Burban *et al.* (1990), Lick (2010), and Bridges *et al*. (2008).

Differences in sediment accretion rates in aquatic systems are controlled by a variety of site-specific habitat factors (*e.g.*, geology, surrounding land use, current velocity, and organic matter). No general rule-of-thumb can be used to assume the sediment accretion rate for a given site and rates must be measured and/or inferred through a carefully designed analysis. It is generally necessary to determine site-specific sedimentation rates to evaluate the use of MNR at a particular site. Subsequent sections will discuss methods to characterize sediment accretion rates and sediment stability.

2.3.2 Physical Properties Related to Sediment Transport. This section identifies and defines sediment physical properties related to sediment erosion, transport, and deposition. Sediment physical properties include sediment grain size, bulk density, and cohesiveness. Each of these properties is quantifiable, and the methods of measurement and the influence of the properties on sediment transport are described in this section.

***2.3.2.1 Sediment Grain Size**.* Knowledge of the particle size distribution (PSD) (also known as grain size distribution) is fundamental to understanding sediment transport processes. Sediment particle sizes range from very fine clays (<0.24 µm) to boulders >0.25 m in diameter. The intermediate sized particles include the silts and sands that make up the sediment beds of most aquatic environments. Table 2-1 provides a description of the typical ranges of particle (or grain) size associated with PSD classifications. Sediment grain size is measured based on phi (ϕ) classification. The ϕ scale is defined in Equation 2.1 as:

$$\phi = -\log_2(d) \qquad \text{(Eq. 2.1)}$$

where *d* is the particle size diameter in mm (Krumbein, 1934).

Table 2-1. Common Grain Size Scale for Sediment Particles (adapted from Blake *et al.*, 2007)

Description	Grain Size (mm)	Grain Size (µm)
Boulder	>256	—
Cobble		—
Large	128-256	
Small	64-128	
Gravel		—
Very coarse	32-64	
Coarse	16-32	
Medium	8-16	
Fine	4-8	
Very fine	2-4	
Sand		
Very coarse	1-2	1000-2000
Coarse	0.5-1	500-1000
Medium	0.25-0.5	250-500
Fine	0.125-0.25	125-250
Very fine	0.0625-0.125	62.5-125
Silt	—	
Coarse		31.3-62.5
Medium		15.6-31.3
Fine		7.8-15.6
Very fine		3.9-7.8
Clay	—	
Coarse		1.95-3.9
Medium		0.98-1.95
Fine		0.49-0.98
Very fine		<0.24-0.49

Most often, natural sediments consist of a mixture of sediment grain sizes, and sediments are described based on the relative proportions of each sediment type (*e.g.*, sandy clay or silty sand). The size and density of a particle will affect its ability to be scoured and transported under various hydrodynamic conditions. For contaminated sediments, concern is generally placed with the smaller particle sizes that have a high surface area-to-mass ratio and tend to sorb contaminants in the environment. The degree of partitioning to sediment particles is controlled by surface area, surface charge, particle composition, and the contaminant's physical and chemical properties.

Poppe *et al.* (2000) provide an overview of a number of methods and discussions for the processing and interpretation of the data. To provide a brief context, only a few common methods are mentioned below. For particles between 32 and 256 mm, templates with square openings can be used to size fractions. Sieve analyses (ASTM, 2004) typically are used for particles between 0.0625 and 32 mm. A settling tube may be used to determine the diameter for particles between 0.0625 and 2.0 mm (ASTM, 2007). Hydraulic settling methods are used for particles less than 0.0625 mm in diameter (ASTM, 2006). These methods include the pipette method, which is considered the most reliable indirect method; the bottom withdrawal method, which can be used if there is not enough material for the pipette method; and the hydrometer method, which is relatively simple and can be accomplished at a lower cost but requires a larger sample quantity (Syvitski, 2007).

2.3.2.2 Sediment Bulk Density. Bulk density (ρ_b) is useful for classifying sediments and quantifying transport properties. It is also used in combination with contaminant concentrations to estimate contaminant mass inventory. The approximate density of the quartz and clay minerals that make up the majority of sediment particles in the natural world is about 2.65 g/cm^3 (Van Rijn, 1993). The bulk density of a sediment bed is defined as the total mass of sediment and water per unit volume of bed material. Bulk density varies with depth depending on the sediment type as seen for cohesive sediments (see definition below). Bulk density generally increases with depth and time for cohesive sediments because of consolidation and pore water displacement. Consolidation is defined as a reduction of space between sediment particles due to an applied stress. This stress can be applied by overlying sediment (overburden), increased depths of water, ice loadings, or periodic atmospheric pressure changes (Skempton, 1969; Weller, 1959). As the bulk density increases, the potential for scour or sediment erosion typically decreases due to consolidation (Jepsen *et al.*, 1997; Mehta and McAnally, 1998). In some sediments, anthropogenic materials (*e.g.*, coke, coal, pitch, and construction debris) can measurably decrease bulk density (Thomas, 2002).

2.3.2.3 Sediment Cohesiveness. Generally, sediments can be classified as cohesive or non-cohesive. In cohesive sediments, interparticle forces are substantial, creating an attractive force (*i.e.*, cohesion) between particles. In non-cohesive sediments, interparticle forces are insignificant and gravitational forces dominate the behavior of the sediment. Sediments composed primarily of clay-sized materials tend to be cohesive because clay-like materials have surface ionic charges that promote strong interparticle forces. Metallic or organic coatings on sediments also contribute to the interparticle forces making them cohesive. Some components of cohesive sediments include inorganic clay minerals (*e.g.*, silica, alumina, montmorillonite, illite, and kaolinite) and non-clay minerals (*e.g.*, quartz, carbonates, feldspar, and mica, as well as organic material such as plant and animal detritus and bacteria). Fine-grained sediments, especially clay minerals, tend to be more cohesive than coarse-grained sediments. Cohesive sediments typically include those with significant fractions of silts and clays (<2 μm) or fine sands (<60 μm). Non-cohesive sediments generally include particle diameters larger than 60 μm. In some cases, mixtures of small percentages of clays into sand sediment can cause sandy sediments to behave in a cohesive manner (Huang *et al.*, 2006; Lick, 2010).

For non-cohesive sediments, sediment erosion and transport rates strongly correlate to particle grain size with the transport rate declining with increasing particle size. This correlation does not hold for cohesive sediments where particle size alone cannot be used to predict transport rates (Mehta *et al.*, 1989; Mehta and McAnally, 1998; Roberts *et al.*, 1998; Van Rijn, 1993) because of the cohesive forces between particles. For cohesive sediments, empirical data are needed to quantify critical shear stress and erosion rates, which can be obtained from devices for measuring sediment critical shear stress (see Section 2.4.3.3a). Additionally, models have been developed to evaluate cohesive sediment processes both empirically and mechanistically relative to how a sediment bed may behave over time. A discussion of such models is generally beyond the scope of this document but McAnally and Mehta (1998) presents an example of one such model for predicting aggregation of cohesive sediments. EPA (2005) provides guidance for selecting and applying models at contaminated sediment sites.

2.3.2.4 Bioturbation. Although not a "sediment property," bioturbation can affect the physical properties of surface sediments, namely bulk density and cohesiveness. Bioturbation occurs in the uppermost layers of sediment (generally 10 to 15 cm) in which most benthic organisms reside (Boudreau, 1998; Clarke *et al.*, 2001) though there are selected species that reside in deeper sediments (*e.g.*, mud-shrimp) (Clarke *et al.*, 2001). Figure 2-2 illustrates that bioturbation activity can vary with depth. *In-situ* characteristics such as particle size, dissolved oxygen (DO), amount and type of organic matter, salinity, and pH will impact the benthic community and the extent of their activity within the biologically active zone (Clarke *et al.*, 2001). This, in turn, will impact the level of bioturbation that can affect physical properties of surface sediments. Polychaetes (annelid worms), crustaceans (crabs, lobsters, and shrimp), and mollusks (snails and clams) are the most common bioturbators in marine and estuarine environments. Their mode of feeding and density has the greatest effect on sediment stability. Secretions associated with tube building can bind sediment particles and increase sediment cohesiveness, whereas burrowing can mix sediments and decrease cohesion and bulk density (Boudreau, 1998; Rhoads and Carey, 1997). Young (1975) found that critical shear stress can be reduced as much as 50% by bioturbating organisms in the laboratory. Conversely, Ravens and Gschwend (1999) discovered that algal mats, produced by polysaccharide-secreting diatoms during fall and spring blooms, more than doubled sediment bed stability.

The effects of bioturbation are site specific and can exhibit spatial and seasonal variations. The net impacts of bioturbation are sometimes considered to be captured in bulk density and erodibility measurements in surface and buried sediment (Mulsow *et al*., 1998). Direct measurements of bioturbation rates and depths can be used in modeling the fate of chemicals, exposure concentrations, and sediment-water fluxes that may result from event erosion. Measurements of bioturbation, however, are not well suited for predicting erosion depth.

Bioturbation contributes to the porosity profiles in surface sediments; therefore, porosity is widely used in the modeling of bioturbation. However, two contrasting theories exist. The first theory suggests that bioturbation decreases porosity gradients by mixing pore water and sediment (Boudreau, 1986). The second theory contends that bioturbation does not modify porosity but only mixes particles in the solid phase (Meysman *et al*., 2005). Therefore, assuming constant porosity, the second theory applies Fick's Law of diffusion to evaluate radio tracer profiles developed from core analysis. Additionally, cores can be analyzed for evidence of bioturbation by visual inspection for the tubes and tunnels in the profile of the core (Orzech *et al.*, 2001).

2.4 Measures of Surface Sediment Contaminant Concentrations

2.4.1 Measuring Changes in Surface Sediment Contamination. Several methods can be used to quantify changes in surface sediment contamination. These methods include core analysis and surface sediment analysis, described in detail below. Other approaches for detecting changes in surface sediment concentration can be used as supportive lines-of-evidence. These include bathymetry that can be used to evaluate changes in the depth to surface sediments and provide insights into erosional and/or depositional

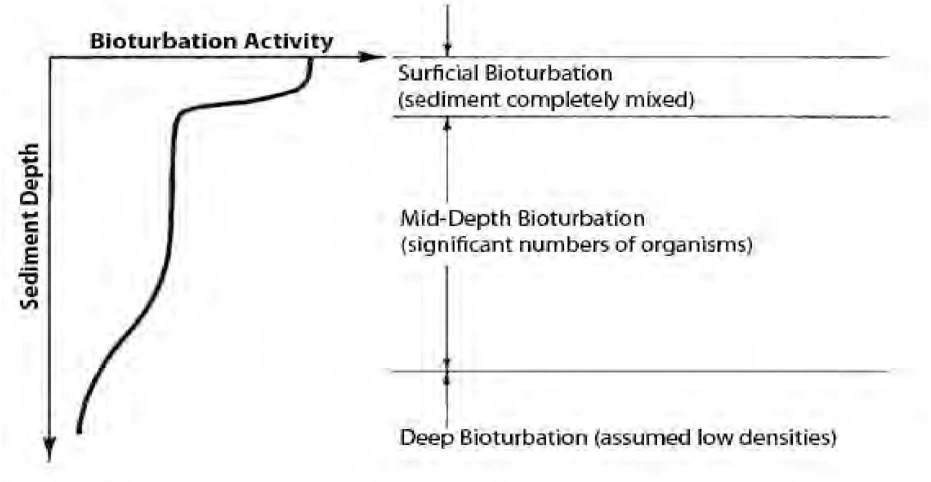


Figure 2-2. Bioturbation Zones (Clarke *et al.*, 2001)

environments. Also, watershed mass balance approaches can be used to estimate transport and fate processes from source zone to deposition.

2.4.1.1 Core Analysis Methods. *Chemical analysis* of sediment cores can be used to create a vertical chemical profile in sediments (ASTM, 2008; Brenner *et al.*, 2002, 2004; EPA, 2001b, 2004; Murdoch and MacKnight, 1994). In depositional environments, the vertical sediment column provides a historical record of the deposition of sediment particles on the bed surface where the sediment-water interface represents the date of sample collection and increasingly older sediments are found with increasing depth below the surface. A typical sediment core profile in these environments includes uncontaminated sediments at the deepest portion of the core, representing sedimentation before the first release of contamination at the site. Above the uncontaminated deepest portion, buried sediment containing maximum contaminant concentrations represents a period of maximum contaminant release into the watershed. Above the maximum concentration horizon, decreasing concentrations approaching the sediment-water interface represent recovery with time after source control or reduction. The uppermost section of the core represents the sediment-water interface where benthic organisms, gas ebullition, and/or erosion and deposition often maintain a high rate of vertical mixing. Not all sites necessarily exhibit reduced surface sediment concentrations with time. Factors that can influence vertical contaminant profiles in sediments with time include: 1) the extent and effectiveness of source control, 2) physical transport and benthic mixing of surface sediment and contaminants, 3) extreme events that mobilize contaminated sediment, 4) the presence of secondary sources that contribute to the suspension and release of contaminants, and 5) sediment deposition rates and contaminant concentrations associated with those sediments.

Table 2-2 outlines commonly-used coring methods and their advantages and disadvantages. Different materials of construction and coring techniques are employed depending on the depth and type of sample to be obtained (EPA, 2001b). As with most methods of analysis, several challenges are faced when conducting chemical analysis of sediment cores (EPA, 2001b, 2008; Murdoch and MacKnight, 1994). According to Rothwell and Rack (2006), challenges lie in the development of: 1) standard measurement and calibration methodologies, and 2) data analysis methods. In order to optimize interpretation of the data and maximize its scientific value, new data visualization tools must be developed. A uniform method of data archiving that will be made available to the entire scientific community, thereby assisting in the interpretation of multiparameter data sets, is also urgently needed.

Table 2-2. Common Coring Methods (adapted from EPA, 2001b)

Device/Dimensions	Use	Sample Depth (cm)	Sample Volume (L)	Advantages	Disadvantages
Fluorocarbon plastic or glass tube (3.5 to 7.5 cm inner diameter [I.D.]: ≤ 120 cm long)	Shallow wadeable waters or deep waters if SCUBA available; soft or semi-consolidated deposits	0 to 10	0.096 to 0.44	• Preserves layering and permits historical study of sediment deposition • Minimal risk of contamination • Rapid; samples immediately ready for laboratory shipment	• Small sample size necessitates repetitive sampling
Hand corer with removable fluorocarbon plastic or glass liners (3.5 to 7.5 cm I.D.: ≤ 120 cm long)	Same as above except more consolidated sediments can be obtained	0 to 10	0.96 to 0.44	• Same advantages as fluorocarbon plastic or glass tube • Penetrates substrate with greater ease through use of handles	• Small sample size necessitates repetitive sampling • Requires careful handling to prevent spillage • Requires removal of liners before repetitive sampling • Barrel and core cutter metal may contaminate sample
Box corer	Same as above but the depth of the unconsolidated sediment must be at least 1 m	0 to 70	≤ 30.0	• Collects large, undisturbed sample; optimal for obtaining intact subsamples	• Difficult to handle • Relatively heavy; requiring larger vessel and power winch to deploy
Gravity corer, phleger corer (3.5 cm I.D. ≤ 50 cm long)	Deep lakes and rivers; semi-consolidated sediments	0 to 50	≤ 0.48	• Reduces risk of sample contamination • Maintains sediment integrity relatively well • Penetrates with sharp cutting edge	• Requires careful handling to avoid sediment spillage • Requires repetitive and time-consuming operation and removal of liners due to small sample size

Table 2-2. Common Coring Methods (adapted from EPA, 2001b) (continued)

Device/Dimensions	Use	Sample Depth (cm)	Sample Volume (L)	Advantages	Disadvantages
Gravity corer, Kajak-Brinkhurst corer (5 cm I.D. ≤ 70 cm long)	Deep lakes and rivers; soft fine-grained sediments	0 to 70	≤ 1.37	• Collects greater volume than the phleger corer.	• Same as phleger corer
Benthos gravity corer (6.6 7.1 cm I.D. ≤ 3 m long)	Soft, fine-grained sediments	0 to 3 m	≤ 10.26	• Retains complete sample from tube because the core valve is fitted to the core liner • Fins promote vertical penetration	• Requires weights for deep penetration so the required lifting capacity is 750 to 1,000 kg • Requires vertical penetration • Compacts sediment sample
Alpine gravity corer (3.5 cm I.D.)	Soft, fine-grained, semi-consolidated substrates	≤ 2 m	≤ 1.92	• Allows different penetration depths due to interchangeable steel barrel	• Lacks stabilizing fins for vertical penetration • May penetrate non-vertically and incompletely • Requires a lifting capacity of 2,000 kg • Disturbs sediment stratas and integrity • Compacts sediment sample
Piston corers	Ocean floor and large deep lakes; most substrates	3 to 20 m	5 to 40	• Typically recovers a relatively undisturbed sediment core in deep waters	• Requires lifting capacity of >2,000 kg • Piston and piston positioning at penetration may fail • Disturbs surface (0 to 0.5 m) layer
MBH-53 piston corer	Waters ≤ 2 m deep with extension rod; soft deposits	≤ 2 m	≤ 2	• Piston provides for greater sample retention	• Cores must be extruded onsite to other containers • Metal barrels introduce risk of metal contamination

Table 2-2. Common Coring Methods (adapted from EPA, 2001b) (continued)

Device/Dimensions	Use	Sample Depth (cm)	Sample Volume (L)	Advantages	Disadvantages
Boomerang corer (6.7 cm I.D.)	Ocean floor (up to 9,000 m deep)	1 m	3.52	• Requires minimal shipboard equipment so small vessels can be used	• Only penetrates 1.2 m • Requires calm water for recovery • Loses 10 to 20% of sample
Vibracorer (5.0 to 7.5 cm I.D.)	Continental shelf of oceans, large lakes; sand, silty sand, gravelly sand substrates	3 to 6 m	5.89 to 13.25	• For deep profiles it effectively samples most substrates with minimum disturbance • Can be used in over 20 m of water depth • Portable models can be operated from small vessels (*e.g.*, 10 m long)	• Labor intensive • Assembly and disassembly might require divers • Disturbs surface (0 to 0.5 m) layer • Special generator may be needed • Heavier models require larger boat and power winch to deploy

2.4.1.2 Surface Sediment Analysis. If the source of the contamination has been removed and clean sediments are depositing (but coring is not a suitable technique), several methods are available for analyzing surface sediments for reduction in contaminant concentrations. These methods also apply to places where natural recovery is proceeding, as evidenced by decreases in contaminant concentrations, without natural deposition and burial taking place, *e.g.*, via biodegradation or metals reduction.

Surface sediment monitoring measures changes in chemical concentrations in surface sediments over time. Surface sediment monitoring is most applicable when conducted at a large site over a long time frame. However, spatial and temporal variability often overshadow short-term temporal trends, so this technique often requires relatively large sample sets and long monitoring periods to identify statistically representative changes in surface sediment concentrations (Connolly *et al*., 2005; Magar and Wenning, 2006). Surface sampling also may be confounded by non-uniform sampling methods.

Sediment traps are devices used to collect surface sediment to evaluate suspended sediment quality. Other surface sediment methods such as sediment dating and mass balance models only measure sediment accumulation rates (Murdoch and MacKnight, 1994). Sediment traps are strategically placed where deposition of sediments is high, the water column has a high concentration of suspended sediments, and the water velocity is reasonably low to prevent resuspension of the material deposited in the trap (Asper, 1987; Iowa Statewide Urban Design and Specifications [SUDAS], 2008). The outlet of the sediment trap usually is designed to allow water to flow out but prevent loss of sediment sample. The primary purposes for deploying sediment traps are to collect material being transported from the surface water to the surface sediment (EPA, 1990). One method of constructing sediment traps is to connect a large funnel to a collecting container surrounded by a steel frame and suspend it in the water column; a few are fabricated from sieve cloths approximately 0.1 mm sieve size mounted on a steel frame (Bischoff *et al.*, 2005).

Sediment traps can be simple to construct and are a cost-effective way to provide useful information on the quality of local suspended solids. Sediment traps can cost from $500 to $7,000 to construct and deploy. Sediment traps, if appropriately deployed, can provide an effective way of intercepting and trapping water column sediment (Iowa SUDAS, 2008). Some of the limitations of sediment traps are: 1) they require a large surface area to allow infiltration and settling of sediment, 2) they may require upstream erosion control to ensure that the data generated are useable, 3) they usually require some sort of protective fencing to prevent them from being distributed by humans and aquatic animals, 4) they cannot be located in streams with high flow rates, and 5) they can provide biased results in systems with bi-directional circulation. Sediment traps require regular maintenance during their deployment and usually need to be removed after high rain events (EPA, 1990).

Radio dating techniques can be very useful in establishing a sedimentation rate for a site. In sedimentary environments, depositional rates and ages of sediment horizons can be determined by the distribution of certain radioactive isotopes. Those radioisotopes most commonly used for sediment chronology are listed in Table 2-3. The age of the sediment containing a radioactive isotope with a known half-life can be calculated by knowing the original concentration of the isotope and measuring the percentage of the remaining radioactive material. The requirements for a radioisotope to be a candidate for "dating" are that: 1) the chemistry of the isotope (element) is known; 2) the half-life is known; 3) the initial amount of the isotope per unit substrate is known or accurately estimated; 4) the only change in concentration of the isotope is due to radioactive decay; and 5) in order to be useful, it must be relatively easy to measure.

Table 2-3. Common Radiological Age Dating Methods for Sediments

Isotope	Half-life	Origin	Location in Sediment Profile	Sediment Application[(a)]
^{234}Th	24 days	Naturally-occurring daughter product of ^{238}U.	0-10 cm depth; dependent on sedimentation and mixing rate.	Due to the short half-life, this isotope is used to determine the mixed layer in surface sediments.
^{7}Be	53 days	Naturally found on atmospheric particles and in surface sediments and soils.	0-15 cm depth; dependent on sedimentation and mixing rate.	Due to the short half-life, this isotope is used to determine the depth of the mixed layer in surface sediments.
^{210}Pb	22.4 years	Naturally found in air, dust, soil, and sediment as a daughter product of radon.	Higher activities in surface sediments, decreasing with depth.	Ratio of ^{210}Pb daughter products ^{208}Po and ^{210}Po is used to calculate excess ^{210}Pb values, which are then used to calculate sedimentation rates and age sediments to about 100 years old.
^{137}Cs	30.1 years	Introduced from above-ground nuclear weapons testing. Peak production occurred in 1963.	Normally subsurface; dependent on sedimentation rate.	Useful for determining sediment age and calculating and verifying sedimentation rates.
^{239}Pu	23,110 years	^{239}Pu is virtually nonexistent in nature. It is made by bombarding ^{238}U with neutrons in a nuclear reactor.	Normally subsurface; dependent on sedimentation rate.	Because it is an alpha emitter and was used in bombs as part of nuclear weapons testing, it was deposited on the earth only during specific times. It is used for dating similarly to the ^{137}Cs method.
^{241}Pu	14.4 years	^{241}Pu is found in association with ^{239}Pu and is virtually nonexistent in nature.	0-50 cm depth; dependent on sedimentation rate.	Because it is an alpha emitter and was part of nuclear weapons testing, it was deposited on the earth only during specific times. It is used for dating similarly to the ^{137}Cs method.

(a) As a general rule, radioactive tracers are appropriate for estimating dates up to four half-lives.

Geochronology profiles using lead-210 (^{210}Pb) or cesium-137 (^{137}Cs) date sediment core segments, resulting in an age profile with depth. The mechanisms that introduce ^{137}Cs and ^{210}Pb into the sediment and the techniques used to interpret the depositional profiles of each isotope are different; using both techniques facilitates independent estimations of deposition rates. Age-dating results provide information on the temporal variations of contaminant release, sediment accumulation rates, and surface mixing depths (Brenner *et al.*, 2004; Matisoff *et al.*, 2002a, 2002b; Koide *et al.*, 1973; Van Metre and Callender, 1997; van Metre *et al.*, 1998, 2000). ^{137}Cs is an event marker associated with atmospheric nuclear testing that uses two specific events, the onset of measurable deposition and the period of maximum deposition, to establish two sediment time horizons. ^{137}Cs dating is most useful in identifying strata deposited in the mid-1950s and early-1960s, periods of atmospheric nuclear testing, while ^{210}Pb is deposited continuously from the atmosphere and can be used to estimate more recent dates. The ^{210}Pb method uses the slope of the concentration to determine a sedimentation rate based on assumptions of a relatively constant natural atmospheric deposition rate, a relatively constant rate of sediment deposition, and a known rate of decay (Holmes, 1998). Because these radioisotopes have physicochemical properties similar to sediment-bound hydrophobic contaminants, have known historical source loading histories, and behave in a well-known manner once deposited, they can be used to reconstruct the historical loadings of sediment-associated contaminants (EPA, 2001b).

^{137}Cs and ^{210}Pb results are interpreted using the following methods (EPA, 2001b):

- ^{137}Cs Horizon Method. Where no local sources occur, ^{137}Cs radioisotopes did not begin to appear in soils/sediments until about 1954. Therefore, in most cases, the initial (deepest) appearance of ^{137}Cs in a core represents the 1954 horizon. The annual sedimentation rate is established by dividing the depth to the 1954 horizon by the number of intervening years since 1954.
- ^{137}Cs Peak Method. The period of maximum atmospheric deposition of ^{137}Cs occurred in 1963. These rates decreased sharply thereafter and were barely measurable by the late 1970s. The maximum ^{137}Cs value in a core profile, therefore, is associated with the 1963 horizon. The annual sedimentation rate is calculated by dividing the depth to the 1963 horizon by the number of intervening years since 1963.
- ^{137}Cs Focusing Factor. A comparison is made between the amount of ^{137}Cs found in a sample and the anticipated atmospheric deposition. The higher the ratio, the greater the degree of sediment focusing in the area. A focusing value greater than 4 indicates a highly depositional environment (Lockhart *et al.*, 1998).
- ^{210}Pb Concentration Slope Method. ^{210}Pb has a half-life of 22.26 years. Therefore, after measuring the profile of ^{210}Pb in the soil core, the sediment's age is estimated from the degree of decay (Sowers *et al.*, 2000).

^{7}Be is produced by cosmic ray reaction with atmospheric nitrogen and oxygen. It is transferred into sedimentary environments through precipitation. Once the ^{7}Be is in the sediments, it becomes associated with the solid phase. Because ^{7}Be attaches strongly to particles, the highest measured activity corresponds to the greatest sediment accumulation rate. ^{7}Be has a half-life of 53 days, which makes its effective range of applicability for dating sediment about 1 year. ^{7}Be may also be used to determine regional short-term sedimentation patterns. Another radioisotope, ^{234}Th, with a half life of 24 days, can also be used to measure short-term sediment dynamics. In particular, analysis of ^{234}Th in the surficial layers of the sediment can reveal the extent of the mixing layer and the depth to which recent sedimentation has occurred. The distribution of the radio nuclides $^{239+240}$Pu in surface sediments can be used as tracers in the modeling of bioturbation. $^{239+240}$Pu become deposited to surface sediments by decay of radon in the atmosphere and testing of nuclear weapons, respectively. The distribution of ^{210}Pb and $^{239+240}$Pu in sediment profiles can be used to predict bioturbation rates and depth (Crusius *et al.*, 2004).

In many cases, all of the above techniques are used to calculate a sedimentation rate. When more than one method returns a usable result, a systematic procedure is needed to determine which technique produced the most reliable, or preferred, sedimentation rate. A typical procedure involves comparing the computed sedimentation rates from the ^{137}Cs horizon method, the ^{137}Cs peak method, and the ^{210}Pb concentration slope method. If these three methods produce comparable sedimentation rates (tolerance limits overlap), the method that produces the smallest tolerance interval may be selected as the predicted sedimentation rate. Other characteristics of both the ^{210}Pb and ^{137}Cs activity profiles are also considered when evaluating a sediment core to determine the sedimentation rate. For example, if the ^{210}Pb data are scattered and produce a low correlation coefficient or a wide tolerance interval, the lead method may be considered less reliable. Similarly, the cesium peak method is considered unreliable if there are multiple peaks in the ^{137}Cs concentration profile or if there is no well-defined 1963 peak. However, when core length is sufficient and both results are available, the 1954 cesium horizon method is chosen most often as the benchmark for determining sediment accumulation rates.

The coring depth and interval thicknesses for chemical and geochronological analyses depend on such site-specific features as the expected contaminant depth, sedimentation rates, uniformity of sediment deposition, surface sediment benthic mixing depths and rates, and the presence of secondary contaminant sources. Sediment age dating also may be guided by the site-specific biological active zone in surface sediment. Resources available for site characterization often limit the number of samples that can be collected and analyzed, which, in turn, will dictate the temporal frequency, spatial distribution, core depth, and interval (core segment) thickness of the sampling program. While more extensive coring can provide information on the heterogeneity of sedimentation rates in a watershed and thinner core segmentation provides more precise age-dating results, the numbers of cores and thickness/frequency of core segment intervals must be weighed against the costs of associated sampling and analysis.

In determining the depth of sediment cores necessary to evaluate the potential appropriateness of MNR, the focus should be on characterizing the potential exposure of ecological receptors and reducing risks. Thus, sediment cores should be sufficiently deep to characterize and differentiate horizons based on sediment contaminant concentrations that are relevant from a risk perspective. Conversely, it is neither appropriate nor necessarily beneficial to extend sediment cores to depths intended to characterize site conditions in the absence of human influence (*e.g.*, prior to the Industrial Revolution). Uniformity of the sediment column with respect to grain size distribution and total organic carbon (TOC) facilitates age dating. Therefore, highly accurate age dating may be impossible in sediments with significant vertical heterogeneity due to heterogeneous depositional environments over time (*e.g.*, varying grain sizes and/or organic carbon content) or environments with substantial resuspension and mixing (Brenner *et al.*, 2002).

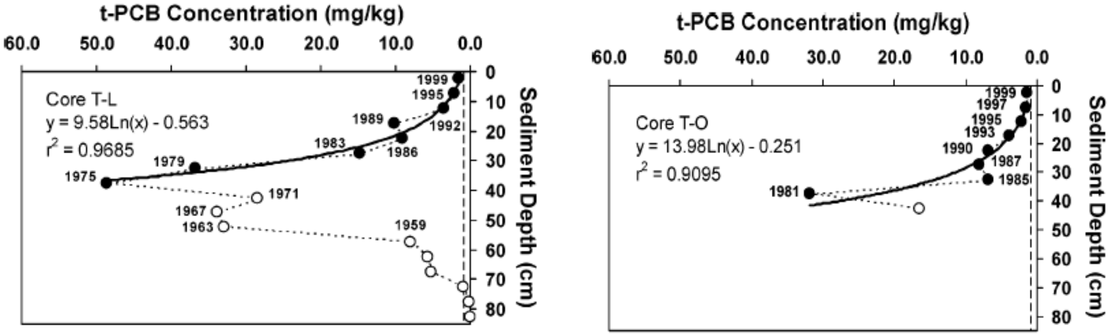
Sediment coring and vertical contaminant profiling, combined with radiochemical methods for age dating, offer the strongest and most immediate measures of recovery in that they verify reduced concentrations in surface sediments over time. An investigator can develop a work plan, collect sediment cores, segment the cores for on- or off-site chemical analyses, analyze the sediments for contaminants of concern, analyze sediments for radionuclides (*e.g.*, ^{210}Pb and ^{137}Cs) and age date the sediment core profiles, analyze the chemical data, and report the results in a short time period. Sediment coring does not rely on repeated field monitoring over time. Using this approach, it may be possible to characterize the rates of recovery of surface sediments quickly, thereby greatly diminishing the time required to perform a feasibility study as opposed to conducting extensive long-term surface sediment monitoring. However, sediment coring is most useful when deposition rates are high and sediments are homogenous. When significant spatial variations exist at a site, core locations should be selected to adequately characterize the range of sediment deposition and recovery. Examples of sediment coring, vertical contaminant profiling, and sediment age dating are provided in Highlights 2-1 and 2-2. Vertical contaminant profiling and age dating were used to evaluate historical changes in surface sediment concentrations in sediments at Lake Hartwell, SC (Highlight 2-1) and White Rock Lake, Dallas, TX (Highlight 2-2) following source control. The Lake Hartwell example demonstrates reduced surface sediment PCB concentrations following industrial point source control. The White Rock Lake example illustrates reduced surface sediment contaminant concentrations resulting from control of non-point sources. The elimination of non-point sources of dichlorodiphenyltrichloroethane (DDT) and lead resulted in statistically significant decreased contaminant concentration trends over time at White Rock Lake. However, when source attenuation was not addressed for another non-point contaminant, the same sediment transport mechanisms that contributed to reduced chemical concentrations in surface sediments also contributed to ongoing deposition and accumulation of PAH-contaminated particles.

Highlight 2-1. Lake Hartwell Surface Sediment PCB Trends

Sediment core profiles were used to establish vertical PCB concentration profiles, age date sediments, and determine surface sedimentation rates and surface sediment contaminant-reduction rates in 18 cores collected from 10 transects in Lake Hartwell, SC. Sediment age dating was conducted using ^{210}Pb and ^{137}Cs concentration profiles in the sediment cores (Brenner *et al.*, 2004). PCB trends showed decreasing surface sediment concentrations since the late 1970s when EPA first regulated PCB use in the United States. The Lake Hartwell experience provides an example of surface sediment reductions following removal of a point source.

Cores were taken to a minimum depth of 100 cm with trace concentrations of PCBs detected at or below 100 cm. Results shown in the figures below indicate these deeper sediments were possibly contaminated by other non-point sources deposited before the onset in 1955 of discharges from capacitor manufacturing by the Sangamo-Weston Plant (the major source of PCB contamination in Lake Hartwell). This deeper contamination also may have resulted from migration of PCBs from overlying contaminated sediments. Maximum concentrations were measured at ~30 to 60 cm below the sediment-water interface, which corresponds to deposition dates between 1960 and 1980. The peak concentrations were followed by a progressive decrease in surface sediment concentrations over time.

Sedimentation rates averaged 2.1 ± 1.5 gm/cm^2/yr for 12 of 18 cores collected. Best-fit curves were applied to the surface sediment recovery results to predict the amount of sedimentation and time required to achieve clean-up goals stipulated in the 1994 Record of Decision (ROD). The ROD cleanup requirement was 1.0 mg/kg t-PCBs, and two additional desirable targets, 0.4 mg/kg t-PCBs and 0.05 mg/kg t-PCBs, were also identified. It was determined that average yearly surface sedimentation requirements to meet the three goals were 1.4 ± 3.7 cm, 11 ± 4.2 cm, and 33 ± 11 cm, respectively (Brenner *et al.*, 2004). Assuming the surface sediment concentrations continue to decline towards background concentrations, surface sediments were estimated to reach the 0.4 mg/kg cleanup level by 2020 and the 0.05 mg.kg level by 2041 (Brenner *et al.*, 2004).



Vertical Sediment Core Profile Illustrating Surface Sediment Recovery in PCB-Contaminated Lake Hartwell Sediments for Two Cores at Transects T-L and T-O (Brenner *et al.*, 2004)

(Reprinted with permission from ES&T.)

Highlight 2-2. Surface Sediment DDT, Lead, and PAH Trends in the United States and in White Rock Lake Sediments

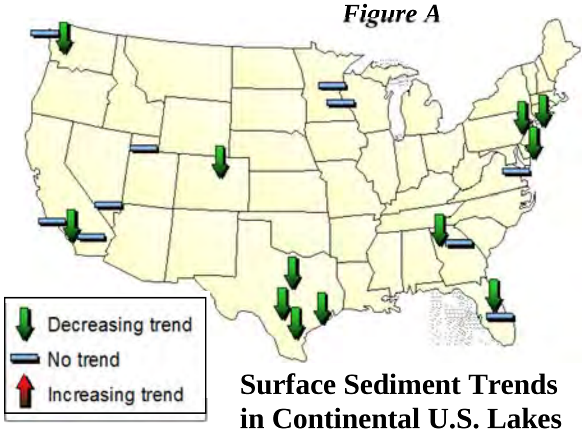
DDT, lead, and PAH trends were examined in sediments of U.S. lakes (EPA, 2004). Decreasing DDT trends were reported in 12 of the 22 lakes examined (Figure A), and all 22 lakes had statistically significant decreasing trends in lead concentrations over time (EPA, 2004). These trends were attributed to decreased DDT use since 1960 and reduced anthropogenic lead releases since the switch in the 1970s to unleaded gasoline, as well as reduced industrial emissions.

White Rock Lake (Dallas, TX) demonstrated surface sediment recovery following removal of non-point sources of DDT and lead. Decreasing surface sediment concentrations are apparent in age-dated White Rock Lake sediment core profiles for total DDT (DDT and DDD, plus DDE) (Figure B) and lead (Figure C) (Van Metre and Callender, 1997; Van Metre *et al*., 2000; EPA, 2004). Sedimentation rates at White Rock Lake were estimated by age dating at 1.13, 0.66, and 0.76 g/cm^2/yr for the periods 1912–1952, 1953–1963, and 1964–1994, respectively (Van Metre and Callender, 1997).

DDT trends identified peak concentrations circa 1960, corresponding to peak DDT use in the United States, followed by decreasing concentrations over time. Sediment lead concentrations also followed historical atmospheric lead levels: peak concentrations (circa 1970) coincided with peak atmospheric levels, followed by decreasing trends with shallower sediment depths.

In contrast, surface sediment PAH concentrations increased with time (Figure D). The trends appear to correlate with vehicle use and urbanization in Dallas. PAHs often exhibit increasing trends with increased urbanization (Van Metre *et al.*, 2000) due to a variety of urban sources including power plant emissions, car/truck exhaust, and oil leaks.

Figure A



Surface Sediment Trends in Continental U.S. Lakes

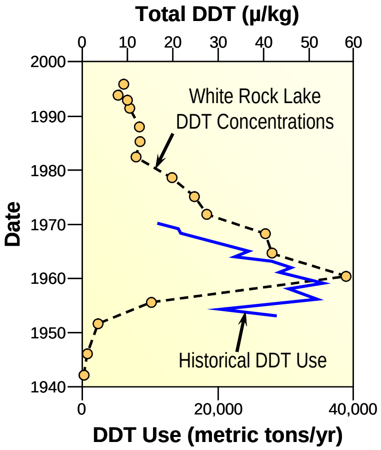


Figure B

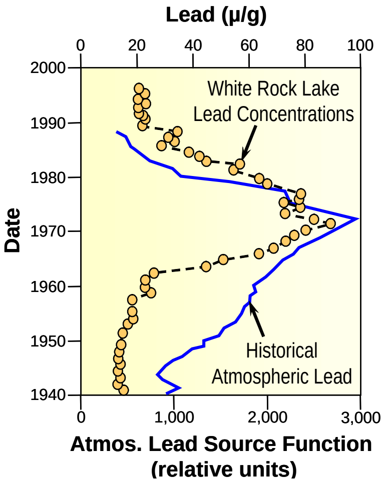


Figure C

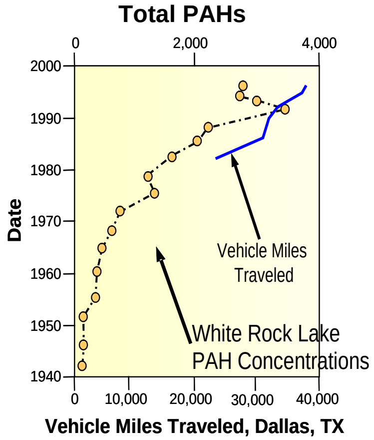


Figure D

White Rock Lake DDT, Lead, and PAH Concentration Trends in 22 U.S. Lakes, and White Rock Lake Sediment Core Profiles (Adapted from U.S. EPA, 2004.)

2.4.1.3 Bathymetry. Bathymetric changes may be studied to monitor sediment bed elevation changes with time. Though this approach cannot detect contaminants directly, if the areas of contaminated sediment are known, inference can be made about the contaminant transport by quantifying sediment movement. Bed depth is obtained by echo sounding that involves a sound pulse traveling from the water surface to the sediment bed. The sound pulse is reflected and monitored. Using the time it takes for the sound to return and the speed of sound in water, a basic calculation can be applied to obtain depth measurements. Repeating bathymetric tests over time in the same water body provides data that can be interpreted to provide information on the erosion and depositional areas in the water body. However, bathymetric measurements may not provide sufficient vertical resolution to measure relatively small changes in sediment thickness, particularly over short periods. When comparing multiple bathymetric surveys over time, it is necessary to ensure that measurement techniques, datum control, and resolution are comparable. Bathymetric accuracy depends on instrumentation and survey procedures. The various measurement techniques (both lateral and vertical) used in past and current bathymetric measurements are subject to error functions, many of which have been explained in the literature and must be considered to arrive at meaningful conclusions (Byrnes *et al*., 2002; Plant *et al.*, 2002; Wilson and Richards, 2006).

2.4.1.4 Watershed Mass Balance. Watershed mass balance calculations are used to address environmental concerns and are an integral part of watershed planning. Development of a watershed mass balance can provide further evidence of the transport and deposition of increasingly clean sediments over time. Mass balance calculations provide information on the manner in which contaminants, sediments, nutrients, and water naturally cycle in a watershed and can assist in defining contaminant fate and transport, the influx and outflow of nutrients, and changes in a watershed due to human impact. The mass of water and the concentration of dissolved and suspended materials entering the watershed are compared to that exiting the watershed. The solids mass balance should provide an average sedimentation rate and be consistent with the weight-of-evidence from water column solids measurements, sediment core profiles, geochronological core profiles, sediment trap data, and bathymetric comparisons, though often on vastly different spatial scales.

Information obtained from watershed mass balance calculations can be incorporated into models to more fully understand the processes that occur in a watershed. Johnson and Gerald (2006) developed mass balance equations to determine the movement of nitrogen, phosphorous, and carbon in a watershed. This information was then incorporated into the watershed model's solute transport component to assist in determining the fate of these nutrients in watersheds that receive runoff waters. Peters *et al.* (2006) evaluated both the monthly and annual water and solute mass balances of five watersheds. The factors calculated to prepare the watershed mass balances included precipitation, solute deposition, and stream discharge. The solutes contained in precipitation and stream discharge were analyzed and included calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), ammonium (NH_4), chloride (Cl), nitrate (NO_3), and sulfate (SO_4). The primary purpose of conducting the watershed mass balance at the five sites was to provide an index of water-resource degradation and determine how human interactions and natural variations affect watersheds, thereby promoting more effective management of these resources (Peters *et al*., 2006). Similar approaches are now being developed for other persistent pollutants.

Some uncertainties may arise in evaluating watershed mass balances. At times, solute concentrations are very low, making it difficult to ascertain the influx and outflow of solutes into the system. Dry deposition of solutes is usually not measured and may be a significant source of contaminants. Spatial uncertainties in rainfall amounts may cause a bias to occur in precipitation measurements.

2.4.2 Uncertainties in Determining Reductions in Surface Sediment Contamination. Combining sediment concentration profiles with age-dating results provides valuable information relative to the amount of time required to achieve surface sediment concentration goals. Nonetheless, uncertainty exists when making future predictions based on past data trends, especially without a mechanistic understanding or a verifiable model of contaminant fate processes. Surface sedimentation and recovery may be affected by temporal changes in the sediment mass balance due to point-source discharge controls, watershed growth and urbanization, or other factors. For example, in engineered reservoirs, long-term stability of the sediment bed may rely on the long-term maintenance of dams and other structures that form the reservoir. Thus, it is necessary to consider potential land use changes that may impact sediment loads and environmental conditions.

Most data collected provide information on past sediment processes and contaminant behavior, changes in future site and water body uses and potential changes to the watershed also must be considered. Recreational and industrial site uses may require navigational dredging that could impact natural recovery processes. Changes to the watershed, including changes in non-point source contaminant loadings, and changes in sediment loads due to increased urbanization or changes in agricultural practices can have long-term impacts. For example, Jaffe *et al.* (1998) report that from 1951 to 1983 the depositional rate in much of San Francisco Bay decreased as sediment supply diminished due to cessation of hydraulic mining in the watershed, upstream flood-control, and water-distribution projects that reduced peak flows.

Immediately following source control, surface sediment contaminant concentrations generally experience a rapid reduction in contaminant concentrations; however, the rate of reduction typically decreases substantially as concentrations decrease. This reduced recovery rate is due to such limiting processes as surface sediment mixing, ongoing contaminant loading, and contaminant recycling through resuspension and repeated cycles of biological contaminant uptake and decay. One way to look at the life-cycle of a site is that exposure concentrations are initially controlled by point source loads, later by ongoing loads from sediment deposits, and finally by uncontrolled non-point source loads (EPA, 1998).

Statistical analysis identifying upper prediction limits based on the data trends can temper expectations of future recovery (Brenner *et al.*, 2004), but it is important to assess whether it is appropriate to use reductions in sediment concentrations over the past several decades as a basis for predictions. It may be possible, for example, that a concentration plateau in surface sediments has been reached where contaminants resurfacing from depth through advective transport and sediment mixing processes, on-going contaminant loading, and contaminant recycling through the food web are at steady state with reductions in surface sediment concentrations through natural burial. For these reasons, a well-designed monitoring plan is a critical component of the natural recovery remedy. Defensible data are necessary to determine the long-term extent of changes in chemical concentrations in surface sediments and the extent to which contaminants persist in surface sediments and the ecosystem and pose a risk to wildlife and humans.

Another consideration in predicting future recovery is that not all contaminants enter aquatic environments as particle-bound contaminants. For relatively mobile contaminants, the “depositional model” for natural recovery may not be appropriate. For example, coal-tar discharges, such as creosote releases from former wood treatment sites, often include non-aqueous phase liquid (NAPL) that can be transported via groundwater as it seeps to the sediment surface (Kueper *et al*., 2003; Patrick, 1998). For NAPL seeps, vertical contaminant profiling may provide little information about recovery (Brenner *et al.*, 2002), which may depend more on hydraulically interrupting groundwater flow and thereby eliminating upward flowing seeps than on deposition of clean sediments alone. Additionally, some metals due to their relatively high solubility can migrate with advective groundwater transport through sediments. Immobilization of contaminated sediments via geochemical processes in sediments, such as the precipitation of divalent metals with reduced sulfides, may have a greater impact on reduced metal bioavailability than burial and isolation by clean sediment. These limitations highlight the importance of a sound CSM that characterizes historical and potential ongoing sources, chemical fate and transport processes, and sediment transport and burial processes. The CSM should be used to ensure that field efforts focus on appropriate metrics that measure processes that influence recovery and, in particular, address those with the greatest uncertainty. Notably, where rates and relative magnitudes of contaminant transport and sedimentary processes are uncertain, sediment coring, age dating, and contaminant profiling can better define those processes and refine the CSM.

2.4.3 Predicting Sediment Erosion and Transport: A Tiered Approach. A successful application of MNR depends primarily on reductions in chemical bioavailability and toxicity in surface sediments over time. In depositional environments, contaminant burial due to net clean sediment deposition is often a major contributor to reduced contaminant bioavailability, which may be further reduced through contaminant transformation, sequestration, and weathering. A phased approach can be used to evaluate sediment transport processes. This approach begins with readily available data and proceeds with more targeted site-specific data collection as necessary. Tier 1 involves estimation of sediment erosion, transport, and deposition potential by measuring conventional sediment properties (*e.g.*, sediment grain size) and estimating water velocities using readily available hydrodynamic data (*e.g.*, rainfall records and U.S. Geological Survey [USGS] records). Tier 2 involves combining direct measurements of sediment erosion, transport, and deposition potential (*e.g.*, bulk density and critical shear strength) with direct hydrodynamic measurements (*e.g.*, currents and waves) to estimate sediment transport potential under normal or high-energy events. Table 2-4 describes processes most commonly associated with sediment transport and outlines data to support Tier 1 and Tier 2 investigations.

2.4.3.1 Tier 1 Estimates of Sediment Transport Processes. Multiple lines-of-evidence are used to evaluate sediment transport in the Tier 1 analysis and support the overall interpretation of sediment transport potential (Blake *et al.*, 2007). The lines-of-evidence commonly used are included in Table 2-4. The Tier 1 analysis relies on data typically collected during the remedial investigation (RI) phase.

Order-of-magnitude calculations are outlined below to demonstrate the steps required to estimate erosion, transport, and deposition potential. For example, if, based on these calculations, significant potential exists for erosion, then direct measurement of sediment shear strength (*e.g.*, by Sedflume) and hydrodynamic forces should be conducted as part of the Tier 2 analysis. The information gathered from these analyses can then be used to assess the potential for unacceptable impacts from erosion.

The Tier 1 analysis takes the user through a series of steps to: a) estimate the processes affecting sediment transport, and b) determine their likely impact. The steps involved are:

- Assemble a CSM by reviewing sediment transport patterns and hydrodynamic characteristics.
- Evaluate the likelihood and magnitude of scour events. This establishes the minimum acceptable storm or flow events against which MNR’s effectiveness will be assessed.
- Estimate the sediment mass balance to determine whether the area is net depositional or net erosional. (This may not be possible at all sites.)
- Calculate the bottom shear stress and critical shear stress. This information is used to determine conditions under which erosion is likely to occur, including natural high-flow events and man-made causes such as ship traffic and propeller wash.
- Based on the predicted shear stress, the potential depth of erosion from the “design” event can be estimated.

Table 2-4. Data Collection for Tier 1 and Tier 2 Sediment Transport Evaluation (modified from Blake *et al.*, 2007)

Parameter	Suggested Tier 1 Data	Suggested Tier 2 Data	Purpose	Questions Answered
Site Characteristics				
Water body configuration and bathymetry (current and historical).	Maps. National Oceanic and Atmospheric Administration (NOAA) or other historical bathymetric charts. Aerial photographs. Information on current and historical site use.	Detailed bathymetric survey using single or multi-beam mapping systems. Shoreline surveys. Side-scan sonar.	Bathymetry, topography, and historical information are used to characterize the physical boundaries of the site and define relevant zones of influence. Bathymetric/shoreline change analyses define long-term depositional/erosional characteristics and rates. Historical information and aerial photographs can identify sediment sources and sinks.	Is the site net depositional or erosional? Have erosion and deposition led to changes in water depth?
Contaminant sources. Horizontal and vertical distribution of sediment contaminants.	Geochemistry and field parameters.	High resolution horizontal and vertical sediment contaminant distribution data using sediment cores.	If flow is unidirectional and contaminant sources and loading history are known, sediment transport patterns can be inferred from horizontal and vertical contaminant distributions.	Have sediment contaminant concentrations changed over time? Has there been a major event causing mixing of the surface sediments? Have sediment contaminants been transported to new areas due to sediment transport processes?
Historical, current, and future anthropogenic activities.	Identification of outfalls, dredging and navigation history, former or planned construction/fill, future use, and anticipated watershed changes.	N/A	The influence of anthropogenic activities must be taken into account during a sediment transport analysis. Also, changes in future site use could alter the potential for sediment erosion, transport, and deposition.	Have there been any anthropogenic activities in the past that may have contributed to transport of contaminated sediments? Are there plans to conduct any activities at the site that can lead to sediment erosion, deposition, or transport?
Water Column Properties				
Waves, tides, and currents. Salinity and temperature.	Available regional or site-specific data. Hydrodynamic data may be available from USGS, U.S. Army Corps of Engineers (USACE), or NOAA gauging stations, including rainfall data or other watershed data.	Site-specific current measurements: acoustic Doppler profilers (ADPs), velocimeters, current meters, and Doppler velocity logs. Tide and wave measurements: ADPs, directional wave meters, and pressure sensors.	The dominant hydrodynamic forces drive sediment transport; when hydrodynamic measurements are combined with suspended sediment measurements, directions and quantities of sediment transport can be described. Analysis of water column transport properties is necessary to determine sediment settling properties and flux. Salinity/temperature profiles to determine hydrodynamics and behaviors or life cycles of aquatic organisms.	What effect do tides and currents have on sediment transport? What is the potential for significant bioturbation?

Table 2-4. Data Collection for Tier 1 and Tier 2 Sediment Transport Evaluation (modified from Blake *et al.*, 2007) (continued)

Parameter	Suggested Tier 1 Data	Suggested Tier 2 Data	Purpose	Questions Answered
Water Column Properties(Continued)				
Suspended sediment concentrations.	Water quality data from USGS, state, or local agencies.	Site-specific suspended sediment concentrations: measuring suspended solids, optical backscatter of ADPs, optical backscatter sensors, or laser *in-situ* sediment transmissometer.	The quantity and characteristics of suspended solids are used to calculate the suspended sediment flux on or off site and determine sedimentation or erosion rates.	What is the quantity of suspended solids in the water column, and where did the suspended solids originate?
Sediment Bed Properties				
Horizontal and vertical PSD.	Grain size data as collected for the RI.	Sieve analysis (>63 µm), laser diffraction methods (<63 µm), and optical methods.	Sediment bed properties are used to infer sediment transport characteristics. Data also are needed for analytic and numeric computations.	According to the grain size of the surface sediments, what is the origin of the sediments? What fraction is the contaminant associated with and is this fraction susceptible to transport?
Water content/bulk density, TOC, and sediment stratigraphy.	Water content data as collected for the RI. TOC data as collected for the RI. Available site data. Sediment core descriptions.	Higher density spatial sampling using Phase I analysis. Sub-bottom profiler.	Bulk density helps to determine the settling properties of the sediment. Stratigraphic information is used to infer depositional environments and sediment bed erosion potential.	What specific properties of the sediment promoted settling? Will the surface sediment be easily eroded? Will deposition continue to take place in the current depositional environment? What is the erosion potential of the surface sediment?
Sediment shear stress tests.	Estimated values for sediment properties and cohesiveness.	Surficial critical shear stress and potential resuspension for cohesive sediments: flume studies. Sediment erosion profiles for cohesive sediments. Side-scan sonar.	Sediment shear strength measurements are used when working with cohesive sediments to determine the potential for sediment erosion and depths of erosion during normal and high-energy events; non-cohesive sediment behavior can be predicted from grain size and bulk density information. These measurements are used to calculate sediment erosion potential and degree of imbeddedness of fine sediments in an armored sediment bed.	What is the likelihood of sediment mixing or off-site transport due to net erosion or, more often, high-flow event erosion?
Sediment accumulation rate.	Bathymetric differences. Dredging records.	Radioisotope analysis. Sediment traps.	Sediment accumulation rates can be used to directly determine rates of burial of on-site sediments. Also, these rates can indicate the susceptibility to high-flow sediment mixing or off-site transport.	At what rate would contaminated sediments be buried at the site? How susceptible is the site to high-flow event driven mixing of surface sediments?

Table 2-4. Data Collection for Tier 1 and Tier 2 Sediment Transport Evaluation (modified from Blake *et al.*, 2007) (continued)

Parameter	Suggested Tier 1 Data	Suggested Tier 2 Data	Purpose	Questions Answered
Sediment Bed Properties				
Depth of biological activity and bioturbation.	Regional and site-specific biological data as available and as collected for the RI.	Qualitative/quantitative benthic surveys. Sediment profile imaging. Push-core observation. Radioisotope profiles. Redox measurements in sediment. Metals speciation.	Vertical physical transport of sediments due to bioturbation must be understood and quantified to characterize potential depths to which contaminated sediments may be exposed and/or transported. ^{7}Be and ^{234}Th radioisotopes can be used to measure actively mixed zones. Oxidized layer of surficial sediment corresponds with most actively mixed sediments.	Would bioturbation and other biological activity reduce or increase the rate of sediment recovery?

2.4.3.1a Using the Conceptual Site Model. A CSM should be developed and reviewed by stakeholders and regulatory agencies before any sampling and analysis are conducted at the site. The CSM is prepared using existing site information and should include a multi-dimensional (temporal and spatial) description of the site (*i.e.*, sources of contaminant, fate and transport of the contaminant through exposure routes, and potential receptors). Both ecological and human risks should be identified. Since site conditions change over time, the CSM should be periodically updated to reflect current site conditions (Apitz *et al.*, 2005a; EPA, 2005a; Fletcher *et al.*, 2008; SPAWAR Systems Center, 2003). The development of the CSM initially should be guided by the site-specific conditions and will likely be independent of remedy. Once the MNR remedy is selected, the CSM should be updated to reflect site and mechanistic processes specific to the MNR remedy. Use of a CSM contributes to the determination of the most cost-effective and efficient manner to protect the environment.

Once the CSM is developed, Tier 1 analysis should be used to identify the dominant sediment transport processes at the site based on the site data collected. The CSM should then lead to the development of sediment management questions: For example: 1) Could erosion of the sediment bed lead to the exposure of contaminated sediments? 2) Could sediment transport lead to the redistribution of contamination within the site or movement of contamination off site? 3) Will natural processes lead to the burial of contaminated sediment by relatively clean sediment? 4) If a site is actively remediated, could sediment transport lead to the recontamination of the site? Erosion, resuspension, transport and deposition must be evaluated when preparing the CSM to guide the Tier 1 analysis (Blake *et al.*, 2007).

2.4.3.1b Mass Balance Estimates. The sediment mass balance is a model of all inputs and outputs of sediment mass in a system. It can be used to determine whether the system is net depositional or erosional and identify sediment transport directions and quantities. Preparation of the mass balance is made easier if the necessary information is gathered during the initial RI phase.

The sediment mass balance is defined as follows:

Sediment mass inflow = Sediment mass outflow + Sediment erosion – Sediment deposition (Eq. 2.2)

Mathematically, the mass balance is expressed as follows:

$$Q_{in}C_{in} - Q_{out}C_{out} - A(D-E) = V\left(\frac{dC}{dt}\right) \qquad \text{(Eq. 2.3)}$$

where Q_{in} and Q_{out} are the incoming and outgoing mass flow rates of water in volume per unit time; C_{in} and C_{out} are the suspended sediment concentrations of the incoming and outgoing water in mass per unit volume; V is the volume of the water body; A is the surface area of the water body; the deposition rate (D) minus erosion rate (E) in mass per unit area per unit time represents that change in sediment due to bed exchange, and dC/dt is the change in suspended sediment in the water column over time, which is zero if the system is in equilibrium or steady state. Flow rates are determined from field measurements or gauging stations. Suspended sediment concentrations are measured. Values of D and E are more difficult to determine but can be obtained from field monitoring of deposition and erosion. The same equation can be rewritten in steady state as follows:

$$Q_{in}C_{in} - Q_{out}C_{out} = A(D-E) \qquad \text{(Eq. 2.4)}$$

The following conditions determine whether the site is depositional or erosional:

- For $Q_{in}\,C_{in} > Q_{out}\,C_{out}$, then $D > E$ and the area is a net depositional environment.
- For $Q_{in}\,C_{in} < Q_{out}\,C_{out}$, then $D < E$ and the area is a net erosional environment.
- For $Q_{in}\,C_{in} = Q_{out}\,C_{out}$, then $D = E$ and the sediment bed is in equilibrium with the influent and effluent solids loads. Here, the assumption is made that the system is at steady state.

During a flood or high-flow events, the above relationships may change, leading to deposition in areas that are more prone to erosion and vice versa. Also, it is important to take into consideration the scale of the area for which the mass balance is developed. Though the study area may have been calculated as either depositional or erosional, there can be very localized scour or deposition occurring due to obstructions, docks, flow restrictions, etc. Though these localized conditions may be small relative to the site, they can play an important role in exposing or redistributing contaminants.

A conceptual sediment mass balance is shown in Highlight 2-3. The example emphasizes the importance of understanding sediment inputs and outputs in characterizing the regional depositional characteristics of an area. Calculation of a sediment mass balance cannot be carried out for all sites, including coastal sites where definable inputs and outputs may not exist.

2.4.3.1c Estimating Bottom Shear Stress. Shear stress is the force that water flow exerts on the sediment surface due to waves, seiche flows, propeller wash, and/or currents. Turbulent shear stress (τ) can be calculated as follows:

$$\tau = \rho C_f u^2 \qquad \text{(Eq. 2.5)}$$

where ρ is the fluid density (kg/m^3), C_f is the coefficient of friction, and u is the average water velocity (m/s). Uncertainty may occur with the use of Equation 2.5 because of the error associated with measurements or predictions of the coefficient of friction and errors with velocity estimates. During Tier 2 analysis, the velocity and coefficient of friction estimates can be improved with direct field measurements of the vertical velocity profile (Cheng *et al.*, 1999).

C_f can be calculated for unidirectional flow using the following equation:

$$C_f = \frac{k^2}{\left(\ln \dfrac{h}{2z_0}\right)^2} \qquad \text{(Eq. 2.6)}$$

where k is von Karman’s constant (0.42), z_0 is the effective bottom roughness, and h is the water depth. A first estimate of the effective bottom roughness is generally selected on the basis of the sediment bed grain size distribution. Typical values for C_f range from 0.002 to 0.004 in rivers and estuaries. The coefficients of friction for environments where waves play a larger role involve more effort in their computation and are described by Van Rijn (1993), Christoffersen and Jonsson (1985), and Grant and Madsen (1979).

Knowledge of the average velocity of a river over the sediment bed is necessary when estimating shear stress in rivers and estuaries. The average velocity of a river can be measured using Doppler current meters, acoustic Doppler velocimeters, and electromagnetic current meters (Westenbroek, 2006). The average velocity in a river at a given flow rate can also be obtained from flow rating curves if the variation of the cross-sectional area with surface elevation is known. Flow rating curves provide an empirical estimate of velocity from flow rate measurements. The USGS has flow rating curve data for most USGS-monitored rivers or streams (http://water.usgs.gov/). These data can serve as a good resource for a first estimate of expected regional flow magnitudes.

Highlight 2-3. Hypothetical Mass Balance Example

The hypothetical system is a lake that receives water and sediments from two rivers (refer to conceptual mass balance figure below). The lake then discharges into a downstream river. The lake is known to be net depositional. The average flow rates of the two inlet rivers are Q_1 and Q_2, and the sediment concentrations in the water column of these two rivers are C_1 and C_2, respectively. The average flow rate and sediment concentration discharging out of the lake are Q_o and C_o, respectively. The volume of the lake (*V*) can be calculated using the dimensions of the lake hypsographic curves (a graph that shows the proportion of area that exists at various elevations by plotting relative area against relative height), or simply using the volume of a cone equation. In order to determine the mass balance in the lake several assumptions are made:

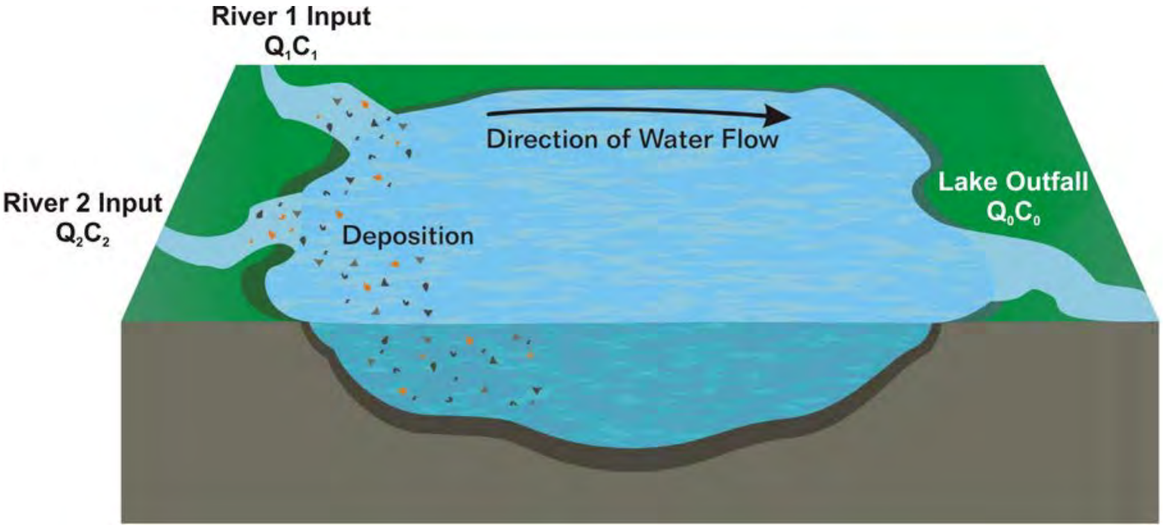
1) Flow is in one direction (from the two input streams to the discharge point of the lake)
2) Shear stresses are minimal, so no erosion occurs.
3) Tides are negligible.

To determine the mass balance, the steady-state mass balance equation used is:

$$Q_1C_1 + Q_2C_2 - Q_oC_o = V(D - E) \qquad \text{(Eq. 2-3.1)}$$

where *E* and *D* are erosion and deposition rates, respectively.

Flow rates are determined from field measurements or gauging stations. Suspended sediment concentrations are measured. Values of *D* and *E* are more difficult to determine but can be obtained from field monitoring of deposition and erosion.



Conceptual Mass Balance Example Showing a Lake Area with Net Deposition

Resources that can be used to predict tides and associated currents in coastal regions in North America are available from NOAA (http://co-ops.nos.noaa.gov). In many navigable locations, NOAA has worked with local agencies to deploy real-time regional current and wave meters. These resources can be used to determine order-of-magnitude shear stresses from waves and currents. More sophisticated instrumentation for directly measuring velocity and shear stress is discussed in Section 2.4.3.3.a.

2.4.3.1d Estimating Critical Shear Stress. Critical shear stress is the minimum amount of shear stress exerted by water currents that can initialize the movement of bottom particles. The erosion potential of the sediments (which can be measured or calculated) determines the critical shear stress required to move sediment particles and, therefore, determines whether contaminated sediments will become exposed or mobilized. Sediments are composed of particles of varying sizes, and erosion generally begins with the particles that are the easiest to move (require the least shear stress). A gradual increase in sediment erosion is then experienced as the shear stress increases. This progression of erosion makes it a challenge to define a specific critical shear stress for the sediment as a whole. Roberts *et al.* (1998) defines critical shear stress as "the shear stress at which a small, but accurately measurable, rate of erosion occurs". In their study, the critical shear stress (τ_{ce}) was calculated using the following equation:

$$\tau_{ce} = \left(\frac{E}{A}\right)^{1/n} \rho^{-m/n} \qquad \text{(Eq. 2.7)}$$

where E is the rate of erosion assumed to be 10^{-4} cm/s, which is considered the rate at which a small but accurately measurable movement of particles can be measured, and A, n, and m are constants that were determined experimentally and are dependent on the size class of the sediment (Roberts *et al.*, 1998).

Van Rijn (1993) estimated the critical shear stress using Shield's curve that determines critical shear stress for erosion using particle diameter as follows. To simplify the calculation of critical shear stresses, a dimensionless particle diameter, d^*, is used:

$$d^* = d\left[(\rho_s - 1)\frac{g}{\upsilon^2}\right]^{1/3} \qquad \text{(Eq. 2.8)}$$

where d is the median particle diameter (cm); ρ_s is the density of the particles (generally assumed as 2.65 g/cm^3); υ is the kinematic fluid viscosity (0.0117 cm^2/s for salt water and 0.0112 cm^2/s for fresh water); and g is the acceleration due to gravity (980 cm/s^2). Using a range of d^* values for the sediment bed, the critical shear stress, τ_{ce}, in dynes/cm^2 for either fresh water or salt water for a particle larger than 200 μm may be calculated as shown in Table 2-5. A typical progression of critical shear stress with grain size is shown in Figure 2-3.

Table 2-5. Critical Shear Stress for Particles Larger than 200 μm

Critical Shear Stress (dynes/cm^2)	Range of Valid d*
$\tau_{ce} = 0.24\, d^{*-1} \left[(\rho_s - 1)gd\right]$	$1 < d^* \le 4$
$\tau_{ce} = 0.14\, d^{*-0.64} \left[(\rho_s - 1)gd\right]$	$4 < d^* \le 10$
$\tau_{ce} = 0.04\, d^{*-0.1} \left[(\rho_s - 1)gd\right]$	$10 < d^* \le 20$
$\tau_{ce} = 0.013\, d^{*0.29} \left[(\rho_s - 1)gd\right]$	$20 < d^* \le 150$
$\tau_{ce} = 0.055\left[(\rho_s - 1)gd\right]$	$d^* > 150$

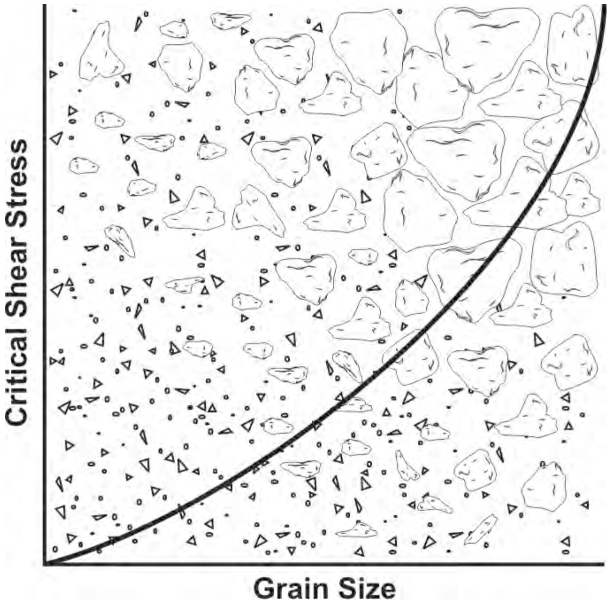


Figure 2-3. Typical Trend in Critical Shear Stress as Sediment Composition Transitions from Sand to Gravel (Adapted from de Linares and Belleudy, 2007.)

No single formula exists to calculate critical shear stress for smaller cohesive sediment particles; however, a conservative estimate of 1 dyne/cm^2 is often used (Ziegler, 2002; Gailani *et al*., 1991). Tier 2 analyses can be used to directly measure critical shear stress for cases where a high degree of certainty is required. It is important to note that contaminants tend to be associated with cohesive sediments. Although no universal equation exists, a simple sediment transport model (either a one-dimensional vertical model or a more complex regional model) can be used to estimate the erosion potential of cohesive sediments. The amount of sediment resuspended during cohesive sediment erosion depends on the turbulent shear stress at the sediment-water interface and the level of consolidation (Krone, 1962; Lick, 2010; Parchure and Mehta, 1985).

This information, including the bed porosity, can be used to calculate the mass of sediment resuspended from a cohesive bed using the following empirical equation (Gailani *et al.*, 1991):

$$E = \frac{a_0}{T_d^m}\left(\frac{\tau - \tau_{\mathrm{cr}}}{\tau_{\mathrm{cr}}}\right)^n, \tau > \tau_{\mathrm{cr}} \qquad \text{(Eq. 2.9)}$$

where E is the resuspension potential (mg/cm^2), a_o and n are site-specific constants related to resuspension properties of cohesive beds (n, the shear stress component, can vary from 2 to 3, while a_o can vary by an order of magnitude), T_d is time after deposition (days), τ is bottom shear stress due to waves and currents, and τ_{cr} is effective critical shear stress (typically 1 dyne/cm^2 at the sediment surface). The consolidation exponent (m) depends on the depositional environment and varies from 0.5 to 2 depending on and inversely proportional to the energy of the body of water. This empirical equation is used because no predictive analytical formulation has been developed to estimate sediment resuspension. However, the maximum sediment resuspension (mg/cm^2) can be estimated based on the maximum expected shear stress using the following equation (Ziegler, 2002):

$$E_{\max} = A\left(\frac{\tau_{\max} - \tau_{ce}}{\tau_{ce}}\right)^{n} \qquad \text{(Eq. 2.10)}$$

where $$A = \frac{a_0}{T_d^m} \qquad \text{(Eq. 2.11)}$$

This equation was developed using data obtained from annular flumes, a method used in Tier 2 analysis. Different flumes measure different physical properties, and, therefore, the values of maximum sediment resuspension are dependent on the flume type used.

Once E_{max} is known, it can be used to calculate scour depth, but, generally, field studies must be conducted to obtain site-specific values for a_0 and n. Also, once E_{max} is known, the scour depth, D_{scour}, (depth in cm), is calculated by the following equation:

$$D_{scour} = \frac{E_{\max}}{1000\,\rho_{dry}} \qquad \text{(Eq. 2.12)}$$

where ρ_{dry} (g/cm^3) is the measured sediment dry density.

2.4.3.1e Identifying Erosional Events. The most significant potential for unacceptable risks resulting from sediment erosion occurs during high-energy events. Such high-energy events may include large storms, extreme tidal events, floods, storm-induced waves, and dam releases that create conditions of high shear stress. The frequency and intensity of such events should be considered in the MNR sediment transport evaluation to assess the potential for sediment scour and exposure and transport of suspended contaminated sediments and the impacts of these processes on potential risk to ecological receptors and human health (EPA, 2005a). Often, a high-energy event with the probability of a 100-year flood occurring in a given year is used as a design benchmark (EPA, 2005a).

At riverine sites, scour events typically involve high flows. USACE (1993) developed a *Hydrologic Frequency Analysis* manual to evaluate hydrographs and determine the frequency and magnitude of high-flow events. For coastal and estuarine sites, storm activities typically most affect regional sediment transport. USACE later developed the *Coastal Engineering Manual* (2002) outlining how to evaluate the maximum wave and water level conditions at a coastal or estuarine site. These manuals can be used to predict the order of magnitude bottom shear stress expected during high-energy events. It should also be noted that the river input into an estuary during such events can significantly alter flow patterns in the region, in which case analyses for both the riverine and estuarine environments should be conducted.

2.4.3.1f Propeller-Induced Scour. The sediment beds of navigable waterways may also be susceptible to scouring from passing and moored ship traffic. Rotating ship propellers accelerate water in order to move a ship. This water has high kinetic energy that can cause scour to a sediment bed. A ship propeller has three components of velocity: the axial component with the rotation of the propeller that is the main contributor and tangential and radial components that are perpendicular and parallel coincident to the rotation of the propeller and parallel coincident to the radii. Ship propeller scour has presented an engineering challenge in the past and has been studied in some detail. With known vessel and waterway characteristics, empirical methods can be used to predict the scour depth as a function of time (Maynord, 2000). Ship propellers produce a wash or jet of localized swirling currents that induces scour on an erodible bed (Figure 2-4). The maximum equilibrium scour depths can be calculated as a function of velocity (V_o), propeller diameter (D_p), distance between propeller tip and sediment bed (C), sediment grain size (d_{50}), and water density ρ (Sumer and Fredsoe, 2002).

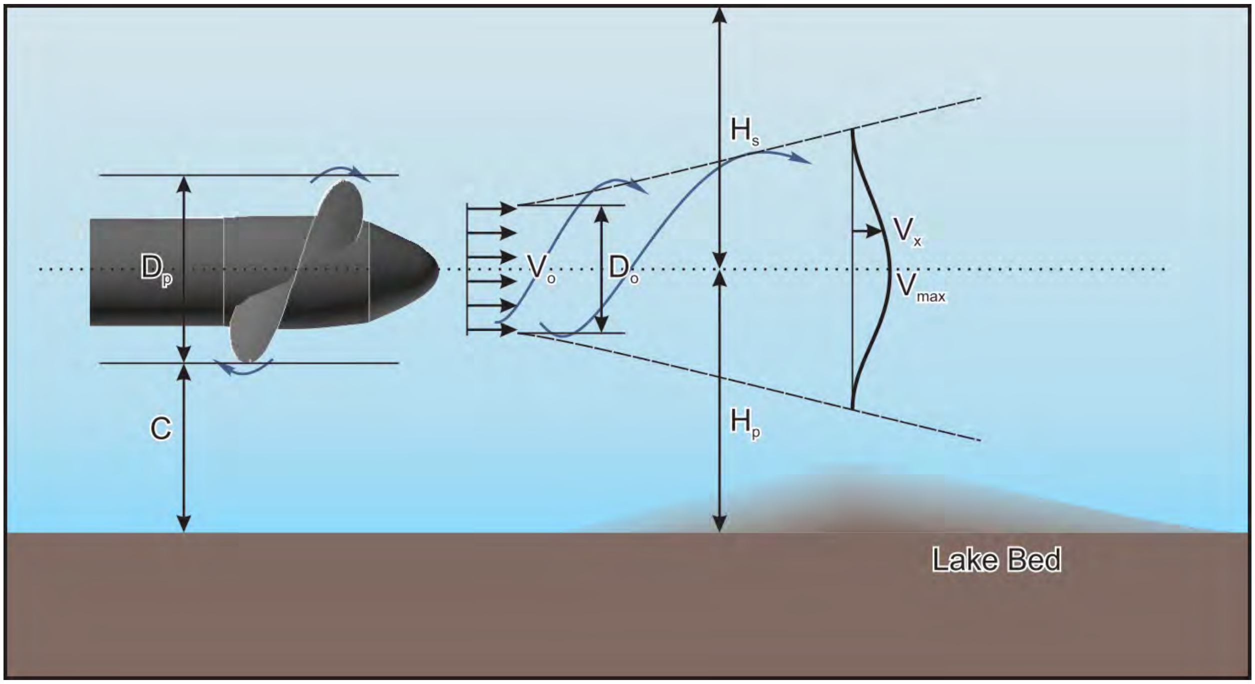


Figure 2-4. Propeller Action that Produces Scour (Modified from Sumer and Fredsoe, 2002.)

2.4.3.1g Wind-Induced Wave Erosion. Wind-induced waves are potentially important at shallow depths (*e.g.*, shoreline areas) and in areas with long fetches (*i.e.*, areas over a body of water where the wind flow is in the same direction). Areas that are prone to wind induced wave erosion are coastal embayments, estuaries, and lakes. Wind effects can be modeled to predict waves and currents under normal- or high-energy events. The best overall summary for predicting wind driven waves is the USACE *Coastal Engineering Manual* (2002). Using techniques outlined in Van Rijn (1993), Christoffersen and Jonsson (1985), and Grant and Madsen (1979), combined wave and current shear stresses can be computed so that the potential for sediment transport can be evaluated. Typical examples can be found in Bailey and Hamilton (1997), Evans (2005), Hamilton and Mitchell (1996), Lou *et al.* (2000), and Luettich *et al.* (1990).

2.4.3.2 Moving from Tier 1 to Tier 2 Sediment Erosion Characterization. The Tier 1 assessment of sediment erosion potential is achieved by calculating hydrodynamic shear stress and sediment critical shear stress values to determine order-of-magnitude erosion rates and scour depths. Tier 1 erosion rates are based on the understanding that these rates vary with applied shear stress due to waves and currents and as a function of sediment bulk properties. However, whereas sediment bulk properties (*e.g.*, PSD, moisture content, organic carbon, and bulk density) can be used to predict critical shear stress values of non-cohesive sediments, they cannot readily be used to predict critical shear stress values for cohesive sediments (Lick, 2010).

Thus, if the Tier 1 assessment shows significant potential for unacceptable risks to ecological receptors and/or human health due to erosion or if cohesive sediments are involved (thereby making it difficult to estimate sediment erosion potential), then direct measurement of sediment shear strength and hydrodynamic forces should be conducted as part of the Tier 2 analysis.

The magnitude and extent of sediment erosion under normal- and high-energy hydrodynamic events is of paramount importance to MNR applications. Few sites are purely depositional. The extent to which sediment erosion is acceptable can be assessed on a site-specific basis depending on the nature of the vertical contaminant profile in the sediment, the potential risks to ecological receptors and human health from erosion, and the potential for increased exposure.

Sediment erosion and scour can pose potentially unacceptable risks to ecological receptors and human health by causing the following possible negative impacts on natural recovery processes:

- Sediment erosion and scour can remove overlying clean surface sediments and expose buried sediments with higher contaminant concentrations. The scour depth influences the magnitude of sediment exposure and the resulting surface sediment contaminant concentrations after the scouring event.
- After erosion takes place, suspension of contaminated sediments in the water column can increase exposures of aquatic animals to contaminants.
- Suspended contaminated sediments may be transported away from the site, increasing the areal extent of sediment contaminants.

Not all scour or erosion, however, will result in unacceptable risk. Sediments eroded from one part of a system may naturally be deposited in other parts of the system. Moreover, movement of sediment itself may not necessarily create an unacceptable risk. EPA's *Contaminated Sediment Remediation Guidance* (2005) notes that the key factor in evaluating the stability of contaminants in sediment is whether movement of contaminated sediment or of contaminants alone is occurring or may occur at scales and rates that will significantly change their current contribution to risks to human health and/or ecological receptors.

At some sites, unacceptable risks to ecological receptors or human health due to impacts from sediment erosion and suspension may persist. Because of these concerns, supporting evidence may be required to evaluate sediment erosion after normal- or high-energy events. Modeling can greatly facilitate predictions of future erosional events and sediment transport behavior, which can aid in the determination of whether unacceptable risks to ecological receptors and/or human health may persist. However, modeling is not always feasible, and at some sites, particularly smaller sites, modeling may not be cost effective.

2.4.3.3 Tier 2 Estimates of Sediment Erosion and Transport. Tier 2 analyses are performed to further the understanding of sediment processes and fill data gaps from a Tier 1 analysis. For cohesive sediments, a great deal of uncertainty is associated with the prediction of erosion rates and scour depth using the Tier 1 approach alone. The primary uncertainty resides in sediment erosion rates that depend on critical shear stress, which are known to be highly heterogeneous from site to site and often within a single site. This uncertainty can be compounded by additional uncertainties regarding current and wave velocities. Accurate estimates of erosion rates and depths increasingly rely on site-specific, field-measured critical shear stress and hydrodynamic velocities. Table 2-4, presented previously, provides a list of information that can be collected to fill the data gaps remaining after a Tier 1 analysis. In some cases, Tier 2 analysis recommends refinement of the procedures used in Tier 1 (*i.e.*, applying site-specific measures as opposed to literature-derived values). In other cases, Tier 2 analysis suggests additional tests and data that would present a better understanding of the site conditions.

2.4.3.3a Site-Specific Sediment Erosion and Critical Shear Stress Measurements. The difficulty of predicting cohesive sediment erosion has led to the development of multiple flume configurations to measure sediment erosion under known hydrodynamic conditions. The general approach involves applying a known hydrodynamic force (*i.e.*, a known flow rate through the flume) on *in-situ* or *ex-situ* sediment columns, and measuring the amount of sediment erosion.

Typically, to conduct a flume study, the flow rate begins below the critical shear stress point of the sediment where no erosion is observed. The flow rate is increased incrementally until the sediments begin to erode. Erosion rates are then measured by the suspended solids concentration in the flume effluent stream or the depth of erosion of the sediment surface. The flumes are also used to measure critical shear stress to identify the critical flow rate at which a measurable amount of sediment is eroded.

Methods used to measure sediment critical shear stress to estimate erosion at different current velocities (usually under laminar flow) and corresponding hydrodynamic shear forces are identified in Table 2-6. The table includes information on flow conditions used for each device, whether the device can be used *in situ* or *ex situ*, the type of sediment transport measured, whether the device can measure the erosion rate, the depth of erosion that can be measured, and the measurable range of shear stresses. All of the devices allow for an indirect measurement of critical shear stress (τ_{cs}) in consolidated sediments with clays, silts, and sand using well-defined flow velocities.

Table 2-6. Comparison of Devices for Measurement of Sediment Critical Shear Stress

Device	Flow Condition	*In Situ* or *Ex Situ*	Measured Transport	Net Erosion per Event	Erosion Rate	Depth Measured	Shear Stress Range	Reference
Straight Flume	Linear/ Oscillatory	Both	Total Load	No	Yes	Surficial Layers	0-4 PA	Ravens and Gschwend, 1999
Annular Flume/ Sea Carousel	Linear	Both	Suspended Load	Yes	No	Surficial Layers	0-1 PA	Maa, 1993; Maa *et al.*, 1995
Sedflume	Linear	*Ex Situ*	Total Load	No	Yes	0-3 m	0-10+ PA	McNeil *et al.*, 1996
ASSET Flume	Linear	*Ex Situ*	Suspended Load + Bedload	No	Yes	0-3 m	0-10+ PA	Jepsen *et al.*, 2002
SEAWOLF Flume	Linear/ Oscillatory	*Ex Situ*	Total Load	No	Yes	0-3 m	0-10+ PA	Roberts *et al.*, 2003a

In-Situ flumes include the annular flume (Figure 2-5) and the straight flume (Figure 2-6). These flumes are placed on the sediment bed and rely on water to be passed over the sediment bed to erode and suspend surface sediments. The flumes themselves remain stationary. The annular flume is a closed system that does not release sediments as they are suspended. Both of the *in-situ* flumes operate in only the surficial layers (a few cm).

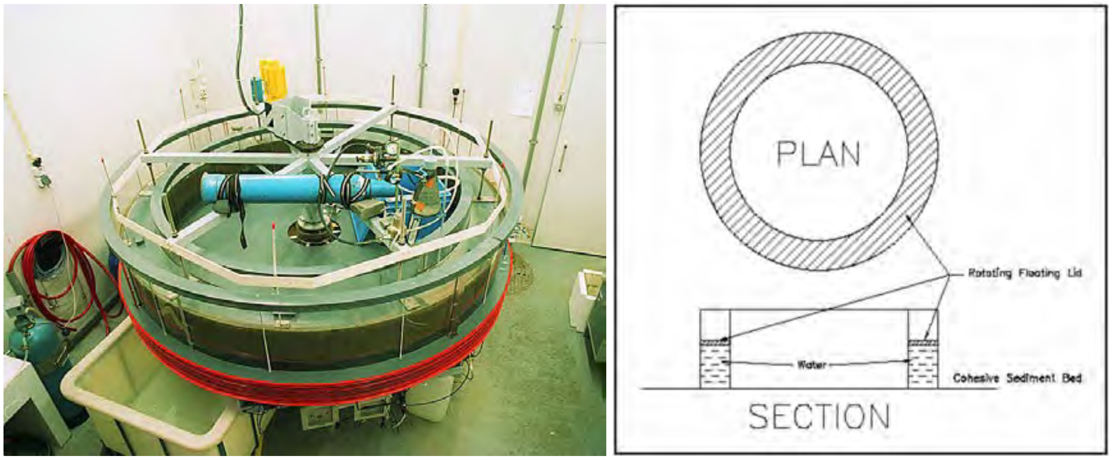


Figure 2-5. Annular Flume Configuration (Image of a Sea Carousel, left, from Deltares hydrologic research facility, the Netherlands; right schematic: USACE, 2002.)

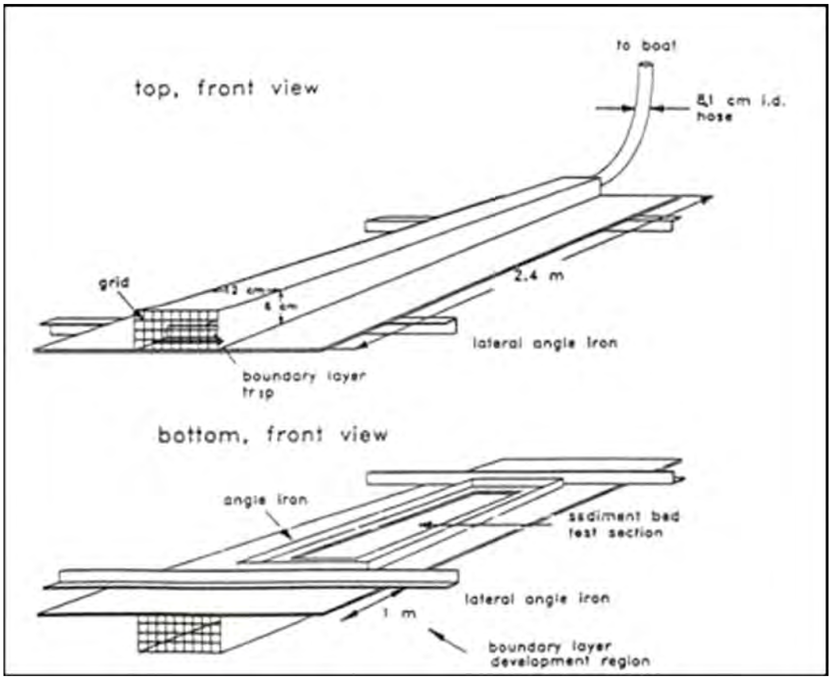


Figure 2-6. Straight Flume Configuration Showing Upright Perspective (top) and Inverted Perspective (bottom) (Ravens and Gschwend, 1999)

Annular flumes are limited in that they can only measure sediment resuspension and shear stresses below 10 dynes/cm^2 of force and, therefore, can only be used in the top few millimeters of the sediment bed (McNeil *et al.*, 1996) as deeper depths cause a greater amount of force to be applied to the instrument. Prior to the development of *ex-situ* flumes, the *in-situ* annular flume was the leading method of erodibility measurement for sediment transport studies (Lick *et al.*, 1995). Either a bed of reconstituted sediments or *in-situ* sediment in a closed circular flow system is subjected to erosion by applying rotation of an overlying water column. At each velocity and associated shear stress, an experiment is run to establish steady-state suspended solids concentrations in the water column, from which event-specific net erosion can be inferred. Subsequent analyses of this approach have identified artifacts, such as sediment accumulation, along the walls of the annulus that may understate event net erosion.

Ex-Situ flumes include the Sedflume (Figure 2-7), the Adjustable Shear Stress Erosion and Transport (ASSET) flume, and the Sediment Erosion Actuated by Wave Oscillations and Linear Flow (SEAWOLF) flume.

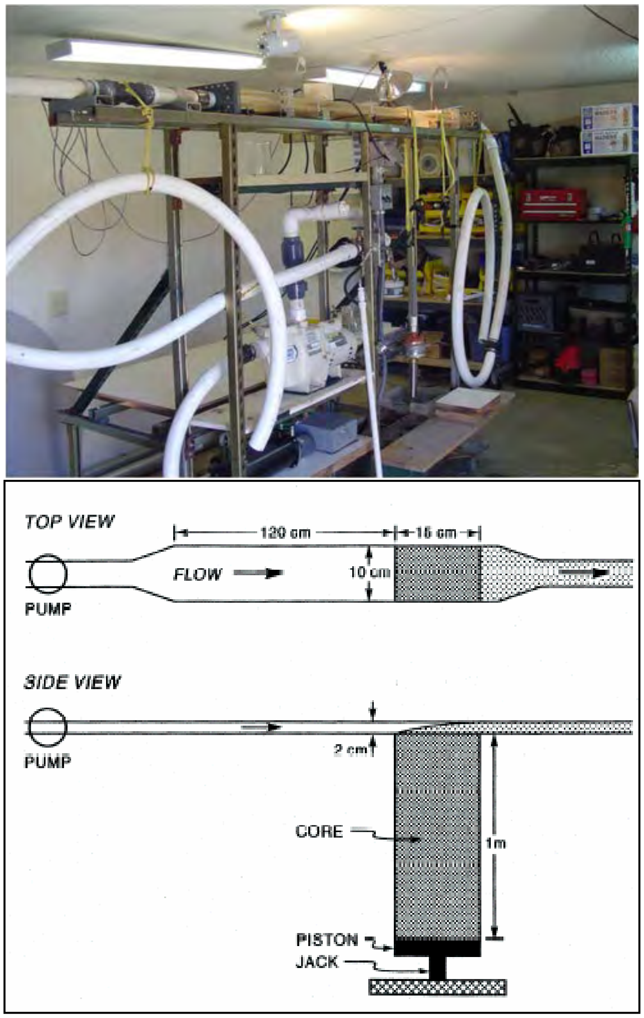


Figure 2-7. Sedflume Schematic
(Upper image adapted from McNeil *et al*., 1996; Lick and McNeil, 2001.
Lower image courtesy of Sea Engineering.)

A Sedflume is a straight flume with a test section containing an open bottom through which a rectangular or circular cross-section coring tube of sediment can be inserted. In general, the main components of a Sedflume are the coring tube; the test section; an inlet section for uniform, fully-developed turbulent flow; a flow exit section; a water storage tank; and a pump to force water through the system. The coring tube, test section, inlet section, and exit section can be made of clear acrylic or polycarbonate to allow observation of sediment-water interactions. During the analysis, water is pumped through the duct and the test section of the Sedflume. The core surface is moved upwards as necessary so that the sediment-water interface remains level with the bottom of the flume. Erosion rates are obtained by measuring the remaining core length at different time intervals, measuring the plunger elevation difference between each successive measurement, and dividing by the time interval. The duration of each erosion test for a specified shear stress is dependent on the rate of erosion and generally is between 0.5 and 10 minutes. Flow rates that induce no measurable erosion also are recorded (Borrowman *et al.*, 2006; Lick, 2010; Stevens *et al*., 2008).

Sedflume measurements were carried out on sediment cores from San Francisco (Jaffe and Foxgrover, 2006). The results revealed increasing critical shear stress values, decreasing erosion, and increasing bulk density with sediment depth. Although age dates are not shown for these sediment cores, it is clear that as sediment cohesiveness generally increases with sediment depth, it also increases with sediment age. Other changes with increasing sediment depth also influence erosion by orders of magnitude. These variations include increasing bulk density and decreasing porosity in sediments of uniform chemical composition. The authors also found that biological processes such as degradation or utilization of organic matter over time result in higher percentages of clay minerals with age and depth.

The ASSET and SEAWOLF flumes are modifications of the Sedflume (James *et al.*, 2005). The ASSET flume maintains the capabilities of the Sedflume, while also quantifying bedload and suspended load transport. In addition to measuring erosion and the variation of erosion with depth below the sediment-water interface, the SEAWOLF flume is able to analyze the impact of oscillatory flows on the sediment erosion rate using two pistons that work in tandem at both ends of the flume. This function may be used to better predict erosion in wave-dominated environments (James *et al*., 2005).

Despite being designed for *ex-situ* operation, these flumes are commonly field mobilized, thereby minimizing the need for long-range transport and disturbance of sediment cores. The primary advantages of *ex-situ* flumes are: 1) they can be used to profile an entire sediment horizon, providing erosion rate profiles with sediment depth, 2) the erosion process is visible to the operator, permitting better control of overflow rates and corresponding shear forces, 3) bedload/suspended transport and erosion rates are measured independently because the use of sediment traps for recirculated water or continuous flow from a source ensures that suspended sediments do not interfere with eroding sediments, 4) complicated underwater deployments are not required, and 5) cores may be reconstructed in the laboratory to study the erosion rates during consolidation of deposited sediments. Estimates made with *ex-situ* flumes often indicate much greater depths of scour than do *in-situ* annular flume estimates for the same site and same assumed shear conditions (Roberts *et al.*, 2003a). Models employing *ex-situ* flume estimates have been developed and are widely used (Roberts *et al.*, 2003a).

The primary disadvantage of *ex-situ* flumes is their reliance on external sediment cores and the potential disruption of sediments during core collection and transport. For this reason, Sedflume studies generally are conducted using push cores or by subsampling box cores. Theoretically, wall effects during core collection and extrusion can also influence Sedflume results; however, wall effects are reportedly negligible for 10-cm (width) by 15-cm rectangular cores (Roberts *et al.*, 2003b). Much of the erosion generated in *ex-situ* flume experiments is also observed to result in bedload. While this portion of erosion has been successfully measured with ASSET, it may be a measurement artifact of other flumes, leading to upward bias in erosion rates (Roberts *et al.*, 2003b).

When considering MNR, the extent to which sediments can erode under normal- or high-energy hydrodynamic conditions must be explored. By combining site-specific flow records with measured erosion data, site managers can begin to develop a quantitative description of sediment erosion potential. Some models use these data to predict long-term sediment transport trends. These models have also employed annular flume estimates of erodibility (Reible, 2004).

Because of potential artifacts in both *in-situ* and *ex-situ* flume methods, it is important to validate estimates made with either method by incorporating them into sediment mass balances and validating them against site-specific water column data and net burial rates inferred from the full range of available evidence (James *et al*., 2005). Not all models can accommodate the results of the different types of flumes; rather, specialized models are often required for different types of flume results. The challenge of measuring and verifying erodibility measurements remains a source of uncertainty in sediment transport modeling (Reible, 2004).

2.4.3.3b Water Column Hydrodynamic Studies. In combination with measurements of critical shear stress and erosion rates of bed sediments, the hydrodynamic forces that drive erosion events must be characterized. Most commonly, these data can be used in concert with measurements of critical shear stress and erosion rate to predict the erosion of sediments as a result of high-energy events. Hydrodynamic forces are site-specific and include river discharge, tidal currents, and wave action.

Erosion and resuspension events in riverine and estuarine environments can be measured at a site by collecting both spatial and time-series measurements of suspended sediment concentrations and current velocity in the water column. These measurements permit determination of the current velocity at which sediments become resuspended, the concentration of sediment in suspension, and the height in the water column to which sediments are being carried.

Extreme weather events, such as floods and hurricanes, can have significant effects on sediment transport at a site. To predict the impact of extreme events, a statistical analysis can be performed. Because extreme conditions are typically difficult to estimate accurately and often have serious economic implications, a number of different techniques have been developed to determine the probability and magnitude of extreme events in different systems (USACE, 1993; 2002). Hydrodynamic and sediment transport models also can be used to estimate sediment transport during high-energy events.

2.5 Summary

Successful application of MNR primarily depends on reductions in chemical bioavailability and toxicity in surface sediments over time. Typically, this is accomplished in a depositional environment. In depositional environments, contaminant burial due to net clean sediment deposition is often a major contributor to reduced contaminant availability, which may be further reduced through contaminant transformation, sequestration, and weathering. As stated in the previous sections, the key to understanding the effectiveness of MNR is the characterization of the dominant processes involved in moving sediments. A phased approach was outlined here that can be used to evaluate sediment transport processes. This approach begins with readily available data and proceeds with more targeted site-specific data collection as necessary.

3.0 FATE OF COMMON ORGANIC CONTAMINANTS IN SEDIMENTS

3.1 Introduction

3.1.1 Monitored Natural Recovery. The primary goal of managing contaminated sediment is to reduce health risks to aquatic/marine receptors, wildlife, and humans. Risk reduction can be accomplished by human intervention (*e.g.*, dredging, capping, and bioremediation) or by natural recovery (Magar and Wenning, 2006). MNR is the management strategy used to determine if natural transformation and fate processes are effective in reducing risks at a contaminated sediment site. MNR involves leaving contaminated sediments in place and monitoring ongoing physical, chemical, and biological processes that contain, transform, destroy, or otherwise reduce the bioavailability of the contaminants until they are no longer a risk to receptors (NRC, 1997). Bioavailability is defined as the extent to which a living organism can take up chemical contaminants by either active or passive processes, or a combination of both. The physical, chemical, and biological processes that contribute to the natural recovery of sediments contaminated with hydrophobic organic compounds (HOCs) that are to be considered in this section include:

- Diffusion and volatilization of HOCs from sediments: Some low molecular weight HOCs are sufficiently volatile or soluble that they can be lost rapidly from contaminated sediments by dissolution, diffusion, and volatilization.
- Reduction in sediment mobility: Sorption of HOCs to stable organic or mineral phases in sediments reduces their mobility.
- Chemical or biological transformation: HOCs can be transformed into degradation products by abiotic and biotic oxidation or reduction reactions that may alter the mobility or toxicity of the contaminants in question.
- Transport of HOCs in sediment pore water: HOCs can be transported through permeable sediments by diffusion or advective processes, such as groundwater or tidal water flow.

3.1.2 Non-polar Organic Compounds of Concern. For sediment, some of the most common contaminants of concern are non-polar organic compounds. These organic compounds are charge-neutral, non-polar organic chemicals characterized by low aqueous solubility and an affinity for association with dissolved or particulate organic matter and hydrophobic liquid, solid, and surface phases. Many HOCs are produced and released to the environment in massive quantities by human activities. When entering an aquatic environment, they tend to sorb to particles and accumulate in sediments. Many HOCs or their degradation products are highly bioaccumulative and toxic to plants and animals because of their high affinity for lipid phases of tissues; they can accumulate to hazardous concentrations in soils and sediments, particularly near point sources. The behavior of different types of HOCs in marine and fresh water bodies and associated sediments is controlled by the physical/chemical properties of the HOCs and the receiving environment. HOCs of major environmental concern are those with:

- High relative toxicity (see below for a detailed discussion of relative toxicity, *e.g.*, toxicity equivalent factors [TEFs]);
- Releases to the environment in large amounts from human activities; and
- High persistence in the environment.

HOCs with high toxicity include PAHs, PCBs, PCDDs, PCDFs, and halogenated pesticides and industrial chemicals, such as DDT and polybromodiphenyl ether fire retardants. The HOCs that have been most studied for their environmental reactivity and toxicity include PAHs, PCBs, and PCDDs/PCDFs (Figure 3-1); therefore, these HOCs will be the focus of this section.

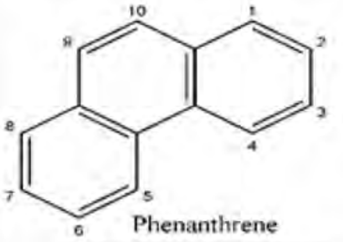
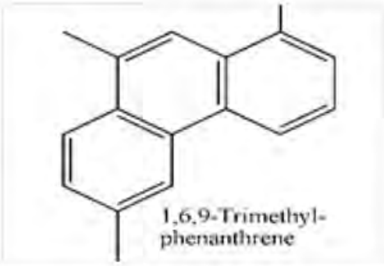
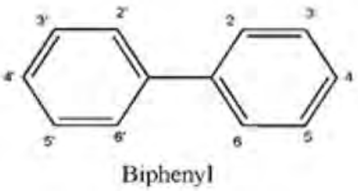
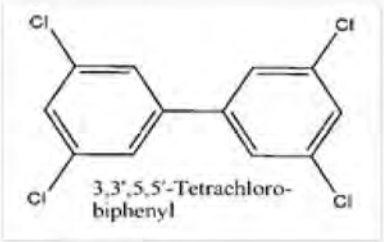
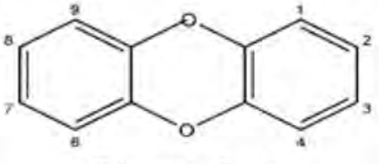
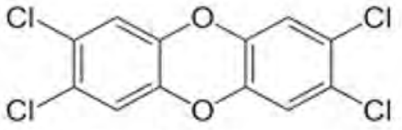
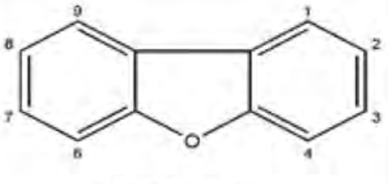
Hydrophobic Organic Compounds (HOCs)	Structure and Carbon Numbering	Examples
Polycyclic Aromatic Hydrocarbon	 Phenanthrene	 1,6,9-Trimethyl-phenanthrene
Polychlorinated Biphenyl	 Biphenyl	 3,3',5,5'-Tetrachloro-biphenyl
Polychlorinated Dibenzo-*p*-dioxin	 Dibenzo-*p*-dioxin	 2,3,7,8-Tetrachlorodibenzo-p-dioxin
Polychlorinated Dibenzofuran	 Dibenzofuran	 Octachlorodibenzofuran

Figure 3-1. Chemical Structure and Carbon-Numbering System of HOC Compound Classes (An example of a typical chemical structure in each HOC class is included.)

- **Polycyclic aromatic hydrocarbons:** PAHs are a class of hydrocarbons containing two or more fused (sharing two carbons) aromatic rings (Figure 3-1). They are derived from the incomplete combustion of organic matter (pyrogenic PAHs), from coal and petroleum (petrogenic PAHs), or from anaerobic degradation of certain plant materials (biogenic PAHs). PAHs may be classified further in terms of their analytical methodological classes (*e.g.*, total PAHs, dissolved PAHs, or extractable PAHs). The extractable class of compounds refers explicitly to that fraction of the total PAHs that can be dissolved or desorbed from a sorbed or otherwise solid phase through the use of an aqueous phase extraction.
- **Polychlorinated biphenyls:** Biphenyl is composed of two benzene rings joined by a single covalent carbon-carbon bond. PCBs are biphenyls containing one or more chlorine atoms covalently bound to the biphenyl carbons. There are 209 possible PCB congeners containing between one and 10 chlorines bonded to any of the 10 available carbons on the benzene rings (Figure 3-1). Only about 130 congeners have been identified in commercial PCB mixtures or environmental samples.
- **Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans:** Dibenzodioxins and dibenzofurans are composed of two benzene rings joined by one or two oxygen atoms (ether linkages), forming rigid coplanar (both benzenes oriented in the same plane) molecules. Chlorinated dibenzodioxins and dibenzofurans contain one or more chlorine atoms covalently bound to the benzene carbons (Figure 3-1). There are 75 possible PCDD congeners and 135 possible PCDF congeners containing between one and eight chlorines. PCDDs and PCDFs are produced as unintended byproducts in the manufacture of some types of industrial chlorinated organic compounds and by combustion of organic matter containing chlorine or treatment of certain organic wastewaters by chlorination. Most of the PCDDs/PCDFs in the environment originate from combustion sources and reach soils and sediments by rainout or fallout of the vapor phase and sorbed (to combustion soot) compounds.

3.1.2.1 Polycyclic Aromatic Hydrocarbons. PAHs are composed of two or more fused benzene rings (Neff, 2002). Naphthalene ($C_{10}H_8$), consisting of two fused aromatic rings, is the lowest molecular weight PAH. PAHs with up to six aromatic rings are commonly found in PAH-contaminated sediments. PAHs with different numbers of fused benzene rings and degrees of alkylation vary in physical/chemical properties (Table 3-1) that affect their fates and effects in the environment. PAHs can be formed by a variety of mechanisms and classified as:

- Pyrogenic PAHs: Very rapid, high temperature (*e.g.*, >700°C) incomplete combustion or pyrolysis of organic materials;
- Petrogenic PAHs: Very slow (over millions of years) rearrangement and transformation of biogenic organic materials at moderate temperatures of 100 to 300 °C to form fossil fuels, such as coal and petroleum;
- Diagenic PAHs: Relatively rapid (days to years) transformation of certain classes of organic compounds in anoxic soils and sediments; and
- Biogenic PAHs: Direct biosynthesis by organisms.

All four classes of PAHs can be found in water, soils, and sediments. Biogenic and diagenic mixtures of PAHs in soils and sediments are composed of just a few specific PAHs. Those few PAHs that are almost exclusively biogenic or diagenic usually are present at low concentrations compared to concentrations of pyrogenic and petrogenic PAHs; however, perylene (a diagenic PAH) concentrations sometimes are high in organic-rich anoxic sediments (Venkatesan and Dahl, 1989). Biogenic/diagenic PAHs are typically of little concern to MNR due primarily to their low relative concentrations in oxidized surface sediments. Pyrogenic and petrogenic PAH mixtures in sediments usually are complex, composed of hundreds of different PAHs, often at high concentrations; therefore, they represent a greater overall risk to environmental health and safety.

Table 3-1. PAH and Related Compounds Typically Used in Hydrocarbon Fingerprinting

Analyte/Analyte Group	Abbr.	Ring #	Analyte/Analyte Group	Abbr.	Ring #
Naphthalene*	**N0**	2	C_3-dibenzothiophenes	D3	3
C_1-naphthalenes*	N1	2	C_4-dibenzothiophenes	D4	3
C_2-naphthalenes*	N2	2	**Fluoranthene***	**FL**	4
C_3-naphthalenes*	N3	2	**Pyrene***	**PY**	4
C_4-naphthalenes*	N4	2	C_1-fluoranthenes/pyrenes*	FP1	4
Biphenyl	Bph	2	C_2-fluoranthenes/pyrenes	FP2	4
Acenaphthylene*	**Acl**	3	C_3-fluoranthenes/pyrenes	FP3	4
Acenaphthene*	**Ace**	3	**Benz(a)anthracene***	**BaA**	4
Dibenzofuran	DdF	3	**Chrysene***	**C0**	4
Fluorene*	F0	3	C_1-chrysenes/benzanthracenes*	C1	4
C_1-fluorenes*	F1	3	C_2-chrysenes/benzanthracenes*	C2	4
C_2-fluorenes*	F2	3	C_3-chrysenes/benzanthracenes*	C3	4
C_3-fluorenes*	F3	3	C_4-chrysenes/benzanthracenes*	C4	4
Anthracene*	**AN**	3	**Benzo(b)fluoranthene***	**BbF**	5
Phenanthrene*	**P0**	3	**Benzo(k)fluoranthene***	**BkF**	5
C_1-phenanthrenes/anthracenes*	P1	3	Benzo(e)pyrene*	BeP	5
C_2-phenanthrenes/anthracenes*	P2	3	**Benzo(a)pyrene***	**BaP**	5
C_3-phenanthrenes/anthracenes*	P3	3	Perylene*	Per	5
C_4-phenanthrenes/anthracenes*	P4	3	**Indeno(1,2,3-c,d)pyrene***	**ID**	6
Dibenzothiophene	D0	3	**Dibenz(a,h)anthracene***	**DA**	5
C_1-dibenzothiophenes	D1	3	**Benzo(g,h,i)perylene***	**BgP**	6
C_2-dibenzothiophenes	D2	3	--	--	--

Bold = 16 PAH priority pollutants identified in the Clean Water Act (CWA).
* = 34 PAHs identified in *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks for the Protection of Benthic Organisms: PAH Mixtures* (EPA, 2003).

Source: Douglas *et al*., 2004

Although coal is generally considered an aromatic material (Berkowitz, 1988), concentrations of extractable total PAHs usually are low, ranging from less than 0.01 to 0.8% (Stout and Emsbo-Mattingly, 2008). Coal is derived primarily from the remains of land plants that accumulated as peat. Upon burial, peat is converted to coal over millions of years of exposure to high temperatures and pressures. Chemical rearrangements during slow diagenesis convert plant debris into a high molecular weight, highly-aromatic, three-dimensional structure (Teichmuller, 1987). There is variation in the number of fused aromatic rings per structural unit in coals of different ranks (hardness and maturity) (Stout and Emsbo-Mattingly, 2008). The aromatic structures are linked together through linear and cyclic aliphatic structures and oxygen and sulfur substituents. Most of the PAHs in coal are tightly bound in the coal structure; they typically do not leach out of coal. However, coal dust and particles have a large surface area and, therefore, are more susceptible to leaching or to adsorption of dissolved PAHs; they may contribute to the total extractable PAHs in sediments receiving coal-associated materials from aerial deposition or runoff (Tripp *et al.*, 1981; Short *et al.*, 1999: Ahrens and Morrisey, 2005). It is important to determine the contribution of coal dust PAHs and pyrogenic PAHs to the total PAHs in contaminated sediments being monitored in MNR investigations. These PAHs typically are bound more tightly than petrogenic PAHs to sediment particles and may contribute little to the PAH hazard of the contaminated sediments (Neff *et al.*, 2005).

Crude oil is derived from the thermal degradation and rearrangement of organic polymers found in source rocks, often sedimentary shales, in the subsurface (Tissot and Welte, 1984). The organic matter in the source rocks usually is derived primarily from sedimentation of dead plants and animals in fresh water and marine sediments. Crude oil represents the material that has migrated away from the source rocks to accumulate in a subsurface reservoir. Crude petroleum contains primarily small molecules (*i.e.*, those able to migrate) unless substantial weathering has occurred to the oil in the reservoir. Most of the PAHs in crude oil are composed of two or three fused aromatic rings (Neff, 2002). Typically, the largest molecules in oil are asphaltenes. Asphaltenes are large, complex compounds composed primarily of 2- to 4-ring PAHs, heterocyclics (mostly thiophenes), saturated cyclic hydrocarbons, and metal porphyrins linked by aliphatic chains (Gray, 2003). The PAHs in asphaltenes are immobile and, therefore, have a low toxicity, similar to that of the PAHs in coal.

Crude oils can contain 0.2% to 7% total PAHs. However, some crude oils that have weathered naturally in the geologic formation may not contain detectable concentrations of any PAHs (Neff, 2002; Wang *et al*., 2003). The abundance of individual aromatic hydrocarbons in petroleum usually decreases markedly with increasing molecular weight. In most cases, the one- through three-ring aromatic hydrocarbons (*i.e.*, benzene through phenanthrene) and related heterocyclic aromatic hydrocarbons (such as dibenzothiophenes) account for at least 90% of the aromatic hydrocarbons that can be resolved in crude oil by conventional analytical techniques (Neff, 2002). Higher molecular weight (4- through 6-ring) PAHs, some of which are either known or suspected carcinogens, are much less abundant in crude oils than they are in most pyrogenic PAH mixtures (Neff *et al.*, 2005). Concentrations of individual carcinogenic PAHs in crude oils range from below detectable levels (about 0.05 mg/kg oil) to 120 mg/kg (Kerr *et al.*, 1999).

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero as determined from analysis of a sample in a given matrix containing the analyte (EPA, 1986c) and can set the lower limits of the ability to study trace-level contaminants in the environment. Modern analytical methods, based on modifications of EPA Method 8270, in which analysis of purified sample extracts is performed by capillary column gas chromatography with quantification by mass spectrometry (GC/MS) operated in the selected ion monitoring (SIM) mode, can attain very low MDLs (Douglas *et al.*, 2004). MDLs for individual parent and alkylated PAHs in sediments range from 0.04 to 0.50 µg/kg (parts per billion dry weight). These detection limits are low enough to detect PAH in sediments below potentially toxic concentrations.

The PAHs in coal and petroleum (*i.e.*, petrogenic PAHs) often contain one or more methyl, ethyl, butyl, or occasionally higher alkyl substituents on one or more of the aromatic carbons (Figure 3-1). As a general rule, these alkyl PAHs are more abundant than the parent compounds in petroleum (Youngblood and Blumer, 1975). Homologues with two to five alkyl carbons usually are more abundant than the less or more highly alkylated homologues (Neff, 2002). Crude oil is refined to produce a wide variety of fuels and hydrocarbon feedstocks (Neff, 1990). Refined petroleum products typically contain the PAHs in the parent crude oil, as well as small amounts of PAHs produced by catalytic cracking and other refining processes. The PAH assemblage in different refined oils varies depending on the refining processes used (*i.e.*, distillation temperature range for the product). Gasoline and other light distillates contain mainly monocyclic aromatic hydrocarbons and low molecular weight PAHs (*i.e.*, naphthalenes and fluorenes [Neff, 2002; Figure 3-2]). Diesel fuels and other middle distillate products may contain aromatic hydrocarbons from benzene through fluoranthene (Figure 3-2). Heavy fuel oils, residual fuel oil (bunker fuel), and crude oil may contain, in addition to the 2- and 3-ring PAHs, small amounts of higher molecular weight, higher boiling 4- through 6-ring PAHs, such as chrysenes and benzopyrenes (Figure 3-2). Petrogenic PAHs can enter fresh water and marine environments from naturally-occurring oil seeps; erosion of coal, peat, and oil shale deposits; and anthropogenic sources such as oil and coal spills, discharges of treated and untreated ballast and bilge water from oil tankers and other ships, effluents from oil refineries, coastal and offshore production platforms, coal-fired power plants, road runoff, storage tank leaks, and municipal wastewater treatment plants (NRC, 1985, 2003b).

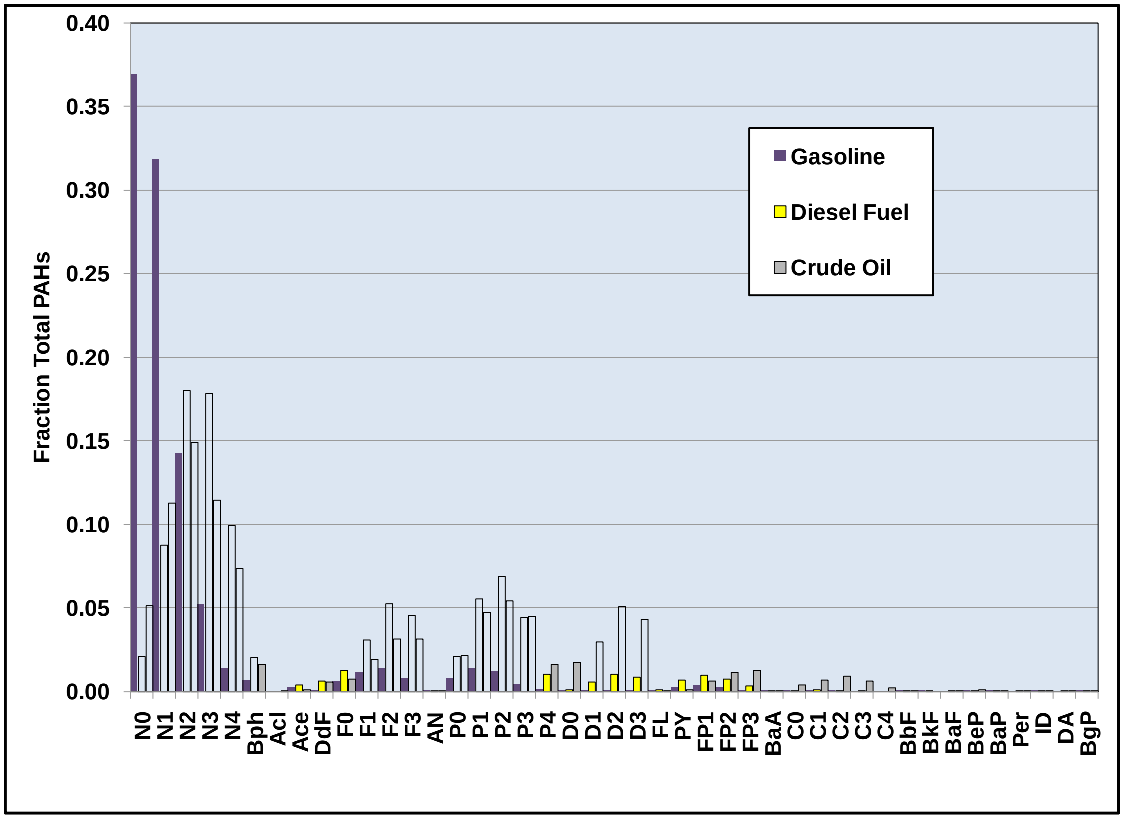


Figure 3-2. Relative Concentrations of Parent and Alkyl PAHs in Petrogenic Mixtures: Gasoline, Diesel Fuel, and a Middle Weight Crude Oil (PAH abbreviations [X-Axis] are defined in Table 3-1.)

Pyrogenic PAHs are differentiated from petrogenic PAHs by the presence and high relative concentrations of higher-molecular-weight PAHs. The major source of high molecular weight 4- through 6-ring PAHs in sediments is from the products of the incomplete combustion of organic matter (Neff, 2002). Combustion of any organic material, including fossil fuels, generates a wide variety of PAHs ranging from naphthalene to complex PAH polymers, particularly if combustion takes place in an oxygen-deficient environment (fuel-rich combustion mixture). During combustion in an oxygen-deficient atmosphere, organic matter is oxidized to low-molecular weight organic molecules that condense as the combustion mixture cools to form complex new molecular structures including PAHs, a process called pyrolysis/pyrosynthesis (Neff, 1979). The PAH yield (or total PAH concentration from a single source) depends on the composition of the organic material being combusted, the combustion temperature, and the oxygen concentration. The PAH mixtures (relative PAH concentrations within single sources) produced by pyrolysis of organic matter are complex and, unlike the mixtures in petroleum, are dominated by 3- through 6-ring PAHs (Figure 3-3). In pyrogenic PAH mixtures, the dominant compound in each homologous series is the unalkylated parent compound or a homologue with only one or two alkyl substituents; more highly alkylated congeners are rare (Sporsol *et al.*, 1983). Unalkylated phenanthrene, fluoranthene, and pyrene often are the most abundant PAHs in pyrogenic PAH mixtures (Figure 3-3). The differences in PAH compositions and ratios of parent to alkyl substituted PAH congeners can be used to help distinguish between petrogenic and various types of pyrogenic PAH assemblages in environmental samples (Stout *et al.*, 2000, 2004).

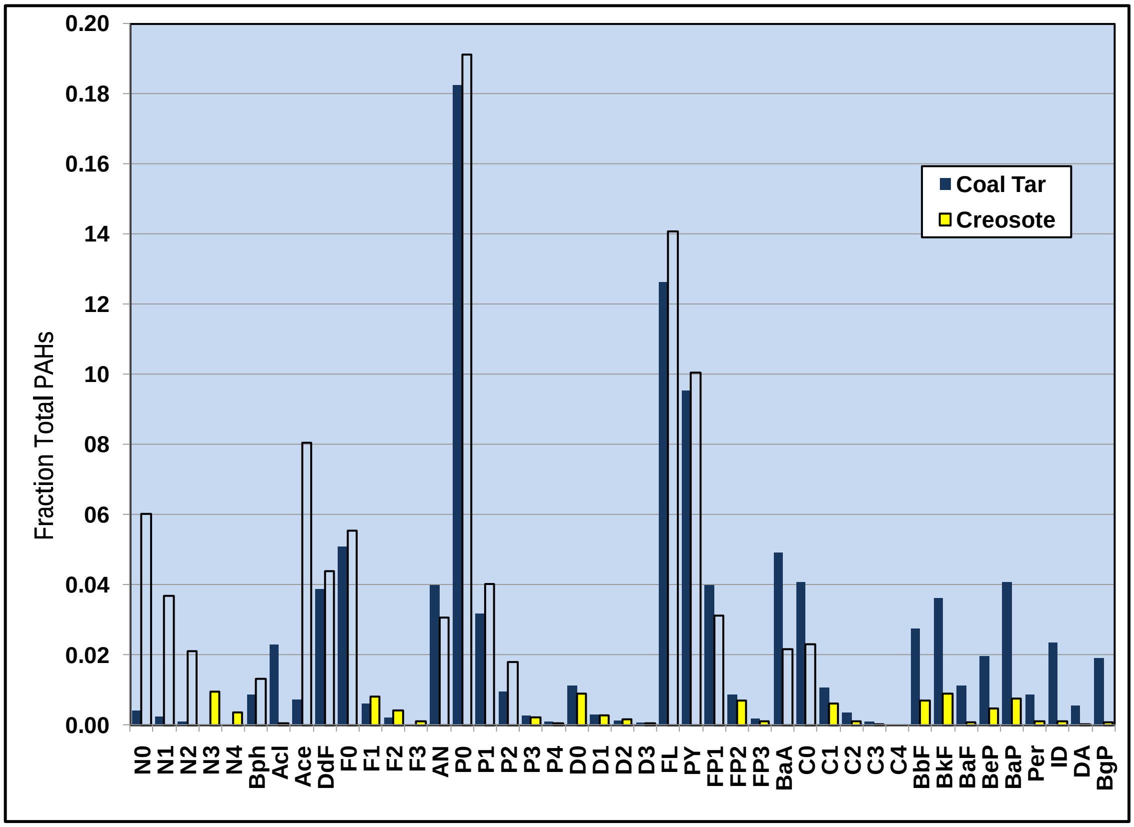


Figure 3-3. Relative Concentrations of Parent and Alkyl PAHs in Representative Pyrogenic Mixtures: Coal Tar and Creosote (Creosote is usually a distillate of coal tar and, therefore, contains higher relative concentrations of 2-ring PAHs. PAH abbreviations [X-Axis] are defined in Table 3-1.)

Natural events, such as forest fires, and industrial and domestic activities, such as the burning of fossil fuels for energy or heat production and internal combustion engines, produce PAHs by pyrolysis and pyrosynthesis. Many facilities that generate heat and electricity burn fossil fuels and emit saturated and aromatic hydrocarbons in liquid, solid, and gaseous waste byproducts (Heit, 1985). Several industrial processes, such as coal coking (Lao *et al.*, 1975); carbonization of coal to produce manufactured gas, coal tars, carbon black, and creosote (Villaume, 1984; Merrill and Wade, 1985; Mueller *et al.*, 1989); catalytic cracking of petroleum feed stocks to produce refined petroleum products (Neff *et al.*, 1994); and aluminum smelting (Thrane, 1987; OSPAR, 2002) produce airborne particulates and solid wastes containing very high concentrations of PAHs. Wood burning stoves, used frequently for domestic heating, produce large amounts of PAHs that are concentrated primarily in the particulate fraction (soot and ash) of the smoke (Ramdahl *et al.*, 1982; Knight *et al.*, 1983). Forest fires and open burning of brush and plant wastes also are important sources of particulate emissions rich in PAHs (Sullivan and Mix, 1983; Freeman and Cattell, 1990).

PAHs produced during combustion of organic matter, as discussed above, also are present in the exhaust gases and ash (or soot) produced during fossil fuel combustion. The lower-molecular weight PAHs in the exhaust gases are primarily present in the vapor phase; the higher-molecular weight PAHs are associated primarily with the particulate (soot) fraction (Dachs and Eisenreich, 2000). Soot is thought to be an agglomerate of peri-condensed PAHs (Venkatesan and Dahl, 1989). PAHs associated with soot particles are part of the particle structure or are tightly adsorbed to the particles through hydrogen bonding and are not easily desorbed. Lower-molecular weight PAHs desorb slowly from airborne soot particles into the vapor phase. Higher-molecular weight PAHs are tightly bound to soot particles (Halsall *et al.*, 1997). The higher-molecular weight PAHs are bound to the finest size soot particles, inhibiting photo-oxidation and facilitating long-range transport in the air (Offenberg and Baker, 1999). The particulate fractions of exhaust from gasoline and diesel-powered vehicles contain from 16 to 2,300 μg/g 4- through 6-ring PAHs (Takada *et al.*, 1991; Oda *et al.*, 1998). Fluoranthene and pyrene represent between 46% and 88% of the total PAHs in diesel engine exhaust and 15% to 17% of the total PAHs in gasoline engine exhaust. They are often the most abundant PAHs in fresh water and marine sediments in urban estuaries (Stout *et al.*, 2004). Nearly all the PAHs derived from vehicular exhaust are deposited within approximately 50 m of roads (Harrison and Johnston, 1985; Hewitt and Rashed, 1990). Much of the deposited PAHs, however, find their way to water bodies in surface runoff from land (Hoffman *et al.*, 1984; Sharma *et al.*, 1994; Stein *et al.*, 2006; Zhang *et al.*, 2008) and are deposited in sediments.

The estimated total input of PAHs to the ocean from all sources (mostly petroleum and combustion) is about 230,000 metric tons per year (Neff, 2002). Releases of petrogenic and pyrogenic PAHs each account for about half the total annual releases to the ocean; however, about 95% of high-molecular-weight, potentially carcinogenic PAHs entering the ocean each year are from pyrogenic sources and 5% are from petrogenic sources. Concentrations of pyrogenic PAHs in near-shore fresh water and marine sediments often are closely correlated with the abundance of spheroidal carbonaceous particles (soot) (Broman *et al.*, 1990). This indicates that PAHs remain associated with the soot after deposition and usually are not modified by photooxidation, dissolution, or biodegradation during transport in the air and water (Readman *et al.*, 1984a,b; Readman *et al.*, 1987; Ghosh *et al.*, 2003; Hartmann *et al*., 2004). Soot-associated PAHs in sediments, which are discussed in greater detail in Section 3.3, have a low bioavailability to aquatic organisms (Farrington and Westall, 1986; Gustafsson *et al.*, 1997) and are extremely resistant to abiotic and biotic degradation. PAH assemblages that have been identified in Cretaceous/Tertiary and Jurassic sedimentary deposits are thought to have been derived from ancient forest fires (Venkatesan and Dahl, 1989; Killops and Massoud, 1992).

3.1.2.2 Polychlorinated Biphenyls. PCBs are synthetic commercial HOCs that have no significant natural sources. PCBs were produced in North America under the trade name *Aroclor* from 1929 to 1977. EPA banned manufacturing, processing, distribution, and use of PCBs in the United States in 1979 (EPA, 2002a), when problems from their environmental persistence and threats to humans and the health of the environment were recognized. However, they are still abundant in the environment because of their extreme stability. Small amounts of PCBs are still in use for special applications.

PCBs were used in a variety of industrial applications (*e.g.*, as dielectric, hydraulic, and heat transfer fluids; plasticizers; flame retardants; carbon paper, etc.) and were produced under many different trade names in several countries, including the United States (Monsanto Corporation: *Aroclor*), Germany (Bayer S.A.: *Clophen*), and Japan (Kanegafuchi Chemical: *Kanechlor*). In the United States, 6.3×10^8 kg of PCBs were manufactured between 1929 and 1977 and sold as mixtures of chlorobiphenyls (CBs). PCBs were manufactured and marketed in many countries as mixtures of 40 to 60 different congeners with different numbers and positions of chlorine atoms on the aromatic carbons. The Monsanto Corporation (Madison, NJ) produced nine technical grades of PCBs under the trade names Aroclors 1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262, and 1268. The last two digits in the numerical suffix indicate the percent chlorine by mass in the technical mixture, with the exception of Aroclor 1016 which contains 42% chlorine. Table 3-2 is a summary of the composition and chemical properties of the different Aroclors. The extent of chlorination, isomeric composition, and resulting physical properties of each mixture are unique, reflecting the reaction conditions and thermodynamics of the manufacturing process. Although 209 congeners of PCBs are theoretically possible, the manufacturing process preferentially creates a limited number of congeners.

Table 3-2. Approximate Molecular Composition (%) and Physical Properties of Seven Commercial Aroclors

Composition and Properties	Aroclor						
	1221	1232	1016	1242	1248	1254	1260
Biphenyl	11.0	6.0	< 0.01	-	-	-	-
Mono-chlorobiphenyl	51.0	26.0	1.0	1.0	-	-	-
Di-chlorobiphenyl	32.0	29.0	20.0	17.0	1.0	-	-
Tri-chlorobiphenyl	4.0	24.0	57.0	40.0	23.0	-	-
Tetra-chlorobiphenyl	2.0	15.0	21.0	32.0	50.0	16.0	-
Penta-chlorobiphenyl	0.5	0.5	1.0	10.0	20.0	60.0	12.0
Hexa-chlorobiphenyl	-	-	< 0.01	0.5	1.0	23.0	46.0
Hepta-chlorobiphenyl	-	-	-	-	-	1.0	36.0
Octa-chlorobiphenyl	-	-	-	-	-	-	6.0
Specific Gravity (@ 25/15.5°C)	1.18	1.27	1.37	1.38	1.41	1.50	1.56
Absolute Viscosity (cp @ 38°C)	5	8	20	24	70	700	resin
Solubility (µg/L @ 25°C)	200	-	240	240	54	12	2.7
Vapor Pressure (mm Hg @ 25°C)	0.0067	0.0046	0.0004	0.0004	0.0004	0.00008	0.00004

Source: Agency for Toxic Substances and Disease Registry (ATSDR), 2000

Only approximately 130 individual congeners have been identified in commercial PCB mixtures (Pereira, 2004). Individual PCB congeners contain between one and 10 chlorines covalently bonded to the available aromatic carbons. Each PCB congener has been assigned a unique identifying number by the International Union of Pure and Applied Chemistry (IUPAC). IUPAC numbers are based on the numbers and positions of chlorines on the biphenyl molecule (Table 3-3). There is continuing discussion of the PCB congener nomenclature (Mills *et al.*, 2007).

Table 3-3. The IUPAC Numbering System for Polychlorinated Biphenyl Congeners and Log K_{0W}

Congener Number	Substitution Pattern	Log K_{ow}	Congener Number	Substitution Pattern	Log K_{ow}
0	Biphenyl	4.09	41	2,2',3,4-	5.69
1	2-	4.46	42	2,2',3,4'-	5.76
2	3-	4.69	43	2,2',3,5-	5.75
3	4-	4.69	44	2,2',3,5'-	5.75
4	2,2'-	4.65	45	2,2',3,6-	5.53
5	2,3-	4.97	46	2,2',3,6'-	5.53
6	2,3'-	5.06	47	2,2',4,4'-	5.85
7	2,4-	5.07	48	2,2',4,5-	5.78
8	2,4'-	5.07	49	2,2',4,5'-	5.85
9	2,5-	5.06	50	2,2',4,6-	5.63
10	2,6-	4.84	51	2,2',4,6'-	5.63
11	3,3'-	5.28	52	2,2',5,5'-	5.84
12	3,4-	5.22	53	2,2',5,6'-	5.62
13	3,4'-	5.29	54	2,2',6,6'-	5.21
14	3,5-	5.28	55	2,3,3',4-	6.11
15	4,4'-	5.30	56	2,3,3',4'-	6.11
16	2,2',3-	5.16	57	2,3,3',5-	6.17
17	2,2',4-	5.25	58	2,3,3',5'-	6.17
18	2,2',5-	5.24	59	2,3,3',6-	5.95
19	2,2',6-	5.02	60	2,3,4,4'-	6.11
20	2,3,3'-	5.57	61	2,3,4,5-	6.04
21	2,3,4-	5.51	62	2,3,4,6-	5.89
22	2,3,4'-	5.58	63	2,3,4',5-	6.17
23	2,3,5-	5.57	64	2,3,4',6-	5.95
24	2,3,6-	5.35	65	2,3,5,6-	5.86
25	2,3',4-	5.67	66	2,3',4,4'-	6.20
26	2,3',5-	5.66	67	2,3',4,5-	6.20
27	2,3',6-	5.44	68	2,3',4,5'-	6.26
28	2,4,4'-	5.67	69	2,3',4,6-	6.04
29	2,4,5-	5.60	70	2,3',4',5-	6.20
30	2,4,6-	5.44	71	2,3',4',6-	5.98
31	2,4',5-	5.67	72	2,3',5,5'-	6.26
32	2,4',6-	5.44	73	2,3',5',6-	6.04
33	2,3',4'-	5.60	74	2,4,4',5-	6.20
34	2,3',5'-	5.66	75	2,4,4',6-	6.05
35	3,3',4-	5.82	76	2,3',4',5'-	6.13
36	3,3',5-	5.88	**77**	**3,3',4,4'-**	**6.36**
37	3,4,4'-	5.83	78	3,3',4,5-	6.35
38	3,4,5-	5.76	79	3,3',4,5'-	6.42
39	3,4',5-	5.89	80	3,3',5,5'-	6.48
40	2,2',3,3'-	5.66	**81**	**3,4,4',5-**	**6.36**
82	2,2',3,3',4-	6.20	125	2,3',4',5',6-	6.51
83	2,2',3,3',5-	6.26	**126**	**3,3',4,4',5-**	**6.89**
84	2,2',3,3',6-	6.04	127	3,3',4,5,5'-	6.95
85	2,2',3,4,4'-	6.30	128	2,2',3,3',4,4'-	6.74
86	2,2',3,4,5-	6.23	129	2,2',3,3',4,5-	6.73
87	2,2',3,4,5'-	6.29	130	2,2',3,3',4,5'-	6.80
88	2,2',3,4,6-	6.07	131	2,2',3,3',4,6-	6.58
89	2,2',3,4,6'-	6.07	132	2,2',3,3',4,6'-	6.58
90	2,2',3,4',5-	6.36	133	2,2',3,3',5,5'-	6.86

Table 3-3. The IUPAC Numbering System for Polychlorinated Biphenyl Congeners and Log K0W (continued)

Congener Number	Substitution Pattern	Log K_{ow}	Congener Number	Substitution Pattern	Log K_{ow}
91	2,2',3,4',6-	6.13	134	2,2',3,3',5,6-	6.55
92	2,2',3,5,5'-	6.35	135	2,2',3,3',5,6'-	6.64
93	2,2',3,5,6-	6.04	136	2,2',3,3',6,6'-	6.22
94	2,2',3,5,6'-	6.13	137	2,2',3,4,4',5-	6.83
95	2,2',3,5',6-	6.13	138	2,2',3,4,4',5'-	6.83
96	2,2',3,6,6'-	5.71	139	2,2',3,4,4',6-	6.67
97	2,2',3,4',5'-	6.29	140	2,2',3,4,4',6'-	6.67
98	2,2',3,4',6'-	6.13	141	2,2',3,4,5,5'-	6.82
99	2,2',4,4',5-	6.39	142	2,2',3,4,5,6-	6.51
100	2,2',4,4',6-	6.23	143	2,2',3,4,5,6'-	6.60
101	2,2',4,5,5'-	6.38	144	2,2',3,4,5',6-	6.67
102	2,2',4,5,6'-	6.16	145	2,2',3,4,6,6'-	6.25
103	2,2',4,5',6-	6.22	146	2,2',3,4',5,5'-	6.89
104	**2,2',4,6,6'-**	**5.81**	147	2,2',3,4',5,6-	6.64
105	2,3,3',4,4'-	6.65	148	2,2',3,4',5,6'-	6.73
106	2,3,3',4,5-	6.64	149	2,2',3,4',5',6-	6.67
107	2,3,3',4',5-	6.71	150	2,2',3,4',6,6'-	6.32
108	2,3,3',4,5'-	6.71	151	2,2',3,5,5',6-	6.64
109	2,3,3',4,6-	6.48	152	2,2',3,5,6,6'-	6.22
110	2,3,3',4',6-	6.48	153	2,2',4,4',5,5'-	6.92
111	2,3,3',5,5'-	6.76	154	2,2',4,4',5,6'-	6.76
112	2,3,3',5,6-	6.45	155	2,2',4,4',6,6'-	6.41
113	2,3,3',5',6-	6.54	**156**	**2,3,3',4,4',5-**	**7.18**
114	**2,3,4,4',5-**	**6.65**	**157**	**2,3,3',4,4',5'-**	**7.18**
115	2,3,4,4',6-	6.49	158	2,3,3',4,4',6-	7.02
116	2,3,4,5,6-	6.33	159	2,3,3',4,5,5'-	7.24
117	2,3,4',5,6-	6.46	160	2,3,3',4,5,6-	6.93
118	**2,3',4,4',5-**	**6.74**	161	2,3,3',4,5',6-	7.08
119	2,3',4,4',6-	6.58	162	2,3,3',4',5,5'-	7.24
120	2,3',4,5,5'-	6.79	163	2,3,3',4',5,6-	6.99
121	2,3',4,5',6-	6.64	164	2,3,3',4',5',6-	7.02
122	2,3,3',4',5'-	6.64	165	2,3,3',5,5',6-	7.05
123	**2,3',4,4',5'-**	**6.74**	166	2,3,4,4',5,6-	6.93
124	2,3',4',5,5'-	6.73	**167**	**2,3',4,4',5,5'-**	**7.27**
168	2,3',4,4',5',6-	7.11	**189**	**2,3,3',4,4',5,5'-**	**7.71**
169	**3,3',4,4',5,5'-**	**7.42**	190	2,3,3',4,4',5,6-	7.46
170	2,2',3,3',4,4',5-	7.27	191	2,3,3',4,4',5',6-	7.55
171	2,2',3,3',4,4',6-	7.11	192	2,3,3',4,5,5',6-	7.52
172	2,2',3,3',4,5,5'-	7.33	193	2,3,3',4',5,5',6-	7.52
173	2,2',3,3',4,5,6-	7.02	194	2,2',3,3',4,4',5,5'-	7.80
174	2,2',3,3',4,5,6'-	7.11	195	2,2',3,3',4,4',5,6-	7.56
175	2,2',3,3',4,5',6-	7.17	196	2,2',3,3',4,4',5,6'-	7.65
176	2,2',3,3',4,6,6'-	6.76	197	2,2',3,3',4,4',6,6'-	7.30
177	2,2',3,3',4,5',6'-	7.08	198	2,2',3,3',4,5,5',6-	7.62
178	2,2',3,3',5,5',6-	7.14	199	2,2',3,3',4,5,5',6'-	7.20
179	2,2',3,3',5,6,6'-	6.73	200	2,2',3,3',4,5,6,6'-	7.27
180	2,2',3,4,4',5,5'-	7.36	201	2,2',3,3',4,5',6,6'-	7.62
181	2,2',3,4,4',5,6-	7.11	202	2,2',3,3',5,5',6,6'-	7.24
182	2,2',3,4,4',5,6'-	7.20	203	2,2',3,4,4',5,5',6-	7.65
183	2,2',3,4,4',5',6-	7.20	204	2,2',3,4,4',5,6,6'-	7.30

Table 3-3. The IUPAC Numbering System for Polychlorinated Biphenyl Congeners and Log K0W (continued)

Congener Number	Substitution Pattern	Log K_{ow}	Congener Number	Substitution Pattern	Log K_{ow}
184	2,2',3,4,4',6,6'-	6.85	205	2,3,3',4,4',5,5',6-	8.00
185	2,2',3,4,5,5',6-	7.11	206	2,2',3,3',4,4',5,5',6-	8.09
186	2,2',3,4,5,6,6'-	6.69	207	2,2',3,3',4,4',5,6,6'-	7.74
187	2,2',3,4',5,5',6-	7.17	208	2,2',3,3',4,5,5',6,6'-	7.71
188	2,2',3,4',5,6,6'-	6.82	209	Decachlorobiphenyl	8.18

Chlorinated biphenyl congeners are identified by the substitution pattern (location of chlorine on different aromatic carbons). The estimated log octanol/water partition coefficient (log K_{ow}) for each congener is included. The toxic coplanar PCB congers are highlighted (Hawker and Connell, 1988; EPA, 2003).

Coplanar PCB congeners are of much greater environmental concern than non-coplanar congeners because of their substantially greater toxicity to mammals, birds, and fish (Van den Berg *et al.*, 1998). The chronic toxicity of coplanar PCBs and PCDDs/PCDFs is expressed through their ability to bind to and activate the aryl hydrocarbon receptor (AhR), which is a cytosolic ligand-activated transcription factor. Activation of this receptor leads to induction (stimulation of enzyme synthesis) of the cytochrome P450 (CYP) mixed function oxygenase system responsible for oxidation of many types of natural (*e.g.*, steroid hormones) and contaminant aromatic hydrocarbons (Safe, 1990). Intense induction of various CYP forms by PCBs and PCDDs/PCDFs may lead to alterations in hormone functions and production of toxic/carcinogenic metabolites. Coplanar aromatics, including PAHs, vary in their ability to bind the AhR receptor, which correlates with toxicity (Van den Berg *et al.*, 1998). Thus, the toxicity of different PCB, PCDD, PCDD, and PAH congeners can be ranked in relation to the most toxic congener, 2,3,7,8-tetrachlorodibeno-*p*-dioxin (TCDD) (Figure 3-1) and expressed as TEF (Table 3-4).

The two benzene rings of a coplanar PCB congener can orient in the same plane, a configuration similar to that of a PCDD or PCDF (see discussion below). Coplanar PCBs contain, at most, two chlorines in the *ortho* position on the biphenyl molecule (Figure 3-4). A PCB with three or four *ortho* chlorines cannot attain a coplanar configuration due to steric hindrance, a configuration essential for metabolic activation and degradation by most prokaryotes and eukaryotes. Coplanar PCB congeners include non-*ortho*, mono-*ortho*, and di-*ortho* congeners with zero, one, or two chlorines in *ortho* positions, respectively. There are four non-*ortho* PCB congeners (numbers 77, 81, 126, 169) and eight mono-*ortho* PCB congeners (numbers 105, 114, 118, 123, 156, 157, 167, 189) of major environmental concern (Tables 3-3 and 3-4). The toxicity of coplanar PCB congeners increases with the number of chlorines in *meta* and *para* positions. The most toxic coplanar PCB congeners (IUPAC Numbers 126 and 169) have chlorines in both *para* positions and at least two *meta* positions. As a rule, non-*ortho* PCB congeners are more toxic than mono-*ortho* congeners which, in turn, are more toxic than di-*ortho* congeners (Safe, 1990; Van den Berg *et al.*, 1998). However, mono- and di-*ortho* PCB congeners usually are more abundant than non-*ortho* congeners in environmental matrices because the latter are more biodegradable. Due to the substantially greater toxicity of coplanar PCB congeners (over non-coplanar), coplanar PCBs represent a much greater environmental risk to humans via direct exposure (*i.e.*, environmental abundance and access) (Parkinson and Safe, 1987; Safe, 1984; Pereira, 2004). Therefore, one focus on MNR investigations should be on monitoring the loss of non-*ortho* and mono-*ortho* coplanar congeners from PCB-contaminated sediments.

Table 3-4. Toxicity Equivalency Factors (TEFs) of PCDDs, PCDFs, Non-*Ortho*- and Mono-*Ortho*-PCBs, and Selected PAHs for Mammals from the World Health Organization (WHO) and Relative Potency of PAHs in Fish

Congener	TEF	Congener	TEF
Polychlorinated Dibenzo-*p*-dioxins (PCDDs)		**Polychlorinated Dibenzofurans (PCDFs)**	
2,3,7,8-TCDD	1	2,3,7,8-CDF	0.1
1,2,3,7,8-PentaCDD	1	12,3,7,8-PentaCDF	0.03
1,2,3,4,7,8-HexaCDD	0.1	2,3,4,7,8-PentaCDF	0.3
1,2,3,6,7,8-HexaCDD	0.1	1,2,3,4,7,8-HexaCDF	0.1
1,2,3,7,8,9-HexaCDD	0.1	1,2,3,6,7,8-HexaCDF	0.1
1,2,3,4,6,7,8-HepatCDD	0.01	1,2,3,7,8,9-HexaCDF	0.1
OctaCDD	0.0003	2,3,4,6,7,8-HexaCDF	0.1
		1,2,3,4,6,7,8-HeptaCDF	0.01
		1,2,3,4,7,8,9-HeptaCDF	0.01
		OctaCDF	0.0003
Non-*Ortho*-Polychlorinated Biphenyls (PCBs)		**Mono-*Ortho*-Polychlorinated Biphenyls (PCBs)**	
3,4,4′,5-TetraCB (81)	0.0003	2,3,3′,4,4′-PentaCB (105)	0.00003
3,3′,4,4′-TetraCB (77)	0.0001	2,3,4,4′,5-PentaCB (114)	0.00003
3,3′,4,4′,5-PentaCB (126)	0.1	2,3′,4,4′5-PentaCB (118)	0.00003
3,3′,4,4′,5,5′-HexaCB (169)	0.03	2′,3,4,4′,5-PentaCB (123)	0.00003
		2,3,3′,4,4′,5-HexaCB (156)	0.00003
		2,3,3′,4,4′,5′-HexaCB (157)	0.00003
		2,3′,4,4′,5,5′-HexaCB (167)	0.00003
		2,3,3′,4.4′,5,5′-HeptaCB (189)	0.00003
Relative Potency of Polycyclic Aromatic Hydrocarbons (PAHs) in Fish			
Phenanthrene	Inactive	Benz(a)anthracene	0.00020
2-Ethylphenanthrene	0.00001	Benzo(a)pyrene	0.00024
Fluoranthene	0.000000002	Dibenz(a,h)anthracene	0.00027
5-Methylchrysene	0.00065	Indeno(1,2,3-cd)pyrene	0.00188

IUPAC numbers are included in parentheses for PCBs (Van den Berg *et al.*, 1998, 2006; Barron *et al.*, 2004).

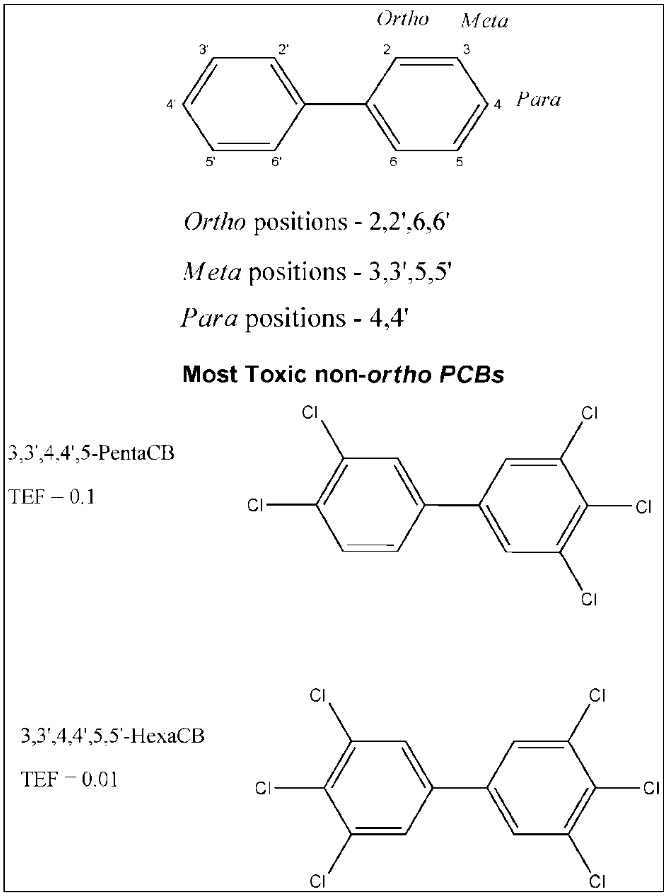


Figure 3-4. Positions of *Ortho, Meta,* and *Para* Carbons in PCBs (Structures of the two most toxic non-*ortho* PCBs are shown based on their TEFs, relative to the toxicity of 2,3,7,8-tetrachloro dibenzo-*p*-dioxin [Table 3-4].)

3.1.2.3 Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans. PCDDs/PCDFs are composed of two non-fused benzene rings. Unlike PCBs, the benzene rings are bound together by one (PCDFs) or two (PCDDs) ether linkages (-O-); the second linkage in PCDFs is a carbon-carbon bond. This creates a rigid molecular structure with the two aromatic rings on the same plane (coplanar configuration). As with coplanar PCBs, each PCDD/PCDF binds with a different affinity to the AhR receptor and, therefore, exhibits a different potency for eliciting biological effects (Safe, 1990; Ahlborg *et al.*, 1994; Van den Berg *et al.*, 1998). The potencies of the different PCDD/PCDF congeners can be normalized to that of 2,3,7,8-TCDD, the most toxic PCDD (Table 3-4). By convention, TCDD is assigned a TEF of 1.0, and the TEFs for other coplanar aromatic compounds with dioxin-like toxic effects range from 0 to 1. When TEFs are derived based on the relative binding affinity to the AhR receptor or induction of cytochrome P450, it is assumed that these biochemical responses correlate with toxicologically important effects (Van den Berg *et al.*, 1998). Coplanar PCDDs/PCDFs and PCBs bind to the specific AhR receptor in eukaryotes, inducing production of cytochrome P450 mixed function oxygenase (MFO) enzyme systems that oxidize aromatic HOCs to more polar, reactive products. The biodegradation products of PCDDs/PCDFs and coplanar PCBs are more toxic than the parent compounds, rendering the coplanar congeners more toxic than the non-coplanar congeners. Because PAHs also are coplanar, some bind weakly to the AhR receptor, inducing chytochrome P1A activity. The strength of binding to the AhR receptor determines the level of induction of MFO and the relative toxicity of the HOC. The most active PCBs and PAHs have TEFs one-tenth less than that of 2,3,7,8-TCDD.

PCDDs/PCDFs are not produced intentionally and have no commercial applications. They are produced as byproducts in the manufacture of other chlorinated chemicals, such as pentachlorophenol and defoliating herbicides, *e.g.*, Agent Orange (a 50:50 mixture of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid), during combustion or intensive chlorination of organic materials in the presence of chlorine (Brzuzy and Hites, 1996; Pereira, 2004). An important source of PCDDs/PCDFs in the environment is bleaching of wood pulp during paper manufacturing. Combustion processes are the major source of PCDD/PCDF emissions to the environment and the cause of the ubiquitous contamination of soils and sediments, with transport processes such as atmospheric dispersal from point sources representing the primary vector for PCDD/PCDF translocation in the environment (Rappe *et al.*, 1987; Brzuzy and Hites, 1996). Most of the PCDDs/PCDFs (typically more than 80%) produced during waste incineration are sorbed to soot particles (fly ash), which is released into the atmosphere unless the combustion gases are scrubbed or filtered (Yan *et al.*, 2007). PCDDs/PCDFs are released into the atmosphere adsorbed to fly ash in the combustion plume and can be transported over long distances; they are ultimately removed from the atmosphere by dry or wet deposition and accumulate in soils and sediments. The major combustion sources of PCDDs/PCDFs and the estimated annual mass emission rates are summarized in Table 3-5 (Brzuzy and Hites, 1996). Total annual global emissions to the atmosphere in 1996 were estimated to be 3,000 ± 600 kg, with the largest emission being from waste incineration. Estimated global deposition of PCDDs/PCDFs from the atmosphere to the land and ocean is 12,500 ± 1,300 kg/year and 610 ± 1,500 kg/year, respectively, for an estimated total global deposition of 13,100 ± 2,000 kg/year (Brzuzy and Hites, 1996). Estimated global deposition is about four-fold times higher than estimated global emissions, likely because emissions are underestimated, particularly for third-world countries.

Table 3-5. Estimated Average Emission Factors (Mass of PCDDs/PCDFs Released per Mass of Fuel Burned) and Total Annual Global Emissions of PCDDs/PCDFs to the Atmosphere from Combustion Sources

PCDD/PCDF Fuel Source	Emissions Factor (μg/g fuel burned)	Global Emissions (kg/year)
Municipal waste incineration	13.0	1130 ± 450
Biomass combustion	0.04	350 ± 140
Ferrous metals production	0.5	350 ± 140
Cement kilns (burning hazardous wastes)	2.6	680 ± 280
Cement kilns (no hazardous wastes)	0.2	320 ± 130
Secondary copper smelting	39.0	78 ± 31
Medical waste incineration	22.0	84 ± 35
Unleaded fuel combustion	320.0	1 ± 0.4
Leaded fuel combustion	2,800.0	11 ± 5
Total emissions		**3,000 ± 600**

Source: Brzuzy and Hites, 1996

3.2 Measuring Fate Processes and Natural Recovery

MNR relies on multiple lines-of-evidence to demonstrate reductions in the bioaccessibility and concentrations of bioavailable HOCs in sediments and the resulting long-term ecological recovery and risk reduction of the affected environment. Several lines-of-evidence should be considered in sediment investigations to support implementation of MNR as a remedy option, including (Magar and Wenning, 2006):

- Documentation and confirmation of source control;
- Evidence of contaminant burial (isolation) and reduction of surface sediment concentrations;
- Evidence of minimal numbers of macrofauna accessing buried, contaminated sediments (bioturbation);
- Measurement of surface sediment mixing, including sediment resuspension events (*e.g.*, floods and/or storm events) to estimate the active sediment benthic layer and determine the surface sediment depth to which remedial objectives should be applied;
- Measurement of sediment stability to assess the risk of contaminant resuspension under normal and high-energy events;
- Evidence of contaminant sequestration, transformation, and risk attenuation commensurate with reduced availability and decreased concentrations;
- Modeling of long-term trends for possible recovery scenarios under various conditions, as evidenced by decreasing concentrations of bioaccessible contaminant in surface sediments, the water column (or pore water), and local biota;
- Monitoring ecological recovery and long-term risk reduction; and
- Knowledge of future site and institutional controls, and a consideration of the risk due to degradation products and the presence of multiple stressors.

In the subsequent sections, focus will be placed on controlling sorption and sequestration of HOCs in sediment. Abiotic and biological transformation of sediment HOCs will also be described. Approaches for assessing HOC sorption, sequestration, and transformation will be discussed in detail.

3.2.1 Physical and Chemical Processes Affecting HOC Fates. It is critical to understand the conditions under which HOCs are bioavailable and the processes by which they become sequestered. To adequately plan and execute successful sediment remediation by MNR, it is essential to understand the principles of HOC fate and transport in sediments (and in the environment as a whole). These processes determine the mobility of HOCs in the aquatic environment and the conditions under which HOCs are bioavailable. An integral part of managing sediment sites contaminated with HOCs, such as PCBs, PCDDs/PCDFs, and PAHs, is estimating the biological risk as defined by the concentrations of mobile, potentially bioavailable forms of HOCs in sediment and selecting natural recovery goals that are protective of sediment-dwelling (benthic) organisms, aquatic life, wildlife, and human health. Fundamental to the selection of recovery goals is an understanding of the mechanisms by which receptors are exposed to bioavailable forms of HOCs.

Natural transformation, sequestration, and weathering of HOCs can contribute to risk reduction and recovery of fresh water and marine sediment ecosystems via contaminant removal, reduced access, detoxification, or reduction in bioavailability. Both biological (aerobic and anaerobic biodegradation) and abiotic chemical reactions (oxidation/reduction) are responsible for contaminant transformations. Sequestration usually is caused by strong sorption of HOCs to sediment organic phases, particularly high-surface area carbonaceous particles, occlusion in pore spaces of particles, and burial in poorly-irrigated, subsurface sediment layers that are inaccessible to surface- or sediment-dwelling biota (Qiu and Davis, 2004). Additionally, HOCs weather naturally after deposition in sediments, particularly in near-surface, aerobic layers. Weathering processes include evaporation, dissolution, diffusion, and dispersion upon discharge from the point sources (*i.e.*, diffusive and advective transport); abiotic oxidation/reduction; and microbial biodegradation (Neff, 1990; Magar and Wenning, 2006). The combined weathering processes can reduce the concentration and bioavailability of HOCs in sediment.

Bioavailability has three components: bioaccessibility, biological availability, and pharmacological availability (Semple *et al.*, 2004; Reichenberg and Mayer, 2006). Bioaccessibility and biological availability are the two components of bioavailability that are of greatest concern in MNR. A contaminant in sediment is bioaccessible if it is in a location in the environment where living organisms can come in direct contact with it either as dissolved (*e.g.*, in pore water), particulate (*e.g.*, sorbed to solids), or colloidal phases. Contaminants buried in deep sediment layers below the depth of bioturbation (which is not a static or well-defined layer and can range from millimeters to meters in depth) or that are tightly bound to sediment particles or large colloids (Cornelissen and Gustafsson, 2005; Hawthorne *et al*., 2007b) may be inaccessible to sediment-dwelling and water column animals.

A chemical has biological availability if it is in a form that can move through or bind to the external epithelia of an organism (*e.g.*, skin, gill epithelium, gut lining, or cell membrane) (Neff, 2002). The most bioavailable form of HOCs is the dissolved form; HOCs adsorbed to small colloids or weakly adsorbed to particles may be slightly less bioavailable. Bioavailable compounds can move through biological membranes in both directions passively, or they can be transported down physico-chemical gradients by enzyme systems. When an aquatic plant or animal is exposed to a non-polar organic chemical dissolved in the ambient water, the chemical partitions into tissue lipids until an equilibrium is reached (Davies and Dobbs, 1984; Bierman, 1990). The octanol/water partition coefficient (K_{ow}) for the chemical is used as a surrogate for a lipid/water partition coefficient because solubility of many non-polar organic compounds in octanol and biological lipids is similar and there are published values for K_{ow} for a large number of non-polar organic chemicals of environmental concern (Connell, 1993). Tables 3-3 and 3-6 contain estimated or measured log K_{ow} values for several PCB, PCDD/PCDF, and PAH congeners. At equilibrium, the rates of absorption into and desorption from the lipid phase of the plant or animal are equal. Active processes controlling bioconcentration include metabolic degradation of the HOCs to more water-soluble products that are easily excreted by the organism. Some aquatic animals (most crustaceans, fish, and higher vertebrates) can metabolize and excrete HOCs more rapidly than predicted by partitioning theory, resulting in lower than predicted equilibrium tissue concentrations.

3.2.2 Application of HOC Partitioning in Sediment to MNR. The first step in reducing bioaccessibility and bioavailability is to reduce the concentration of the dissolved contaminant in the aqueous phase. Dissolution increases the concentration in the aqueous phase by partitioning from the solid phase (*e.g.*, dissolution or desorption) and, thereby, increases the bioavailability of sediment HOCs. In contrast, in some instances, evaporation and the combination of abiotic and microbial degradation reduce HOC concentrations in sediments and associated pore waters, decreasing the amount of HOCs available for bioaccumulation by sediment-dwelling organisms. Therefore, an MNR evaluation should include an assessment of the long-term risk reduction that is achieved as a result of reduction in concentration and bioaccessibility of HOCs in sediment; these are achieved through natural burial (isolation), capping, and the combined weathering processes (Qiu and Davis, 2004; Magar and Wenning, 2006). Burial or capping of HOC-contaminated sediments is a common MNR strategy (Palermo *et al*., 1998; Brenner *et al*., 2004). However, contaminated sediment burial may not be required to achieve acceptable risk because contaminant binding, sorption, or partitioning to solid phases often is sufficient to sequester HOCs from the dissolved phase. Model predictions and empirical evaluations of partitioning of HOCs from aqueous to non-aqueous (*e.g.*, adsorbed/absorbed) in site-specific sediments is an essential line-of-evidence for MNR. An evaluation of HOC partitioning can provide an estimate of the risk-based allowable concentration of HOCs in sediments. For example, high-molecular weight PAHs, particularly those from combustion sources, can be tightly bound to particulate organic carbon (POC), particularly combustion soot carbon (Thorsen *et al.*, 2004), in sediment, which may result in a large reduction in their bioavailability to aquatic organisms (Neff *et al.*, 2005).

Contaminant sequestration in sediments contributes to the recovery of fresh water and marine sediment-associated ecosystems and reduces the health risk to wildlife and human receptors by reducing the biological accessibility and biological availability of in-place HOCs. Sequestration results from the sorption of HOCs to organic coatings on sediment mineral particles, organic particles, and organic colloids in sediment and the associated geochemical reactions with the sediment matrix and pore water. The most bioavailable and toxic forms of HOCs are in solution in sediment pore water or the overlying water column; sequestration of HOCs in sediment particles and colloids usually substantially reduces the bioavailability and toxicity of in-place HOCs (Qiu and Davis, 2004). This reduction in soluble forms of the contaminant reduces the concentration of dissolved HOCs in the aqueous phase and the efflux of bioavailable forms of HOCs from sediments into the overlying water column. However, this binding may also be responsible for diminished rates of contaminant degradation (Bressler and Gray, 2003).

The limiting step for accessibility of HOC contaminants to sediment-dwelling organisms usually is the rate of dissolution/desorption from sediment particles. HOCs that partition from sediment solids into sediment pore water may be subjected to diffusive and advective transport, which further dilutes the HOCs. The net effect of the combined weathering process is to generally reduce concentrations of the bioavailable forms of HOCs in site sediments - the first critical step in sediment recovery. On the other hand, weathering and transformation alone (in some instances) may not be sufficiently rapid to attain safe levels of certain HOCs, including higher molecular weight PCBs, PAHs, PCDDs/PCDFs, and organochlorine pesticides, in sediments in a reasonable amount of time. However, because of the strong sorption of high-molecular-weight HOCs to sediment TOC, there may be little risk associated with the presence of high-molecular-weight HOCs in sediment, whether or not they are buried by cleaner sediments.

3.2.3 Influence of Sediment-Water Partitioning on HOC Bioavailability. Burial and sorption to sediment solids and colloids decrease the bioaccessibility and bioavailability of HOCs. Sorption-desorption processes are one of the most important processes controlling the bioavailability of sediment-bound HOCs, such as PAHs, PCBs, PCDDs/PCDFs, and several highly non-polar organochlorine pesticides because these processes control the concentration of HOCs in solution in sediment pore water and overlying waters (Lamoureux and Brownawell, 1999; White *et al.*, 1999; Kraaij *et al.*, 2001; Kukkonen *et al.*, 2004). An understanding of sorption-desorption kinetics and how they affect HOC bioaccessibility and bioavailability, gained by gathering sufficient empirical HOC partitioning data for different types of sediments, is critical for predicting exposure to and ecological risks of sediment HOCs during MNR. The inherent uncertainty about the fractions of total sediment HOCs and their forms that are bioavailable is the key element in quantifying exposure in human health and ecological risk assessments that often are the basis for derivation of sediment quality criteria (EPA, 2003).

Due to their hydrophobic nature, non-polar organic chemicals, such as PAHs, PCBs, and PCDD/PCDFs, tend to have a strong affinity for phase boundaries, such as the surface microlayer of the water body and the surface of particles (Olsen *et al.*, 1982). They also have a high affinity for low-dissolved, colloidal, and solid organic phases in sediments. Because of the strong affinity of dissolved, non-polar organic chemicals for solid or liquid organic phases, they tend to partition from the water and sorb to available organic phases, such as tissue lipids of aquatic organisms, organic coatings on sediment particles, and organic particles and colloids (*e.g.*, humic materials and organic detritus) (Karickhoff *et al.*, 1979; Knezovich *et al.*, 1987).

The concentrations of dissolved HOCs in sediment pore water and the overlying water column are dependent on their relative affinities for inorganic and organic sediment and suspended particles, DOC, and the dissolved phase. HOCs introduced into fresh or marine water bodies in dissolved, particulate, and colloidal forms partition among the different phases according to their relative affinities for the different phases (Karickhoff *et al.*, 1979; Karickhoff, 1981; Neff, 2002).

The tendency for an HOC in solution to adsorb to suspended or deposited particles, a process that removes HOCs from solution in the aqueous phase and, therefore, limits bioavailability, can be expressed as a linear sediment-water partition coefficient, K_d. However, fresh water and marine sediments are an extremely heterogeneous mixture of different particle types and sizes. Because of this heterogeneity, the K_d for a particular HOC is widely variable, depending on the chemical composition and grain size of the sediment used for the K_d determination. Strongest adsorption is to organic coatings on inorganic and organic sediment particles and organic colloids. Therefore, some of this variability can be reduced by normalizing K_d to the concentration of TOC in the sediment (Karickhoff *et al.*, 1979; Karickhoff, 1981). The TOC-normalized partition coefficient, K_{oc}, can be calculated if the K_d and the weight fraction of TOC in sediment are known according to the following formula:

$$K_{oc} = K_d/f_{oc} \qquad \text{(Eq. 3.1)}$$

where f_{oc} is the fraction of organic carbon in the sediment. The value for K_{oc} can be estimated easily for a particular compound because it is correlated to the octanol/water partition coefficient, K_{ow} (Hansch and Leo, 1979), and the aqueous solubility (Karickhoff *et al.*, 1979) of the compound. There are published values for K_{ow} for a large number of HOCs of environmental concern (Chiou *et al.*, 1982; Connell, 1993; Schwarzenbach *et al.*, 2003; Mackay *et al.*, 2006). A regression of the log K_{ow} versus the log K_{oc} for non-polar organic compounds spanning a wide range of molecular weights yields a good linear correlation between the two partition coefficients (Karickhoff, 1981). The log K_{oc}/log K_{ow} regression of Karickhoff (1981) for PAHs has the form:

$$\text{Log } K_{oc} = 0.989 \log K_{ow} - 0.346 \qquad \text{(Eq. 3.2)}$$

EPA (2003) used a slightly different regression derived by Di Toro (1985) for estimating equilibrium partitioning sediment benchmarks (ESBs) for a large number of HOCs, including PAHs:

$$\text{Log } K_{oc} = 000028 + 0.983 \log K_{ow} \qquad \text{(Eq. 3.3)}$$

Farrington (1991) summarized several other regression equations for estimating log K_{oc} values of different types of HOCs from their log K_{ow} values. The linear relationship between K_{ow} and K_{oc} appears to be slightly different for different homologous series of PAHs, PCBs, and PCDD/PCDFs (Vowles and Mantoura, 1987). However, there is a reasonably good correlation between K_{ow} (and thus K_{oc}) and aqueous solubility for most PAHs, PCBs, and PCDD/PCDFs (Table 3-6).

The empirical or literature values of K_d, K_{oc}, and K_{ow} can be used to yield model predictions of the concentrations expected in the dissolved phase and subsequently estimate bioavailability, toxicity risk and the recovery time for HOC-contaminated sediments. Values for log K_{oc} can be used to predict leaching or partitioning of HOCs from sediment particles into sediment pore water and the overlying water column. Log K_{oc} and log K_{ow} values also can be used to predict the bioaccumulation and toxicity of HOCs to benthic marine animals, based on the equilibrium partitioning theory (Di Toro *et al.,* 1991; Di Toro and McGrath, 2001). HOCs with high log K_{oc} have low bioaccessibility because they are tightly bound to sediment organic matter (Qiu and Davis, 2004; Reichenberg and Mayer, 2006; Hawthorne *et al.*, 2007a; Burgess, 2009).

Table 3-6. Physical/Chemical Properties of Importance in Environmental Fate Estimations of Representative PAHs, PCBs, PCDDs, and PCDFs

Hydrophobic Organic Contaminant	Molecular Weight (g/mol)	Vapor Pressure (Pa)	Solubility (mg/L)	Log K_{ow} (unitless)
PAHs				
Naphthalene	128.2	36.8	31	3.37
2,6-Dimethylnaphthalene	156.2	9.27	1.7	4.31
Phenanthrene	178.2	0.113	1.1	4.57
Fluoranthene	202.3	8.7×10^{-3}	0.26	5.22
Chrysene	228.3	1.1×10^{-4}	9.0×10^{-3}	5.86
Benzo(a)pyrene	252.3	2.1×10^{-5}	4.0×10^{-3}	6.04
Dibenz(a,h)anthracene	278.4	9.1×10^{-9}	6×10^{-4}	6.75
PCBs				
2,2′-DichloroCB	223.1	0.428	1.2	4.65
3,3′,5,5′-TetraCB	292.0	2.0×10^{-3}	1.2×10^{-3}	6.48
2,2′,4,5,5′-PentaCB	326.4	3.6×10^{-3}	6.7×10^{-3}	6.38
2,2′,4,4′,5,5′-HexaCB	360.9	5.9×10^{-4}	8.6×10^{-4}	6.92
2,2′,3, 3′,5,5′,6,6′-OctaCB	429.8	$<1 \times 10^{-6}$	4.0×10^{-4}	7.24
DecaCB	498.7	$<1 \times 10^{-6}$	7.0×10^{-6}	8.18
PCDDs				
Dibenzo-*p*-dioxin	184.0	0.51	0.84	4.30
2-ChloroDD	218.5	0.10	0.28	5.00
2,7-DichloroDD	253.0	8.1×10^{-3}	4.0×10^{-3}	5.75
2,3,7,8-TetrachloroDD	322.0	1.2×10^{-4}	$2.0 \text{ x } 10^{-3}$	6.80
1,2,3,4,7-PentachloroDD	356.4	4.3×10^{-6}	$1.2 \text{ x } 10^{-3}$	7.40
1,2,3,4,7,8-HexachloroDD	391.0	1.5×10^{-6}	$4.0 \text{ x } 10^{-5}$	7.80
OctachloroDD	460.0	1.2×10^{-7}	$7.0 \text{ x } 10^{-7}$	8.20
PCDFs				
2,8-DichloroDF	237.1	1.5×10^{-2}	1.4×10^{-2}	5.44
2,3,7,8-TetrachloroDF	306.0	1.9×10^{-4}	$4.1 \text{ x } 10^{-4}$	6.10
2,3,4,7,8-PentachloroDF	340.4	1.7×10^{-5}	$2.4 \text{ x } 10^{-4}$	6.50
1,2,3,4,7,8-HexachloroDF	374.9	3.6×10^{-6}	$1.8 \text{ x } 10^{-5}$	7.20
OctachloroDF	443.8	1.0×10^{-7}	$1.2 \text{ x } 10^{-6}$	8.00

Data from Shiu *et al.*, 1988; Mackay *et al.*, 2006; Nakajoh *et al.*, 2006

3.2.4 Sorption to Organic Colloids. Organic colloids and suspended mixed-phase organic solids usually are present at higher concentrations in sediment pore water than in overlying water (Chin and Gschwend, 1992; Mackay and Gschwend, 2001). Organic colloids are particles, generally less than 0.1 to 0.2 μm in diameter, that pass through conventional filters and cannot be sedimented by centrifugation (Wells and Goldberg, 1991; Gschwend and Schwarzenbach, 1992). They usually are humic acids formed from biodegradation of natural terrestrial, fresh water, and marine plant materials (Chin and Gschwend, 1991, 1992). They represent most of the DOC in most fresh water and marine sediments.

Natural organic colloids in sediments and the water column have a high affinity for absorption and binding of HOCs (Wijayaratne and Means, 1984a,b). This association increases the apparent solubility and concentration of low-solubility HOCs in the water phase. Apparent solubility of HOCs tends to increase in sediment pore water as the concentration of DOC increases because the HOCs form non-covalent associations with hydrophobic domains within the DOC molecular framework (Raber *et al.*, 1998). Sorption of HOCs to colloids plays an important role in HOC fate and transport because HOC association with colloids: 1) behaves like dissolved solutes, facilitating advective transport in pore water; and 2) reduces the concentration of bioavailable HOCs in pore water, limiting exposure to sediment biota (EPA, 2003).

The significance of suspended colloid concentrations to HOC sorption dynamics is underscored by previous studies of sorption processes during the development of the equilibrium partitioning (EqP) theory. Gschwend and Wu (1985) showed that a large fraction of PCBs in sediment pore water was sorbed to colloidal materials and proposed that equilibrium partitioning models should include the colloidal phase for three conditions: purely dissolved, sorbed to non-settling particles or macromolecular colloids, and sorbed to settling solids. Others proposed models for estimating the distribution of HOCs among the aqueous phase solids of various compositions, such as humic substances and other organic polymers (Chin and Weber, 1989; McCarthy and Jimenez, 1985).

Other studies highlighted the importance of the nature of the colloidal material on sorption processes. For example, Chin and Gschwend (1992) measured organic carbon-normalized, colloid/water partition coefficients, $Koc_{colloid}$, for pyrene and phenanthrene and found that the values varied substantially between sediment samples collected from two different areas of Boston Harbor. The authors hypothesized that the difference in colloid-binding coefficients was due to differences in organic matter functional group characteristics in sediments from the two locations. $Koc_{colloid}$ for pyrene was substantially higher for the sample collected from the location where the sediment organic carbon phase contained a higher concentration of lipids. Thus, for pyrene the greater affinity for colloids could be explained either by sorption to colloidal lipids or to organic matter from the location where a greater degree of binding was observed. Therefore, the characteristics of the sediment organic fraction of the sediment are important for controlling HOC sorption and, consequently, HOC bioaccessibility.

McGroddy and Farrington (1995) measured concentrations of dissolved PAHs and PAHs sorbed to colloids in sediments from Boston Harbor and calculated sediment-water distribution coefficients. When PAHs are bound to the colloids in the water, the solid-water distribution coefficient is lower than a coefficient for a system with little or no colloids present because PAHs sorbed to the colloids contribute to the total PAH load measured in the water phase, rather than in the sediment phase. However, the authors found that K_d values in the Boston Harbor sediments were much higher than expected, despite the additional PAH load sorbed to colloids in the water, due to the presence of soot particles in the sediment that contain high relative concentrations of PAHs. Black carbon (combustion soot carbon) has a very high adsorption capacity for HOCs (discussed below). McGroddy and Farrington (1995) noted that the ratios of $K_{occolloid}$ to $K_{ocsediment}$ for pyrene were greater for samples collected at one location where there was greater anthropogenic activity and sediment lipid concentrations were higher. The $K_{occolloid}$ values for sediments from locations disturbed to a greater degree by anthropogenic activity and urban discharges, compared to remote locations where anthropogenic disturbance is not significant, contain colloidal material with a higher proportion of natural humic substances.

These studies collectively illustrate the importance of sorption processes of organic colloids, including the importance of functional group composition of the organic material of the colloids in HOC partitioning in sediments. However, this phenomenon is not limited to PAH distribution between sedimentary (aqueous), suspended (colloidal), and solid phases. For example, the concentration of total PCBs in pore water of heavily contaminated sediments from New Bedford Harbor, MA, increased with depth in the sediment core (Brownawell and Farrington, 1986). The concentrations of many of the higher-molecular weight, less soluble (typically those with greater chlorine content) PCB congeners exceeded the reported solubilities of CB isomer groups in a mixture of Aroclor in sea water. Profiles of DOC and PCB concentrations in sediment cores were similar, suggesting that PCBs were non-covalently associated with DOC molecules and/or colloids, thereby increasing their apparent or effective solubilities in sediment pore water. The PCB concentration profiles of interstitial water as a function of depth suggested a diffusional flux to the overlying water column.

Consideration of sorption to individual components within heterogeneous sorbent material is necessary to more adequately describe fate and transport of HOCs in sediments that frequently display non-linear sorption dynamics to organic carbon-rich sediment and sedimentary colloidal material. These studies show the important role that colloidal and dissolved organic matter (DOM) can play in governing HOC partitioning and sorption within sediments, and hence the large role they may have in determining the fate and transport of HOCs *in situ*. Thus, at sites where MNR is implemented, the potential for enhanced transport of HOCs, such as PAHs, PCBs, and PCDDs/PCDFs, due to sorption to more mobile colloids must be considered and addressed to ensure that best estimates are made for retention or movement of HOCs in the remediation site. To achieve this objective, a more comprehensive mechanistic understanding of HOC sorptive processes to sedimentary material must include interpretation of existing data via linear and non-linear modeling efforts.

3.2.5 Non-Linear and Non-Equilibrium Sorption. A fundamental assumption in using PAH ESBs and other regulatory guidelines that are based on EqP is that the dissolved, bioavailable HOC concentration is directly proportional to the concentration of HOCs sorbed to sediment organic matter (EPA, 2003). The organic matter-normalized linear EqP model was proposed decades ago and was corroborated by results from studies showing that the distribution of HOCs between soil or sediment organic matter and water could be treated similarly to the partitioning of HOCs between an organic solvent phase (octanol) and water (*i.e.*, the linear relationships between K_{ow}, K_{oc}, and K_d as defined above) (Lambert, 1968; Karickhoff *et al.*, 1979; Chiou *et al.*, 1983). However, the validity of the assumptions inherent in the EqP approach has been challenged based on the results of several field and laboratory studies.

An example of how the EqP model is used to establish cleanup criteria for PAH-contaminated sediment sites is found in EPA's *Procedures for the Derivation of ESBs for the Protection of Benthic Organisms: PAH Mixtures* (EPA, 2003). PAH ESBs are a function of the sum of the concentration of 34 individual PAHs or PAH congener groups in sediment, and concentrations below the benchmark are considered to be non-deleterious to benthic organisms in a given sediment environment. The ESB is estimated by calculating the concentration of total PAHs in sediment pore water that is in equilibrium with the critical body residue (CBR) of total PAHs in tissues of sediment-dwelling macrofauna in contact with the sediment. The CBR is the molar concentration of total PAHs in tissues that cause harmful effects by neutral narcosis (McCarty *et al.*, 1992). Equilibrium concentrations of total PAHs in bulk sediment, sediment pore water, and animal tissues may be predicted from partition coefficients between sediment and water and between water and animal tissues. Because dissolved PAHs are the most bioavailable form in sedimentary environments, and because most toxicity data are for PAHs in the dissolved phase, the final chronic falue (FCV) for total PAHs from the National Water Quality Criteria Guidelines is used as the toxicity endpoint for PAHs in sediment pore water at equilibrium. The FCV, usually reported as μg PAH/g sediment organic carbon, is defined as the concentration of PAHs in sediment that is protective of the presence of aquatic life. FCVs for 18 or 34 PAHs are summed to obtain a FCV for total PAHs. If the ratio of the measured concentration of total PAHs in sediment to the FCV is ≥1, a risk of toxicity of the PAHs to sediment biota exists.

A necessary part of an MNR evaluation is to understand the physical and chemical factors that cause differences between modeled and actual sediment-water distribution coefficients for HOCs. Sound scientific evidence is available to support the use of the EqP model to make predictive estimates of contaminant bioavailability for most situations (EPA, 2003). However, as previously acknowledged, the EqP model may not accurately represent actual sorption processes that are occurring in some situations. If the *in-situ* sorption processes are complex or not at equilibrium, the calculated exposures to HOCs may not be accurate descriptions of *in-situ* exposures and the use of EqP models may result in either overly or insufficiently protective sediment quality criteria. An evaluation of measured versus modeled concentrations of HOCs will help in determining whether the physical forms of the HOCs and physical/chemical conditions at a site are suitable for use of the EqP model to set remediation criteria and natural attenuation goals.

Sorption isotherms of various HOCs (*e.g.*, PAHs and PCBs) onto geologic substrates (*e.g.*, sediments or aquifer solids) were found to be non-linear in several studies (Miller and Weber, 1986; Ball and Roberts, 1991a; Weber *et al.*, 1991, 1992). In these investigations, it was observed that the ratio of sorbed HOC concentration to aqueous HOC concentration changed as a function of initial HOC concentration. Further, sorption of HOCs in environmental systems often does not reach equilibrium in time scales relevant to environmental fate and transport processes, and sorption must be described using non-equilibrium (*i.e.*, Freundlich) models, rather than strictly Langmuir-type sorption models that inherently assume finite sorption sites and, therefore, a linear relationship between initial aqueous phase concentration and observed adsorption (Ball and Roberts, 1991b; Brusseau *et al.*, 1991). These observations of non-linearity and non-equilibrium have been modeled primarily by describing various sorption heterogeneities in geosorbent material (*i.e.*, organic versus mineral phases) (Weber *et al.*, 1992; Brusseau *et al.*, 1991), often related to physico-chemical properties of the specific sorbent components with linear and non-linear and equilibrium and non-equilibrium sorption processes attributed differently to the various compartments of the geosorbent material under investigation.

Weber *et al.* (1992) proposed that sorption in any natural system is inherently dependent on many local sorption phenomena and that a distributed reactivity model is most appropriate. Investigations of non-linear and non-equilibrium sorption components have resulted in a few general concepts for explaining the observed results. These general types of models are described below and include intraparticle diffusion; intraorganic matter diffusion (IOMD); and a greater degree of irreversible sorption to “hard,” “condensed,” or “black” carbon (BC) sorbents. BC, synonymous with combustion soot, charcoal, coal particles and kerogens, or activated carbon (Fernandez and Brooks, 2003), is of particular significance to the discussion of non-linear and non-equilibrium sorption due to the high capacity of this material to irreversibly absorb significant quantities of HOCs, particularly on a mass-normalized basis. With the current available analytical techniques, the absolute amount of these materials is difficult to quantify in environmental matrices. These materials also defy molecular-level description of the sorptive surfaces. Weber *et al.* (1992) described and modeled the sorptive properties of these materials and hypothesized that sorption to BC is described by partitioning to two types of organic carbon domains, soft (or rubbery) and hard (or glassy). Sorption to soft carbon was characterized by equilibrium, linear partitioning, and sorption to hard carbon was characterized by non-equilibrium and non-linearity. Adsorption of HOCs to these organic matter domains is notoriously non-linear and irreversible, attributes that are credited to contaminant diffusion into particles, the organic matter matrix, and absorption into the glassy/rubbery domains of organic matter, all of which are affected by the composition of the native sedimentary organic matter and the extent of diagenetic alteration of the sorbent matrix. Accardi-Dey and Gschwend (2002) expanded on this premise by removing soft carbon from sediments by combustion, then measuring sorption. By accounting for absorption into natural organic matter (NOM) and adsorption onto BC, they were able to explain non-linear isotherms and the strong sorption of PAHs. At equilibrium, the overall solid-water distribution coefficient (K_d) could be calculated using:

$$K_d = f_{oc}K_{OC} + f_{BC}K_{BC}C_W^{\,n-1} \qquad \text{(Eq. 3.4)}$$

where f_{oc} is the weight fraction of organic carbon in the solid phase and K_{OC} is the organic carbon-normalized distribution coefficient for the compound of interest. C_w is the truly dissolved concentration,

f_{BC} is the weight fraction of BC in the solid phase, K_{BC} is the BC-normalized distribution coefficient, and n is the Freundlich exponent, appropriate for each PAH-BC combination of interest.

3.2.6 Intraparticle and Intraorganic Matter Diffusion. Wu and Gschwend (1986, 1988) and Ball and Roberts (1991b) proposed models in which HOCs diffuse radially within mineral solids to explain non-equilibrium sorption observed in earlier experiments. The general concept of these intraparticle sorption models is that dissolved HOC molecules within the pores of mineral grains diffuse in water from areas of high concentration to areas of low concentration. The rate of HOC diffusion is affected not only by those parameters that affect diffusion in water (*e.g.*, physical and chemical characteristics of the HOC molecules, water temperature, etc.), but also the sorption and steric properties (*e.g.*, hydrophobicity and size) of the HOCs and the tortuosity of the substrate. Their movement is retarded by sorption to mineral surfaces or steric hindrance as they move through the pores.

Hamaker *et al.* (1966) proposed IOMD to explain rate-limited sorption of organic chemicals. Brusseau and Rao (1989a, 1989b) and Brusseau *et al.* (1991) proposed IOMD as the rate-limiting sorption process to explain non-equilibrium partitioning. NOM has been described as a flexible, amorphous polymeric material into which HOCs diffuse. As studies have demonstrated how organic matter characteristics strongly affect sorption processes, the IOMD model was expanded to include two general types of organic matter matrices — an expanded amorphous or rubbery polyacetal domain and a condensed microcrystalline or glassy polystyrene domain (Weber and Huang, 1996; LeBoeuf and Weber, 2000; Xing and Pignatello, 1997; Weber and Young, 1997; Cornelissen *et al.*, 2000).

Weber and Huang (1996) proposed that natural soil and sediment sorbents could be modeled as consisting of three domains: a mineral nonporous domain; a condensed (hard, glassy) soil organic matter (SOM) domain; and an expanded, amorphous (rubbery) organic matter domain. They hypothesized that sorption within the condensed SOM is non-linear and that the rate is affected by sorbate concentration and also the SOM characteristics.

3.2.7 Enhanced Sorption to Black Carbon Sorbents. Additional levels of model sophistication have been invoked to explain observations of non-linear and non-equilibrium processes. In addition to intraparticle diffusion and IOMD, the extent of sorption to BC sorbents (defined above) has been identified as contributing to empirically observed sorption non-linearity based on the diagenetic state of the organic material. Early studies of sorption, such as those by Grathwohl (1990) and Weber *et al.* (1992), showed that the age characteristics of sorbent material significantly affect the extent, linearity, and reversibility of sorption. Grathwohl (1990) and Achten and Hofmann (2009) demonstrated that geologically older carbon sorbents, such as the organic matter in unweathered shale or anthracite (older) coal, have greater capacity to adsorb HOC contaminants than do SOM or bituminous (younger) coal. These results demonstrate an inverse relationship between the amount of oxygen-containing functional groups and sorption, suggesting a positive correlation between the degree to which SOM had undergone diagenesis and sorption strength. Furthermore, Weber *et al.* (1992) observed that sorption of 1,2,4-trichlorobenzene to "hard" or "glassy" carbon was mechanistically different from sorption to "soft" or "rubbery" carbon, the former showing non-linearity and the latter showing linear partitioning behavior.

McGroddy and Farrington (1995) expanded on insights from studies by Grathwohl (1990) and others regarding the importance of sorbent characteristics in predicting sorption behavior. The authors measured sediment and pore water PAH concentrations in sediment samples from three locations in Boston Harbor. They calculated K_{oc} values for several PAHs based on measured PAH concentrations in sediment pore water and found that the measured pore water concentrations were much lower than predicted by equilibrium partitioning models. In contrast, measured aqueous concentrations of PCBs with log K_{oc}s similar to those of the PAHs studied were in agreement with concentrations predicted by equilibrium partitioning models. Based on calculations of the fractions of phenanthrene and pyrene that were available for equilibrium partitioning (AEP), they hypothesized that PAHs from pyrogenic sources were preferentially associated with soot particles in sediments and were less AEP than PAHs from petrogenic sources or pyrogenic PAHs from liquid sources (*e.g.*, creosote). Thus, the source of PAHs deposited to sediments as well as the sorbents present in sediments will strongly affect how PAHs will be distributed among solid and aqueous phases (Neff *et al*., 2005). This distribution can affect the concentrations of bioavailable PAHs to which benthic organisms are exposed and also must be considered in establishing clean-up levels for a particular site.

3.2.8 Sorption of PAHs, Coplanar PCBs, and PCDDs/PCDFs to Black Carbon Sorbents. Strong and often nearly irreversible sorption of PAHs, PCBs, and PCDD/PCDFs to BC has been observed (Persson *et al*., 2002; Ghosh *et al*., 2003; Lohmann *et al*., 2005; Ghosh and Hawthorne, 2010; Werner *et al*., 2010). Most of the BC in sediments is combustion soot composed of irregular, microscopic carbon particles generated during combustion of organic matter. The presence of BC in sediments and its effects on HOC binding play a key role in PAH, coplanar PCB, and PCDD/PCDF fate and transport. PAHs are the HOCs that usually exhibit the strongest binding to BC (Readman *et al*., 1987; Broman *et al*., 1990), partly because they are generated during the formation of combustion soot and adsorb strongly to the soot particles as they cool (Fernandez and Brooks, 2003). Concentrations of pyrogenic PAHs and PCDDs/PCDFs in near-shore marine sediments often are closely correlated with the abundance of carbonaceous particles of soot, kerogen, and coal (Broman *et al*., 1990; Lohmann *et al*., 2002; Yunker *et al*., 2002; Achten and Hofmann, 2009), indicating that these HOCs remain associated with the particles after deposition and may not be extensively modified by photooxidation, dissolution, or biodegradation during transport in the air and water (Prahl and Carpenter, 1983; Readman *et al*., 1987). Readman *et al.* (1987) used a linear free energy sediment-water exchange model to simulate PAH partitioning and exchange of individual unalkylated (primarily pyrogenic) PAHs in the surface mixed layer of sediment and the overlying water column of the Tamar River Estuary, England. They showed that the concentrations of PAHs in the sediments are between two and five orders of magnitude higher than those expected from equilibrium partitioning with concentrations of PAHs in the associated water. Their observations indicated that most of the PAHs in the sediments were sequestered on BC and were chemically unreactive and resistant to abiotic transformations. Sorptive exchange with water and, therefore, bioavailability of PAHs to marine organisms appeared to be restricted by the existence of occluded and other micro-morphologically inert forms of particle-bound PAHs.

McGroddy *et al.* (1996) tested the hypothesis that only a fraction of PAHs in sediment is AEP. They measured desorption and equilibrium sediment and pore water concentrations, calculated the predicted aqueous concentrations based on existing equilibrium partitioning models, and compared their results to calculated AEP values. Previously established EqP models overpredicted the aqueous PAH concentrations. However, they found that by utilizing their equation for partitioning and the AEP values calculated from a previous study they could predict the aqueous concentration of PAHs. In contrast to PAHs, aqueous PCB concentrations were predicted well by the previous models. They concluded that the PAHs that were not AEP were released to the environment by pyrolysis of organic matter and were associated with the soot particles that were generated simultaneously. On a broader scale, they noted that PAHs and PCBs interact with sediment solids via fundamentally different geochemical mechanisms. It is important to note that the PCBs studied by McGroddy and Farrington (1995) and McGroddy *et al.* (1996), PCBs 101 and 138, were non-coplanar. As discussed below, the degree of coplanarity of compounds composed of benzene rings (PAHs, PCBs, and PCDDs/PCDFs) strongly affects sorption/desorption behavior.

Irreversible binding of PAHs to BC renders pyrogenic PAH assemblages that are chemically stable for long periods of time, especially after deposition in soil and sedimentary environments. Desorption of PAHs from carbonaceous particles is very slow as indicated by the low bioavailability and toxicity of pyrogenic PAHs in sediments to aquatic organisms (Cornelissen *et al*., 1998; Farrington and

Westall, 1986; Gustafsson *et al.*, 1997; Rust *et al.*, 2004; Thorsen *et al.*, 2004; Cornelissen and Gustafsson, 2005). Particle-bound PAHs in marine sediments near Norwegian and Canadian aluminum smelters (a source of PAH-rich soot particles) produce fewer adverse effects on local benthic communities than expected based on laboratory studies with dissolved PAHs (Knutzen, 1995; Paine *et al.*, 1996). The PAHs in effluents from aluminum smelters are pyrogenic and tightly bound to soot particles; they have limited bioavailability to marine organisms (Naes *et al.*, 1998).

An important aspect of understanding and quantifying the role of soot in HOC sorption is the quantification of soot in soils and sediments. Gustafsson *et al.* (1997) developed a method for quantifying soot in sediments. The method involves removing organic carbon by thermal oxidation, removing inorganic carbonates by acidification, and measuring the remaining BC using carbon, hydrogen, and nitrogen elemental analysis. The authors proposed that previously measured large K_{oc} values for PAHs in sediment could be explained by the partitioning of HOCs to high-affinity sorption sites of the measured concentrations of BC particles, as evidenced by approximations of BC-water partition coefficients (K_{BC}s) that were obtained from studies of PAH sorption to activated carbon. By measuring PAH, organic carbon, and BC concentrations in sediments, Gustafsson and Gschwend (1997) found that PAH sorption correlated strongly with BC. They also calculated K_{BC}s and hypothesized that PAH interactions with BC were similar to interactions with activated carbon. The authors suggested that there may be π-π bond interaction between planar HOCs and sorbents with a significant aromatic ring structure such as BC.

Gillette *et al.* (1999) showed that the concentration of PAHs on particles at the microscale could be measured directly in a 40-µm diameter spot in the sample by microprobe laser desorption/laser ionization mass spectrometry. In the past, studies of HOC sorption to geosorbents had to rely on observations at the particle macro-scale. Ghosh *et al.* (2000) demonstrated that the majority of PAHs in Milwaukee Harbor sediments are sorbed to the wood/coal fraction of sediment, though these types of particles only comprise a small fraction of the total sediment mass. They used these mass spectral measurements of PAHs on BC particles to demonstrate that PAHs are concentrated primarily on the outer few microns of the coal-derived particles. Their data indicated that the concentrations of PAHs were highest in patches of organic matter on sediment particles. This was the first particle-scale direct observation of the association of HOCs with organic matter in specific locations on sediment particles and provided a detailed view of how PAHs sorb to these types of particles.

Ghosh *et al.* (2000) also investigated the kinetics of desorption from the two general classes of particles studied: more dense mineral particles, such as clay and sand; and less dense organic particles, such as wood and coal-derived particles. They showed that PAHs desorbed from the less dense fraction (*e.g.*, wood and coal-derived particles) more slowly than from the denser mineral fraction. Higher activation energies were associated with PAH binding to coal-derived particles than with binding to clay/silt particles (Ghosh *et al.*, 2001). Furthermore, Cornelissen *et al.* (2000) demonstrated rapid desorption from linearly sorbing organic matter, but slow desorption from non-linearly sorbing sites based on the nature of the non-covalent interactions between the condensed (glassy, more dense) and amorphous (rubbery, less dense) domains of the organic sorbent material. These results have important implications for MNR because desorption is an integral part of HOC fate and transport in sediments. For example, if site sediment is likely to have significant amounts of coal- or soot-derived BC particles, PAHs present in the sediment probably are less bioavailable for uptake by benthic organisms than if the PAHs were associated with mineral phases in sediments (Cornelissen and Gustafsson, 2005; Neff *et al.*, 2005). Thus, higher sediment PAH concentrations may be acceptable due to the lower associated bioaccessibility and risk.

These studies emphasize irreversible binding of PAHs to low density organic particles found in sediment. However, PAHs (and also PCDDs/PCDFs) can be associated with BC particles beginning with their release to the environment at their point of origin. BC is produced during the incomplete combustion of organic matter. Combustion produces a variety of PAHs that escape with the smoke or exhaust gases and condense onto the BC particles as they cool (Neff, 1979). PCDDs/PCDFs produced by combustion of organic matter in the presence of high concentrations of chlorine also are released to the environment in the combustion gases and tend to condense on BC particles in the exhaust plume as it cools. These PAHs and PCDDs/PCDFs are entrapped in the aromatic matrix of the BC particles. PAHs in the fuel or those produced during combustion are entrapped in BC particles released to the environment. Therefore, a feasible explanation for observations of a strong PAH association with coal-derived particles and BC is co-generation in addition to strong sorption mechanisms.

In contrast to the situation with PAHs and PCDDs/PCDFs, PCBs rarely are produced or released during combustion of wastes. Because of the aromatic structure, large surface area, and high K_{oc} of BC, BC particles deposited in fresh and marine water bodies scavenge dissolved PAHs, PCBs, PCDDs/PCDFS, and other HOCs from the water or sediments (Ghosh *et al*., 2003; Lohmann *et al.*, 2005). The PAHs and PCDDs/PCDFs that condense on the cooling BC in the combustion gases and the HOCs that adsorb to the BC particles in the environment are tightly bound to the BC particles and are deposited in soils and sediments. Aerial deposition of BC to the Laurentian Great Lakes ranges from 0.02 to 0.89 mg/m^2/year, representing annual mass loadings of BC that range from 2.3×10^3 tons onto Lake Superior to 420×10^3 tons onto Lake Michigan. Only 0.01%, on average, of the total mass of PAHs in the lakes is adsorbed directly from the water phase (Buckley *et al.*, 2004). Because of their lower aqueous solubility and higher K_{oc}s, even less PCDDs/PCDFs associated with sediment BC is adsorbed from the water phase. However, PCBs associated with sediment BC are adsorbed from dissolved and particulate phases in the water. Thus, much of the pyrogenic PAHs, PCDDs, and PCDFs are tightly bound to the particulate BC phase and have low accessibility and bioavailability to sediment-associated organisms. PCBs are less tightly bound to sediment organic phases and may be more mobile in sediments and water.

Accardi-Dey and Gschwend (2003) proposed a new method for describing the distribution of HOCs between water and sediment solids that contain relatively high concentrations (a few percent TOC) of BC. They proposed that, by accounting for the presence of BC sorbents (using the BC-normalized distribution coefficient, K_{bc}) in addition to K_{oc}, they could quantify PAH distribution between water and particulate phases. Lohmann *et al.* (2005) estimated K_{bc} values for other PAHs, PCBs, and PCDDs in Boston and New York Harbor sediments based on K_{bc} values for pyrene and phenanthrene calculated by Accardi-Dey and Gschwend (2002) and Accardi-Dey and Gschwend (2003), respectively. K_{bc} values for most HOCs were one order of magnitude or higher than the corresponding K_{oc} values.

Bucheli and Gustafsson (2000) measured K_{bc} for PAHs using diesel particulate matter as a model BC sorbent. The K_{bc} values calculated were some of the highest solid-water distribution coefficients ever measured and were up to 250 times higher than predicted K_{oc} values. Their results provided additional evidence to support the hypothesis that sorption to BC is a probable explanation for the extensive and often irreversible PAH sorption in sediments shown in previous studies. Hawthorne *et al.* (2007b) measured K_{oc} and K_{bc} for parent and alkylated PAHs in more than 100 historically contaminated sediments (mainly at manufactured gas plant [MGP] sites). Both K_{oc} and K_{bc} values varied by up to three orders of magnitude for individual PAHs in sediments containing 0.3 to 42% by weight TOC, 0.1 to 30% BC, and total PAH concentrations (16 priority pollutant parent PAHs) from 0.2 to 8,600 μg/g. PAH partitioning in sediment was not explained more clearly by the combined K_{oc} and K_{bc} partitioning models than by the K_{oc} model alone. This was unexpected because log K_{bc} was larger than log K_{oc} for all PAHs in all sediments (Table 3-7). The fraction of TOC in sediment that is BC determines the effects of PAH sorption to BC in modeling PAH partitioning in sediments. Evidence from several recent studies suggests that sorption of HOCs in soils and sediments occurs as absorption within amorphous organic matter (AOM) and adsorption to BC. Strong sorption to BC leads to: 1) solid-water distribution coefficients higher (by up to two orders of magnitude) than what would be expected based upon sorption to AOM; 2) lower-than-expected bioavailability of HOCs to sediment-dwelling organisms, including the microbiota responsible for HOC biodegradation in sediments; and, as a result, 3) much slower-than-expected biodegradation of sediment HOCs (Cornelissen *et al.*, 2005).

3.2.9 Partitioning of PAHs from Sediment NAPL. Petrogenic PAHs from petroleum and pyrogenic PAHs from creosote and coal tar in sediments may be complexed with the colloidal and particulate organic fractions of sediment. Additionally, PAHs can be associated with a NAPL, such as petroleum or coal tar, or an oil coating on sediment particles. PCBs also may be present in sediment in an oil-like NAPL phase, *e.g.*, the mixtures of different chlorinated biphenyls in commercial PCB mixtures (Table 3-2), such as Aroclor 1254, a viscous liquid. Since the affinity of PAHs and PCBs is higher for the NAPL phase than for the sediment NOM and sediment pore water phases, but probably not for the sediment BC phase, partitioning of PAHs or PCBs into solution in sediment pore water is controlled primarily by the affinity of the HOCs for the NAPL phase (Eisenhut *et al.*, 1990; Neff *et al.*, 2005). No information is available regarding the partitioning of HOC between NAPL and BC phases. The rate of partitioning of HOCs from NAPL to sediment pore water phases is dependent on the relative surface area of contact between the water and NAPL, the viscosity of the NAPL (which controls diffusion within the NAPL layer), and the NAPL/water partition coefficients for the different HOCs. Thus, in estimating the partitioning of PAHs or PCBs between the NAPL phase (petroleum, coal tar, creosote, and Aroclor) and the dissolved phase, PAH and PCB concentrations should be normalized to some measure of total organic matter in the NAPL.

The PAHs in sediment NAPLs are distributed among the dissolved (pore water), NAPL, and sediment organic carbon phases of the sediment in accordance with their relative affinities for the three phases. This distribution between the NAPL and water phases can be described by an oil/water partition coefficient (K_{oil}) (Lee *et al.*, 1992a, 1992b), and the distribution between sediment organic carbon and water can be described by K_{oc} as discussed above. The K_{oc} for most HOCs and colloidal-particulate organic matter in sediments is lower than the K_{ow} (Karickhoff, 1981; Di Toro *et al.*, 1991), whereas the K_{oil} for PAHs in most crude and refined petroleum products and liquid coal tars and creosote is about the same as or higher than the K_{ow} and tends to increase with average molecular weight of the NAPL material (Shiu *et al.*, 1990; Lee *et al.*, 1992a, 1992b).

Use of K_{ow}, K_{oc}, and K_{oil} to make predictive estimates of HOC partitioning behavior tends to overestimate concentrations of dissolved PAHs in pore water for sediments that are contaminated primarily with pyrogenic PAHs. However, partition coefficients can provide a reasonable upper-limit estimate of dissolved phase PAHs in pore water of petroleum-, creosote-, or coal tar-contaminated sediments if the oil or other NAPL phase is still liquid and in physical contact with sediment pore water (Pope *et al.*, 2010). The NAPL, particularly if it is crude oil or coal tar, may develop a surface “skin” of resins-asphaltenes or other high-molecular-weight polar compounds, decreasing NAPL/water partitioning (Nelson *et al.*, 1996). When pore spaces are filled with NAPL or oil, the permeability of the sediment may be substantially decreased, thus decreasing the effective NAPL/water interface and limiting accessibility of the PAHs to partitioning into sediment pore water. Site-specific, empirically-determined K_d values (particle-water partition coefficients) may be best for estimating sediment-water partitioning of pyrogenic PAHs or PAHs from weathered crude oil.

Neff *et al.* (2006, 2011) observed that bioavailability to intertidal animals of PAHs from subsurface deposits of weathered North Slope crude oil in shoreline sediments 12 years after the *Exxon Valdez* oil spill was negligible. The PAHs in the oil, which had persisted buried in shoreline sediments for 12 years after the spill, were observed to be immobile and have low bioaccessibility (Boehm *et al.*, 2007).

Thorsen *et al.* (2004) measured the bioavailability of sediment PAHs to benthic animals as the biota sediment accumulation factor (BSAF: lipid-normalized PAH concentration in tissue/sediment organic carbon-normalized PAH concentration in sediment). BSAF values for petrogenic PAHs were greater than those for pyrogenic PAHs, indicating that the petrogenic PAHs were more bioavailable than the pyrogenic PAHs in sediments. Bioavailability of pyrogenic PAHs in sediment decreased with increasing BC concentration in sediments, but bioavailability of petrogenic PAHs in sediment was not affected by BC concentration, indicating that pyrogenic PAHs, but not petrogenic PAHs, were strongly sorbed to BC.

Table 3-7. Mean Measured log K_{oc} and log K_{BC} Values for PAHs in More than 100 Historically Contaminated Sediments Containing 0.2 to 8,600 μg/g Dry Weight Total PAHs

Polycyclic Aromatic Hydrocarbon	Measured Log K_{oc}	Measured Log K_{bc}
Naphthalene	3.02	4.73
2-Methylnaphthalene	3.36	5.03
1-Methylnaphthalene	3.16	4.76
C2-Naphthalenes	3.63	4.84
C3-Naphthalenes	3.33	4.85
C4-Naphthalenes	3.34	4.93
Acenaphthylene	4.02	5.54
Acenaphthene	3.37	4.89
Fluorene	3.65	5.17
C1-Fluorenes	3.94	5.23
C2-Fluorenes	3.67	5.25
Phenanthrene	4.18	5.65
Anthracene	4.60	6.20
C1-Phenanthrenes/Anthracenes	4.38	5.79
C2-Phenanthrenes/Anthracenes	4.64	6.04
C3-Phenanthrenes/Anthracenes	4.74	6.31
C4-Phenanthrenes/Anthracenes	4.77	5.84
Fluoranthene	4.74	6.28
Pyrene	4.70	6.32
C1-Fluoranthenes/Pyrenes	4.75	6.46
Benz(a)anthracene	5.48	7.03
Chrysene	5.50	7.08
C1-Chrysenes	5.49	7.30
Benzo(b+k)fluoranthenes	5.87	7.39
Benzo(e)pyrene	5.53	7.17
Benzo(a)pyrene	5.68	7.22
Perylene	5.88	7.25
Indeno(1,2,3-cd)pyrene	6.41	8.17
Dibenz(a,h)anthracene	6.13	7.37
Benzo(ghi)perylene	6.11	7.73

Source: Hawthorne *et al.*, 2007b

3.2.10 Physical/Chemical Transformation

3.2.10.1 HOC Dissolution and Evaporation. Aqueous solubilities of PAHs, PCBs, and PCDDs/PCDFs are low and decrease with increasing molecular weight (Table 3-6). Solubility also decreases with decreasing ambient temperature and increasing salinity or dissolved solids concentration (Doucette and Andren, 1988; Eastcott *et al.*, 1988; Shiu *et al.*, 1988; Abrajano *et al.*, 2005). Single-phase fresh water solubilities of HOCs, such as those listed in Table 3-6, represent the theoretical maximum aqueous phase concentration of HOCs in sediment pore water at 25°C and ionic strength less than 0.5M without DOC.

Most HOCs have a low volatility and do not readily evaporate from sediment or water. Evaporation of HOCs from subsurface sediments is slow and is not a significant route of HOC loss from contaminated fresh water and marine sediments. Most of the available information on evaporation of HOCs is for hydrocarbon evaporation from slicks of spilled oil on the water surface (Neff, 1990).

Compounds in petroleum that boil at temperatures below about 250°C, or have vapor pressures greater than about 0.1 mm Hg (13.3 Pa), tend to evaporate rapidly from the surface of the oil. Included in this category are alkanes from methane to *n*-dodecane and aromatics from benzene through naphthalene (Bobra *et al.*, 1979). All PCB and PCDD/PCDF congeners have vapor pressures below 1 Pa (Table 3-6), indicating their low volatility. The evaporation rates of different HOCs are directly proportional to their vapor pressures (Table 3-6), which are inversely proportional to their molecular weights (Mackay and Leinonen, 1975). A Canadian mid-weight crude oil exposed to the air and flowing water at low light intensity for 24 days lost all *n*-alkanes up through C_{10} and all monoaromatic hydrocarbons (Wang and Fingas, 1995). Evaporation of 44.5% of the oil mass resulted in a loss of 52% of the total naphthalenes and 5.7% of the total fluorenes. Less than 1% of the total phenanthrenes, dibenzothiophenes, and chrysenes were lost by evaporation. Thus, light aliphatic and aromatic hydrocarbons up to at least dodecane and methylnaphthalene readily evaporate from deposits of petroleum products on the water surface or on soils and sediments. Evaporation from buried oil deposits is much slower and depends on the diffusion rate in the sediments (which is a function of porosity and concentration gradients).

Low-molecular-weight saturated and aromatic hydrocarbons in air remain primarily in the gas phase and do not adsorb to a significant degree to airborne particles (Dickhut and Gustafson, 1995a, 1995b; Gundel *et al.*, 1995). Gas phase aromatic hydrocarbons are degraded rapidly by photolysis (Atkinson and Arey, 1994). For example, naphthalene reacts rapidly with atmospheric hydroxyl radical and has an atmospheric lifetime of approximately 8 hours. However, some of the photolytic reactions of PAHs in the atmosphere produce mutagenic products (Atkinson and Arey, 1994). Mutagenic products of PAH photooxidation in the atmosphere include 2-nitronaphthalene, 3-nitrofluorene, and 2-nitrobenzopyranone.

Very little HOCs evaporate from contaminated sediments. However, the presence of a wide variety of low-molecular-weight PAHs and less chlorinated PCBs in the vapor phase of the atmosphere indicates that some HOCs do transfer to the atmosphere in the form of vapor or particulate- or aerosol-associated contaminants (Eitzer and Hites, 1991; Gigliotti *et al.*, 2000; Su *et al.*, 2007). A strong inverse relationship exists between temperature and the vapor pressure of HOCs. Thus, the rate of evaporation of volatile hydrocarbons from NAPL on the sea surface, dispersed oil in the water column, or in shoreline sediments increases sharply as the temperature of the NAPL increases (Reijnhart and Rose, 1982; Edgerton *et al.*, 1987). Super-cooled liquid vapor pressures from the liquid phase of most PAHs, PCBs, and PCDDs/PCDFs are much lower than 10 Pa at 25°C (Table 3-6). However, PAHs with molecular weights up to that of pyrene are volatile enough that a significant fraction of the total PAHs may be present in the vapor phase of a combustion plume (Gundel *et al.*, 1995) or in the atmosphere. The concentration of total PAHs (36 measured) in the vapor and particulate fractions of air samples from Sandy Hook, a coastal community in New Jersey, are 2.8 to 42 ng/m^3 and 0.15 to 4.0 ng/m^3, respectively (Gigliotti *et al.*, 2000). The most abundant PAHs in the vapor phase are phenanthrene and alkylphenanthrenes. The higher-molecular-weight PAHs that are produced by flame pyrolysis are associated primarily with the BC particulate fraction (Dachs and Eisenreich, 2000). PAHs with molecular weights lower than that of phenanthrene are present in the winter primarily in the vapor phase of arctic haze over northern Canada and Russia; higher-molecular-weight PAHs are bound to BC particles (Halsall *et al.*, 1997).

PCBs and PCDDs/PCDFs, despite their very low vapor pressures, do evaporate in small amounts from water, soils, and sediments (Eitzer and Hites, 1989; Bobet *et al*., 1990; Su *et al.*, 2007). Su *et al.* (2007) measured 0.006 to 0.15 ng/m^3 total PCBs in air over forested and cleared land in southern Ontario. Higher concentrations have been recorded in air samples collected at heavily-contaminated segments of the Snake River. These PCBs probably are derived from evaporation from the soil or water surface. PCDDs/PCDFs enter the air primarily in emissions from incomplete combustion of municipal and chemical wastes (Table 3-5) (Brzuzy and Hites, 1996; Friesen *et al.*, 1996; Hites, 1990). Because of the steep decrease in vapor pressure with increasing chlorination, only the lower chlorinated congeners persist in the vapor phase when the combustion gases cool.

In air, the lower chlorinated PCDDs/PCDFs in the vapor phase are removed from the atmosphere primarily by photodegradation with an estimated half-life in hours (Koester and Hites, 1992; Mackay *et al*., 2006). Particle-bound and vapor-phase higher chlorinated PCDDs/PCDFs photolyze more slowly in the atmosphere, with air residence times of 1 to 3.7 days for some PCDDs/PCDFs (Kwok *et al*., 1995). Harrad (1996) reported average concentrations in British urban air samples of 6.1×10^{-6} ng/m^3 of 2,3,7,8-TCDD (the most toxic PCDD), 3.3×10^{-5} ng/m^3 of 2,3,7,8-TCDF, and 0.11 ng/m^3 of 2,2′,5,5′-tetrchlorobiphenyl. Nearly 100% of total PCDDs/PCDFs in the United Kingdom are in soil (99.5%) and the top 5 cm of fresh water sediments (0.45%). Thus, much of the PCBs and PCDDs/PCDFs in the atmosphere are derived from combustion emissions and evaporation from soil, surface waters, and sediments. The atmospheric HOCs are distributed between the vapor and particulate phases in the air, with higher concentrations of lower-molecular-weight HOCs than higher-molecular-weight HOCs in the vapor phase.

Sediments act as reservoirs from which PAHs, PCBs, and PCDDs/PCDFs are slowly released to water via desorption. In water, HOCs can be removed by photodegradation to oxygenated products or less chlorinated derivatives and/or slow anaerobic/aerobic biodegradation with a half-life time in days (Travis and Hattemer-Frey, 1987).

3.2.10.2 Electrophilic Substitution. PAHs, PCBs, and PCDDs/PCDFs are extremely stable in the environment. However, they can undergo three chemical reactions: electrophilic substitution, oxidation, and reduction. For many years, it was thought these reactions could occur abiotically (in the absence of metabolic reactions of living organisms). However, there is growing evidence that abiotic chemical transformation, except photolysis, of organic compounds usually occurs at extremely slow rates, but can contribute to destruction or alteration of contaminants over years or decades, rates probably too slow for MNR. However, most of these chemical transformation reactions also can be catalyzed by metabolic activity of microorganisms in water, soils, and sediments (Vogel *et al*., 1987). Microbially-mediated chemical reactions usually are much faster than the corresponding abiotic reactions.

Electrophilic substitution reactions involve exchanging a hydrogen atom on the organic molecule for a substitute functional group (or alternative electron-rich nucleophile). These substitution reactions include hydrolysis reactions, conjugation, and other functional group substitutions. Hydrolysis is a chemical reaction occurring between an organic chemical and water or a hydroxide ion in the following manner:

$$\text{R-X} + \text{H}_2\text{O} = \text{R-OH} + \text{H}^+ + \text{X}^- \qquad \text{(Eq. 3.5)}$$

$$\text{R-X} + \text{OH}^- = \text{R-OH} + \text{X}^- \qquad \text{(Eq. 3.6)}$$

Substitution reactions are generally of the following form:

$$R\text{-}X + Nu^- = R\text{-}Nu + X^- \qquad \text{(Eq. 3.7)}$$

where Nu is a nucleophilic group such as HS^{-1}. Microbially-mediated electrophilic substitution reactions usually are orders of magnitude more rapid than abiotic reactions under most physical/chemical conditions in water and sediments (Vogel *et al.*, 1987).

3.2.10.3 Oxidation/Reduction. Because oxidation and reduction reactions require removal or addition of electrons, external electron acceptors or donors must be present in the reacting system. For example, carbon atoms in hydrocarbons are in a reduced state and tend to undergo oxidation reactions such as hydroxylation, halosyl oxidation, and epoxidation. Substituting halogen atoms for hydrogen atoms effectively increases the oxidation state of the carbon, so highly halogenated organics are more susceptible to reduction reactions such as hydrogenolysis, dihalo-elimination, and coupling.

Reduction processes of common inorganic electron acceptors in environmental systems (*i.e.*, oxidizing agents) include reduction of O_2 to H_2O, nitrate to nitrite, SO_4^{-2} to HS^{-1}, and $2H^+$ to H_2. Oxidative processes of inorganic electron donors (*i.e.*, reducing agents) that are commonly available in the environment include oxidation of H_2 to $2H^+$ and Fe^{+2} to $Fe(OH)_3$. Oxidation or reduction of organics can be carried out directly or catalyzed by microorganisms. Microbial mediated reactions typically occur at higher rates than abiotic oxidation or reduction reactions.

PCDDs and PCDFs are chemically stable and not likely to be degraded at significant rates by abiotic hydrolytic reactions under environmental conditions. Juttner *et al.* (1997) detected similar concentrations of PCDDs/PCDFs at all levels in dated lake sediments dating back to the 17th century, implying that little degradation occurred following burial in anoxic sediment layers.

3.2.10.4 Photooxidation. Abiotic photolysis is an effective and sometimes rapid mechanism of degradation of PAHs, PCBs, and PCDDs/PCDFs in the air, surface waters, or deposits on the surface of near-surface sediments (Atkinson, 1991; Neff, 2002; Pereira, 2004). PCDDs in soils and shallow-water surface sediments appear to be resistant to photochemical degradation (Crosby *et al.*, 1971). Photolytic half-lives of PCDDs/PCDFs in surface waters range from 1 to 225 days in winter and up to 550 days in surface sediments (Atkinson, 1991). PCBs and PAHs adsorbed to quartz sand and spiked into several moist soils in the presence of a TiO_2 catalyst were photooxidized rapidly when the soil was exposed to sunlight (Krauss and Wilcke, 2002). Adsorption to SOM inhibited photooxidation. These studies show that PCBs in surface layers of sediments may be degraded by photooxidation.

Photolysis is the most important degradation mechanism of gas phase PCDDs/PCDFs in the atmosphere (Deriziotis, 2004). Photolysis rates are highest for the less chlorinated congeners and decrease with increasing chlorination (Orth *et al.*, 1989). The photolytic half-lives of TCDD and octachlorodibenzodioxin (OCDD) were 0.4 to 17 hours and 6.8 to 82 hours, respectively, depending on light intensity (Pennise and Kamens, 1996). Atmospheric PCDDs/PCDFs adsorbed to airborne particles, particularly soot, are resistant to photolysis (Kwok *et al.*, 1995).

The estimated atmospheric lifetime of vapor-phase PAHs and their photooxidation products ranges from 1.3 hours for anthracene to 2.7 days for 1-nitronaphthalene (Atkinson and Arey, 1994). Photodegradation rates of different PAHs vary widely; degradation rates may depend on concentrations of PAHs and photosensitizers in the oil, and on the physical form of the PAH assemblage (Mill *et al.*, 1981; Valerio and Lazzarotto, 1985). PAHs bound to soot particles are less sensitive than dissolved PAHs to photooxidation (Valerio and Lazzarotto, 1985; Kamens *et al.*, 1988). Most dissolved alkyl-PAHs and heterocyclic compounds are more sensitive to photolysis than are the parent, unalkylated compounds

(Ehrhardt *et al.*, 1992). High molecular weight four- through six-ring PAHs tend to be most sensitive to photooxidation (Mill *et al.*, 1981). The sensitivity of PAHs in solution to direct photolysis increases with increasing molecular weight. For example, the half-life of naphthalene (MW 128.2 daltons) in surface fresh water in sunlight equivalent to 40ºN latitude in mid-summer is 61 hours, compared to a half-life of 8 hours for phenanthrene (MW 178.2 daltons) and 0.54 hours for benzo(a)pyrene (MW 252.3 daltons).

Sorption of PAHs to suspended or bottom sediments or colloids may decrease or increase photolysis rates. David and Boule (1993) showed that sorption to silica particles increases the rate of photolysis of anthracene, phenanthrene, and benz(a)anthracene. Ferric oxide, montmorillonite clay, and cellulose sorbents decrease photolysis rates. The major photolysis products of silica-sorbed PAHs are quinones and hydrogen peroxide. PAHs associated with suspended particles of soot or CB are relatively refractory to photooxidation reactions.

3.2.10.5 Advective and Diffusive Transport Affecting Dispersal of Sediment-Associated HOCs.

Dispersion and weathering processes affect the fate of HOCs and complex HOC mixtures (*e.g.*, NAPLs) in sediments. The most important of these are diffusion, advection, dispersion, and bed (sediment) transport. Diffusion is the process whereby dissolved species in water are transported by random molecular motion from an area associated with higher concentrations, usually the contaminated particle/water interface, to an adjacent area associated with a lower concentration. Diffusion is too slow to cause significant dispersion of the HOC in the absence of advection. Advection is movement of a chemical or a mixture vertically or horizontally through an environmental medium, such as sediment, in association with water movement through the medium. Migration of dissolved HOCs with sediment pore water flow is considered advection. Dispersion of fine-grained particles and organic colloids in sediment pore water facilitates the advection of particle-bound, dissolved colloid-bound, and dissolved HOCs, and NAPLs vertically or horizontally in sediments and into the overlying water column (Neff *et al.*, 1994; Friedman *et al*., 2011). Combined diffusion and advection usually result in spreading of subsurface HOCs and, in the process, the contaminant becomes diluted. Advective dispersion rarely is uniform; the leading edge of migrating contaminant usually advances more rapidly than the centroid due to the wide variability in actual permeability and flow paths within the porous medium.

The rate and extent of migration of HOC NAPLs composed of oils, coal tars, or creosote into and through sediments depends on the viscosity, density, and interfacial tension of the NAPL and the permeability of the sediment (Strain, 1986; Vandermeulen *et al.*, 1988). NAPLs of crude, refined, and residual petroleum; creosote; coal tars; and different PCB mixtures (*e.g.*, Aroclors) vary widely in density, interfacial tension, and viscosity. Most crude and refined/residual oils have densities less than that of fresh and salt water and, therefore, will tend to migrate to and float on the upper interface of pore water in periodically emergent sediments (*e.g.*, intertidal zone of the ocean or estuary) and will not penetrate submerged sediments. PAHs also may partition slowly from a buried oil NAPL and be advected to the sediment surface by colloid transport or sediment bioturbation (Wilcock *et al.*, 1996; White *et al*., 2005). The water table in intertidal marine and estuarine sediments moves up and down with the tides, and NAPLs can penetrate permeable intertidal sediments during the falling tides and be retarded there by the reduced sediment permeability caused by the oil. Any upward percolation of water through the sediment column with the incoming tide or submarine groundwater discharge will tend to push the NAPL upward in the sediment (Strain, 1986).

Commercial PCB mixtures are denser than fresh water (Table 3-2), and, as a result, an Aroclor NAPL tends to be advected horizontally or downward in pore water with substantial retardation due to the high viscosity of the mixtures (Brenner *et al*., 2004). However, less chlorinated PCBs may partition from the NAPL and adsorb to fine-grain silt/clay sediment particles and be carried with them to the sediment surface (Lee *et al.*, 2006). Advection of NAPL or dissolved/dispersed HOCs toward the surface of fresh water and near-shore sediments also can occur due to upward groundwater flow through contaminated sediments into the overlying water column. Sediments containing high concentrations of clay have very low hydraulic conductivities; diffusion and advection of low-molecular-weight, low viscosity HOCs and NAPLs are very slow in such sediments (Mott and Weber, 1991).

Some heavy crude, residual oils, coal tars, and highly chlorinated Aroclors (classified as dense non-aqueous phase liquids [DNAPLs]) are denser than water and sink when spilled in open water. They are so viscous that their rate of penetration into and migration through any but the coarsest sand and gravel/cobble sediments is very slow (Gerhard *et al*., 2007). However, in locations where DNAPLs have been disposed of or spilled on land or in disposal sumps, there may be substantial migration of even the heavy compounds, viscous oil, tar, PCBs, and organic solvents through sand/silt sediment columns. Sediments composed of fine-grained silt or clay particles, as well as sandy sediments containing more than a few percent silt/clay, have very low permeabilities (Scheidegger, 1957).

Advective transport, dispersion, and diffusion rates for dissolved HOCs in soils and sediments are controlled by the permeability of the media and the sediment-water partitioning behavior of the HOCs and site sediment particles. As discussed above, the strength of HOCs binding to sediment is dependent on the quality and concentration of organic matter in the sediment. Natural capping by fine-grained silt/clay sediments may provide a barrier to the upward migration of HOCs (Brenner *et al*., 2004); the effectiveness of that sediment barrier depends on the properties and thickness of the natural capping material. Therefore, knowledge of sediment pore water flow characteristics is needed to evaluate the significance of a contaminant's advection and diffusion characteristics and its potential to transport HOCs laterally out of the contaminated site or vertically into the water column. The rate of migration of dissolved HOCs is slow relative to groundwater transport due to interactions between the dissolved HOCs and the soil or aquifer solids. Retention of the HOCs by the aquifer or sediment materials occurs when the contaminant is sorbed onto the substrate (particularly clay-sized sediment particles), sediment organic particles, or organic coatings on fine-grained sediment particles. The contaminant velocity can be estimated using the groundwater flow rate at the site and the retardation factor for the contaminant of interest (Domenico and Schwartz, 1998). The retardation factor, R, is derived by the following equation:

$$R = 1 + \rho_b K_{oc}/n \qquad \text{(Eq. 3.8)}$$

where, ρ_b is the bulk or mass density of the porous medium, n is the porosity of the medium, and K_{oc} is the sediment organic carbon/water partition coefficient (see Section 3.2.3 for discussion of K_{oc}). Table 3-8 summarizes the estimated retardation factors for several PAHs in soils or sediments containing different concentrations of TOC. The two sediments used in the study contained either low concentrations of TOC (0.1%, similar to 'cleaned' or washed sand) or relatively high concentrations of TOC (5.0%, similar to nearshore sediments). These data clearly demonstrate the profound effect of partitioning to organic fractions in contaminated sediments on the migration of sediment-associated HOCs. From these data, it can be surmised that PAHs and other HOCs with R values greater than about 100 will migrate through sediment dissolved in pore water very slowly, if at all. High-molecular-weight HOCs with high log K_{oc} values (> 4.0 mL/g) generally will not migrate rapidly through sediments containing higher than trace concentrations of TOC. This includes all PCB and PCDD/PCDF congeners; they have log K_{ow} values ranging from 4.3 to 8.2 (Mackay *et al*., 2006) (Tables 3-3 and 3-6).

Table 3-8. Log K_{oc}, K_d, and Retardation Factors (R) for Several PAHs in Sediments Containing 0.1% or 5% Organic Carbon

PAH	Log K_{oc} (mL/g)	K_d (mL/g) (0.1% OC)	R (0.1% OC)	K_d (mL/g) (5% OC)	R (5% OC)
Naphthalene	3.11	1.30	9	65	391
2-Methylnaphthalene	3.93	8.50	52	425	2,551
Dibenzothiophene	4.87	74.13	446	3,707	22,240
1-Methylphenanthrene	4.93	85.11	512	4,256	25,535
Benz(a)anthracene	6.14	1,380	8,281	69,000	414,000
5-Methylchrysene	6.21	1,622	9,732	81,091	486,544
Benzo(a)pyrene	6.74	5,500	33,000	275,000	1,650,000

The sediment used to generate these data had a density of 1.80 g/cm^3 and a porosity of 0.30.
Source: Neff *et al*., 1994

As discussed above, natural organic colloids in sediments and the water column have a high affinity for absorption and binding of HOCs (Gschwend and Schwarzenbach, 1992). Because colloids behave like dissolved macromolecules, they are readily transported by diffusion, advection, and dispersion through sediment pore water flow. Transport of HOCs adsorbed to colloids differs from transport of HOCs that are not sorbed. Despite their high K_{oc} values, high-molecular-weight HOCs can migrate through and out of sediments adsorbed to colloids. The retardation factors of HOCs adsorbed to organic colloids are much lower than those of HOCs in solution in pore water. The reduction of the retardation factor is approximately proportional to the ratio of the $K_{oc,colloid}$ to the K_{oc}. Thus, it is important to measure colloid concentrations and their effect on HOC migration in site sediment when performing a site-specific ecological risk assessment.

Although diffusion is a relatively slow process, diffusion-driven mass transport always occurs if concentration gradients are present. For example, a diffusive flux for PCBs from sediments was estimated for a 6.75-mile stretch of the Grasse River near the confluence to the St. Lawrence River at 22 g/d for the entire area (Ortiz *et al*., 2004). This estimate was calculated using a mass transfer coefficient of 0.02 m/d and diffusion rate to show that diffusive flux was a significant mechanism for PCB transport to the water column. Consequently, diffusion can produce a significant flux of contaminants through a saturated porous medium in the absence of advection (Palermo *et al.*, 1998), although diffusion is the slower of these two processes. Thus, the mass flux of interest to MNR is usually driven by advection (Fetter, 1994). Diffusion is expected to be significant for contaminated sediment layers that are in direct contact with the water column, whereas burial of contaminated sediments will retard the diffusive transport of contaminants to the water column. It should be noted that as contaminated sediments recover (*i.e.*, become less toxic), recovering populations of benthic organisms can mix sediments by bioturbation, causing rates of advective transport to increase.

3.3 Biological Transformation of HOCs in Sediments

3.3.1 PAH Biodegradation. Nearly all fresh water and marine water bodies and sediments contain populations of bacteria and fungi that are capable of biodegrading bioaccessible PAHs, PCBs, and PCDDs/PCDFs to some degree (Leahy and Colwell, 1990; Abramowicz, 1995; Barkovski and Adriaens, 1996; Bressler and Gray, 2003). Water column and sediment bacteria and fungi exhibit considerable diversity and adaptability in utilizing different types of organic molecules as a sole or supplemental carbon source. Thus, after a period of time through the activity of local microbial communities, sediments may be rendered non-toxic even though some HOCs are still present. Many groups of microorganisms oxidize saturated hydrocarbons and, to a lesser extent, most low-molecular-weight aromatic hydrocarbons and heterocyclic compounds completely to carbon dioxide during heterotrophic respiration (Bressler and Gray, 2003). Selected soil and sediment fungi are adapted to metabolizing plant lignins, rich in aromatic structures and, thus, possess the enzymatic assemblage necessary to degrade some PAHs completely to carbon dioxide (CO_2) and water (Field *et al.*, 1992; Cutright, 1995).

Weathering of petroleum in sediments usually results in a decrease in sediment toxicity due to a decrease in the concentration of bioaccessible and bioavailable hydrocarbons, including PAHs and their degradation products (Jonker *et al.*, 2006). Often, however, PAHs and heterocyclic compounds are metabolized only partially, yielding a variety of polar, oxygenated metabolites (Fedorak and Westlake, 1984; Bossert and Bartha, 1986; Kuhn and Suflita, 1989; Qiu and McFarland, 1991), some of which can be more toxic than the parent PAHs. A variety of ketones, quinones, and organic acids may be formed during incomplete biodegradation of high-molecular-weight PAHs in sediments and water (Pothuluri and Cerniglia, 1994; Wischmann and Steinhart, 1997). In some cases, however, reactive intermediates of PAH biodegradation become covalently and irreversibly bound to sediment organic matter (Qiu and McFarland, 1991), ultimately mitigating the toxicity of these weathering products by rendering the covalently bound adducts non-bioavailable.

Following contamination of sediments with petroleum, coal tar, or creosote, different hydrocarbon classes are simultaneously or sequentially degraded by indigenous microbiota in sediments, but at widely different rates (Atlas, 1995; Gough *et al.*, 1992; Kaplan *et al*., 1996; Oudot *et al.*, 1998; Brassington *et al.*, 2007). Low-molecular-weight *n*-alkanes with chain lengths of 10 to 22 carbons are metabolized most rapidly, followed by isoalkanes and higher-molecular-weight *n*-alkanes, olefins, monocyclic aromatic hydrocarbons, PAHs, and, finally, highly-condensed cycloalkanes, resins, and asphaltenes. Degradation of some sulfur heterocyclics, such as dibenzothiophene and its alkyl homologues, seems to require mixed microbial assemblages and co-substrates (Kropp *et al.*, 1994; Dyreborg *et al.*, 1996). Usually these mixed microbial assemblages and co-substrates are present in oil-contaminated sediments where dibenzothiophenes biodegrade at rates similar to those for PAHs of similar molecular weight (Douglas *et al.*, 1996; Burns *et al.*, 1997). Following the *Exxon Valdez* oil spill, ratios of various alkyl dibenzothiophenes to alkyl phenanthrenes in marine sediments remained stable for several years and were useful for identifying the spilled oil in environmental samples (Douglas *et al.*, 1996).

Highly-branched or cyclic alkanes and alkenes are resistant to biodegradation and tend to be persistent in sediments (Robson and Rowland, 1987; Wang and Stout, 2007). Alkanes from C_{11} to C_{35} and PAHs from naphthalene to dimethylfluorenes were biodegraded nearly completely in bench-scale microcosm incubation experiments during 1 month of exposure of a weathered light Arabian crude oil to sea water containing a natural assemblage of marine bacteria (Dutta and Harayama, 2000). Only C_4-dibenzothiophenes and C_6- and C_7-phenanthrenes were resistant to biodegradation under these experimental conditions. Crude oils and some heavy fuel oils contain a wide variety of complex cyclic alkanes (steranes and triterpanes) derived from plant precursors during petrogenisis in source rocks. These hydrocarbons are resistant to biodegradation in surface sediments and, therefore, are frequently used as biomarkers of the sources and weathering of the petroleum residues in sediments (Wang *et al.*, 2006).

Some high-molecular-weight PAHs, such as chrysene, dibenzanthracene, and perylene, are degraded only very slowly in a variety of sediments (Bossert and Bartha, 1986; Heitkamp and Cerniglia, 1987). In 9 months, 40 ± 7% of total oil, 83 ± 6% of aliphatic hydrocarbons, 49 ± 10% of cyclic alkanes, and 55 ± 18% of aromatic hydrocarbons were biodegraded in intertidal sediment plots contaminated with a weathered, emulsified light Arabian crude oil (Oudot *et al.*, 1998). Resins and asphaltenes were not biodegraded during this time. However, after the 1991 Gulf War, indigenous microbes from waters and sediments of the western Arabian Gulf degraded PAHs and related sulfur-containing heterocyclic compounds more rapidly than they degraded normal alkanes under low nutrient conditions (Fayad and Overton, 1995).

Differences between prokaryote (bacteria) and eukaryote (algae, fungi, and higher organisms) metabolic pathways for degrading PAHs may be important with respect to production of mutagenic or carcinogenic byproducts. In bacteria, a dioxygenase enzyme system incorporates two oxygen atoms into the aromatic ring structure to form a dioxethane intermediate (Figure 3-5). The dioxethane is oxidized further to a *cis*-dihydrodiol and then to various dihydroxy products, the most common of which are catechols (Cerniglia, 1993; Wilson and Jones, 1993: Pothuluri and Cerniglia, 1994; Sutherland *et al.*, 1995). These intermediates are not mutagenic or carcinogenic.

Most eukaryotes use a monooxygenase system, the cytochrome P450 MFO system, to incorporate one oxygen atom into the aromatic ring structure to form an arene oxide, which either isomerizes spontaneously to form a phenol, or is hydrated by epoxide hydrase to form a *trans*-dihydrodiol or a phenol (Cerniglia, 1993; Sutherland *et al.*, 1995) (Figure 3-5). As with prokaryotes, the dihydrodiol may be oxidized to a dihydroxy product, such as a catechol.

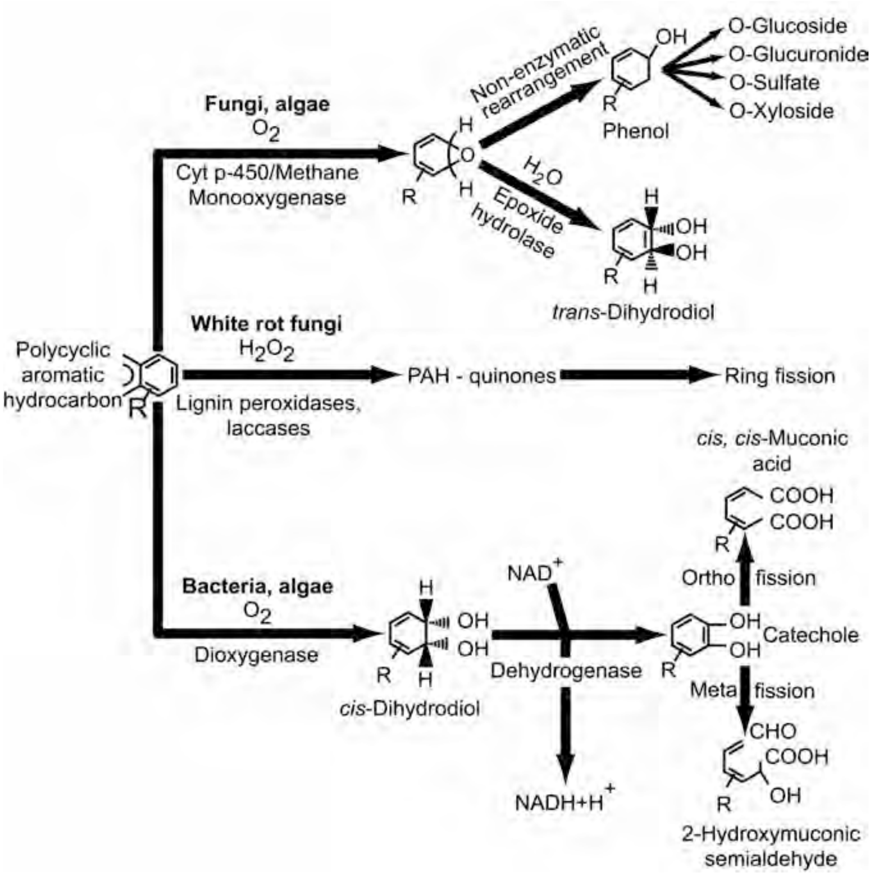


Figure 3-5. Initial Steps in Biodegradation of PAHs by Prokaryotes (Bacteria) and Eukaryotes (Fungi, Algae, Plants, Animals)
(*Trans*-dihydrodiols of some higher-molecular-weight PAHs produced by eukaryotes are carcinogenic [redrawn from Cerniglia, 1993].)

In those PAHs that can be enzymatically activated to mutagens or carcinogens (selected 4- through 6-ring PAHs, such as benz[a]anthracene, benzo[a]pyrene, and dibenz[a,h]anthracene) (Table 3-4), the reactive metabolites that interact with cellular DNA to induce cancer or mutation are *trans*-diol-epoxides (Hall and Grover, 1990; Guengerich, 1992; Luch and Baird, 2005). For example, the most carcinogenic metabolite of benzo(a)pyrene is benzo(a)pyrene-7,8-diol-9,10-oxide (Hall and Grover, 1990). The prokaryotic (bacterial) pathway does not produce arene oxide and epoxide intermediates; therefore, the products of bacterial degradation of PAHs are less mutagenic and carcinogenic than the products of PAH biodegradation by fungi and higher organisms.

Crude oil contains only traces of mutagenic/carcinogenic PAHs. Most of the PAHs in crude oil are low-molecular-weight, 2- and 3-ring aromatics, related heterocyclic aromatic compounds (*e.g.*, dibenzothiophene), and their alkylated homologues. These compounds are toxic but not mutagenic/carcinogenic (Neff, 2002; Di Toro *et al*., 2007; McGrath and Di Toro, 2009). Microbial degradation of these low-molecular-weight PAHs produces a variety of phenols, quinones, dihydrodiols, alcohols, and acids as short-lived intermediates (Liu *et al.*, 1992; Volkering and Breure, 2003). Some of these intermediates are more toxic than the parent compounds (Aprill *et al.*, 1990; Wang *et al.*, 1990; Belkin *et al.*, 1994; Hund and Traunspurger, 1994); however, these intermediates do not persist long in aerobic water and sediments (Heitkamp and Cerniglia, 1987). Ultimately, the low- and medium-molecular-weight aromatic hydrocarbons in petroleum are degraded to low-molecular-weight organic acids, most of which are not toxic. Under oxidizing conditions, these organic acids are degraded rapidly by sediment microbiota to CO_2 and water and can serve as important nutrients (primarily as a readily degradable form of carbon) for sediment microorganisms.

All available evidence indicates that rates of hydrocarbon degradation are much lower under anoxic than under aerobic (oxygen-rich) conditions, even though many species of bacteria and fungi are able to metabolize petroleum hydrocarbons, including PAHs and heterocyclic compounds, in the absence of oxygen (Johnston, 1970; Bauer and Capone, 1985; Kuhn and Suflita, 1989; McFarland and Sims, 1991; Karthikeyan and Bhandari, 2001; Rothermich *et al.*, 2002; Seo *et al.*, 2009). Part of the negative effect of low oxygen concentrations on the microbial degradation of hydrocarbons in sediments may be related to availability of primary nutrients (nitrogen and phosphorus). Mineralization of NOM, resulting in release of inorganic nitrogen and phosphorus, is very slow in anoxic sediments. Hydrocarbons being rich in carbon but deficient in nitrogen and phosphorus are an inadequate nutrient source but a rich carbon source for microbes in the absence of exogenous sources of available primary nutrients. Addition of primary nutrients may stimulate hydrocarbon degradation in anoxic and hypoxic sediments (Scherrer and Mille, 1989; Mills *et al*., 2004). Excess nutrient addition, however, may favor alkane over PAH biodegradation. During early attempts to bioremediate oiled sediments on the shore following the *Exxon Valdez* oil spill, the mineralization potential of indigenous bacteria for aromatic hydrocarbons was high; however, a year later (after extensive application of fertilizers), the mineralization potential was higher for alkanes than for aromatic hydrocarbons (Sugai *et al.*, 1997).

Availability of a suitable alternative to oxygen as the electron acceptor may also limit PAH degradation in anoxic sediments. The predominant electron acceptor processes in anoxic sediments are iron-, manganese-, and sulfate-reduction and methanogenesis; sulfate is abundant in sea water and marine sediments, so sulfate-reduction, mediated by anaerobic sulfate-reducing sediment bacteria, is the quantitatively most important source of electrons for hydrocarbon oxidation in anoxic marine sediments (Ashtok and Saxena, 1995; Sharak Genthner *et al.*, 1997; Rothermich *et al.*, 2002). Coates *et al.* (1996, 1997) reported that naphthalene, methylnaphthalene, phenanthrene, fluorene, and fluoranthene, but not pyrene and benzo(a)pyrene, were degraded to CO_2 and water under sulfate-reducing conditions in heavily contaminated sediment from San Diego Bay, CA. PAH oxidation likely is performed by anaerobic, sulfate-reducing bacteria (SRB) in these sediments. Biodegradation of naphthalene in anaerobic sediment columns is more efficient when sulfate rather than nitrate or manganese is available as the electron acceptor (Langenhoff *et al.*, 1996). Sharak Genthner *et al.* (1997) reported only limited PAH biodegradation under nitrate-reducing, sulfate-reducing, and methanogenic conditions in creosote-contaminated anaerobic sediments. A wide variety of organic acids accumulate in small amounts in petroleum-contaminated groundwater as a result of anaerobic microbial degradation of saturated and aromatic hydrocarbons under anoxic conditions (Cozzarelli *et al.*, 1994). Thus, hydrocarbons including PAHs from oil, coal tar, creosote, and other combustion sources may be persistent in anoxic or hypoxic sediments, particularly if the sediments are fine-grained and contain high concentrations of organic matter (Burns *et al.*, 1993; Floodgate, 1994; Xia and Wang, 2008). The degradation rate of low-molecular-weight PAHs as reported for the sediments evaluated in these studies was inversely related to sediment organic carbon concentration (Hinga, 2003) and also to the concentration of expandable clay in the sediments (Hwang and Cutright, 2003).

The main limitation on both the degradation rate and extent for PAHs in sediments is bioaccessibility and bioavailability (Weissenfels *et al.*, 1992; Cerniglia, 1993; Richnow *et al.*, 1993; Bressler and Gray, 2003). PAHs, in particular the higher-molecular-weight 4- through 6-ring PAHs (including the pro-carcinogens [PAHs that can be activated to carcinogens enzymatically, as described above]), have low solubilities and tend to bind strongly to sediment organic matter (Tan and Tomson, 1990; Amy *et al.*, 1991; Scheunert *et al.*, 1992; Weissenfels *et al.*, 1992; Richnow *et al.*, 1995; Carmichael *et al.*, 1997; Reemtsma and Mehrtens, 1997) or polymerize to form complex new compounds that can be found in the asphaltene phase of the weathered oil (Bossert and Bartha, 1984; Qiu and McFarland, 1991). As part of the asphaltene phase, these contaminants are not bioavailable to the local microbial communities for biodegradation. Richnow *et al.* (1993) reported that a large fraction of the PAH metabolites produced by microbes during degradation of an oil in contaminated soil from Germany were covalently bonded to soil humic substances through stable ester bonds. Selective chemical degradation methods were required to release the PAH metabolites from the soil humic substances that were tightly sorbed to the soil humic material. These covalently-bonded or physically-sorbed PAHs had low bioavailability and toxicity. Sorption of low-molecular-weight PAHs, such as naphthalene, to organic colloids in sediments does not affect their bioavailability or rate of microbial degradation (Meredeth and Radosevich, 1998); however, this trait could be due to the low relative mass of PAHs sorbed to colloids relative to that sorbed onto solids. It is widely accepted that only desorbed (dissolved) PAHs are bioavailable for biodegradation by sediment microorganisms (Bressler and Gray, 2003). This appears to be true for PAHs that are tightly bound to BC (and unavailable) in sediments (Beckles *et al.*, 2007). However, Xia and Wang (2008) demonstrated that hydrocarbon degradation was more rapid at the sediment particle-water interface than in the aqueous, pore water phase in sediments. Bressler and Gray (2003) showed that bacteria on the surface of hydrated sediment particles are able to translocate and metabolize lightly adsorbed PAHs. Thus, sorption of PAHs and other hydrocarbon-derived HOCs may not completely inhibit biodegradation and bioavailability.

PAHs are potentially bioavailable to sediment microorganisms and higher benthic and water-column organisms when they remain in the oil phase (NAPL) in the sediment; their bioavailability is reduced when the oil weathers, increasing its viscosity, as described above; the PAHs are covalently bound to the asphaltene phase; or the oil weathers to a solid asphaltic mass. However, if PAHs are leached by water-washing of the oily sediment into pore water or surface water, they tend to sorb to natural sediment organic matter, mostly high-molecular-weight humic materials. After long equilibration times, these sorbed PAHs become tightly bound to the sediment organic fraction and become less bioavailable to sediment organisms. PAH metabolites produced by bacteria and fungi, as well as photooxidation products of hydrocarbons, are highly reactive and tend to react or complex with sediment organic matter. Some PAH degradation products become covalently bound to sediment organic matter and can only be analytically detected by destructive pyrolysis of the sediment organic matter (Richnow *et al.*, 1995). This tight binding or sequestration of PAH degradation products in the sediment has the effect of decreasing their bioavailability, microbial metabolism, and toxicity to sediment plants and animals (Alexander, 1995). Thus, after a period of time, the sediment may become non-toxic due to low PAH bioavailability even though PAHs may still be present at concentrations exceeding established threshold values.

The scientific literature contains several estimates of the rates of degradation of petroleum hydrocarbons, including PAHs, in water and sediments. Atlas and Bronner (1981) estimated that petroleum hydrocarbons from the 1978 *Amoco Cadiz* crude oil spill were being degraded at a rate of 1.5 g/m^2/month in the upper 5 cm of intertidal sediments along the Brittany coast of France. After 8 years, concentrations of alkanes that were originally present at concentrations of 2,400 to 17,000 μg/g, and aromatic hydrocarbons that were originally present at concentrations of 740 to 5,500 μg/g, had dropped to near background levels in soft intertidal sediments near the spill site (Page *et al.*, 1989). Massie *et al.* (1985) estimated that the rate of degradation of naphthalene in off-shore marine sediments near oil production platforms ranges from 0.06 to 93.6 g/m^2/month; the degradation rate of benzo(a)pyrene rarely exceeds 0.8 g/m^2/month.

About 40% of the crude oil spilled from the tanker *Exxon Valdez* in Prince William Sound, AK, in March 1989 was washed onto the coarse boulder/cobble/gravel shore sediments and accumulated in subsurface deposits. The buried oil weathered rapidly in the first few years after the spill. Boehm *et al.* (1995) estimated half-lives for total petroleum PAHs in intertidal sediments during the year and a half after the spill of 2 months in the upper intertidal zone and 3.8 months in the lower intertidal zone. By the summer of 1991, 2 years after the spill, PAH degradation half-lives had increased to the range of 7.4 to 16.0 months, likely due to reduced leaching and bioavailability of PAHs from highly weathered oil in shoreline sediments. In the year after the spill, the oxidation rate potential for PAHs by microbial communities in intertidal sediments ranged from 5 to 30 μg PAHs mineralized/g dry sediment/day (Sugai *et al.*, 1997). Numbers of hydrocarbon-degrading bacteria increased in intertidal and subtidal sediments from the spill zone during the year after the spill (Braddock *et al.*, 1995). Some oil deposits on the shore developed an asphalt-like coating (Ramaswami *et al.*, 1994) or sank into coarse upper intertidal sediments and were protected from weathering by an armor of rocks and boulders. PAHs in these deposits were nearly immobile, and biodegradation was very slow. Percent loss relative to the original total PAHs from buried oil residues on the shore increased slowly from an average of 66% in 1989-1993 to an average of 82% in 2004-2006 (Atlas and Bragg, 2007). Most of the oil residues on the shore within a few years after the spill had ≥70% PAH depletion, and the PAH fractions were resistant to further biodegradation.

3.3.2 PCB Biotransformation. The compositions of PCB congener mixtures present in the environment differ substantially from those of the original, technical Aroclor mixtures released to the environment. This is because several processes collectively referred to as “environmental weathering” change the composition of PCB mixtures over time after release into the environment. This weathering is a result of the combined effects of processes such as differential volatilization, solubility, sorption, anaerobic dechlorination, and aerobic and anaerobic biodegradation; these processes result in changes in the composition of PCB mixtures over time and differences in PCB compositions during trophic transfer and biomagnification in marine food webs (Froese *et al.*, 1998). Generally, less-chlorinated PCBs are lost most rapidly due to volatilization and metabolism, while more-highly-chlorinated PCBs often are more resistant to degradation and volatilization and sorb more strongly to particulate matter (Abramowicz, 1995). More-highly-chlorinated PCBs tend to bioaccumulate to a greater degree than do less-chlorinated PCBs in tissues of animals and have a high potential to biomagnify in fresh water and marine food webs (Hoekstra *et al.*, 2003).

Biodegradation of PCBs in sediments requires consortia of microorganisms with broad specificity and modes of oxidative or reductive attack (Seo *et al.*, 2009). There are three general ways that PCBs are biodegraded:

- Aerobically as a growth substrate: aerobic bacteria degrade less-chlorinated PCB congeners as a source of biomass accretion (Costa *et al.*, 2004).
- Aerobically by cometabolism: aerobic bacteria or fungi use non-polar organic substrates as a primary energy source and, in the process, biodegrade some PCB congeners (Abramowicz, 1995).
- Anaerobically: sediment microbes reductively dechlorinate more-highly-chlorinated PCBs by replacing chlorines on the biphenyl skeleton with hydrogens (Brown *et al.*, 1987; Zanaroli *et al*., 2006; Bedard, 2008).

Several aerobic sediment microorganisms can completely mineralize some less-chlorinated PCB congeners through aerobic oxidation (Abramowicz, 1995; Van Briesen *et al.*, 2004). More-highly-chlorinated PCB congeners can be reductively dechlorinated by anaerobic bacteria, including sulfate-reducing and methanogenic bacteria, in anoxic sediments producing less chlorinated mono-, di-, and tri-chlorobiphenyls (Brown *et al.*, 1987; Zanaroli *et al*., 2006). If conditions are right, complete removal of PCBs from contaminated sediments can be accomplished by sequential activities of anaerobic and aerobic bacteria (Evans *et al.*, 1996). Gradients of oxygen concentration with depth in sediment control the oxidative and reductive processes (Van Briesen *et al*., 2004), with most degradation occurring in the transition region of the sediment column, *i.e.*, the redox potential discontinuity where redox potential (Eh) is near zero.

The more-highly-chlorinated PCB congeners are reductively dechlorinated in the suboxic layers of sediment below the redox potential discontinuity. Anaerobic bacteria couple oxidation of sediment organic matter to reductive dechlorination of PCB congeners serving as the electron acceptor. Under aerobic conditions, the less-chlorinated PCB congeners are metabolized by aerobic microorganisms with the PCB congener as the sole or secondary carbon source and electron acceptor.

The major limitation to these processes being carried out concurrently in time and space is that one process requires oxygen and the other is inhibited by the presence of oxygen. The sequential oxidative and reductive degradation of PCBs can take place at and just above and below the redox potential discontinuity in the upper layer of sediments, particularly if microscopic algae or aquatic plants occupy the near-surface layers of the sediments. The plants cause the depth of the redox potential discontinuity to sink deeper in sediments during the day when oxygen is released into the sediments by photosynthesis and to rise toward the surface at night when plant respiration removes oxygen from the sediments (Catallo, 1999; Aldridge and Ganf, 2003).

Aerobic PCB biodegradation involves the initial oxidation of the biphenyl nucleus by the addition of oxygen at the 2,3-position by a 2,3-dioxygenase enzyme, with subsequent dehydrogenation of the catechol followed by ring cleavage (Harkness *et al.*, 1993; Abramowicz, 1995). This pathway leads to the production of chlorobenzoic acid intermediates that can build up and inhibit pure cultures of PCB degrading organisms, but that are readily hydrolyzed by other aerobic bacteria in diverse microbial communities.

Aerobic biodegradation of PCBs usually is limited to the congeners containing fewer than four chlorine atoms, but a few strains of aerobic bacteria have the ability to degrade tetra-, penta-, and hexa-chlorobiphenyls (Bedard *et al*., 1986, Abramowicz, 1990). Because the majority of congeners in Aroclors 1221, 1232, 1016, and 1242 contain fewer than four chlorine atoms, it is possible to demonstrate significant levels of PCB mass removal with aerobic biodegradation. In fact, reductions of between 50% and 85% by mass have been reported in sediments contaminated with up to 1,000 parts per million (ppm) of Aroclors 1221 through 1248. One study reported a 67% drop in the molar concentration of weathered Aroclor 1248 from soil slurry microcosms with low organic carbon content (Evans *et al.*, 1996). The main disadvantages of aerobic PCB biodegradation include: 1) the inability of microorganisms to break down the more-highly-chlorinated, more toxic congeners, and 2) the limited availability of oxygen in most contaminated sediment environments, rendering most sediment layers anaerobic at depths more than a few millimeters from the sediment-water interface. The absence of or very slow aerobic biodegradation of more highly-chlorinated PCBs results in their persistence in aerobic environments.

In contrast to aerobic biodegradation that destroys PCBs via ring cleavage, microbially-catalyzed anaerobic, reductive dechlorination simply removes chlorine substituents from PCBs, particularly from the more highly-chlorinated congeners with three or more chlorines. In general, reductive dechlorination preferentially removes chlorines from the *meta* and *para* positions and replaces them with hydrogen atoms, resulting in depletion of highly-chlorinated PCB congeners accompanied by an increase in concentrations of less-chlorinated *ortho*-substituted PCB congeners (Natarajan *et al*., 1998; Seeger *et al.*, 2001; Zanaroli *et al.*, 2006; Bedard, 2008). Because the most toxic PCB congeners are those with chlorines in the *meta* and *para* positions in the biphenyl molecule and no more than two chlorines in the *ortho* position (coplanar PCBs), reductive dechlorination causes a substantial reduction in carcinogenicity and dioxin-like toxicity of PCB mixtures in sediments (Quensen *et al.*, 1998; Abramowicz, 1995; Zanaroli *et al*., 2006). Dechlorination contributes to detoxification of PCB mixtures primarily through two mechanisms: 1) elimination of coplanar congeners that may exhibit dioxin-like toxicity (McFarland and Clarke, 1989; NRC, 2001; Quensen *et al.*, 1998), and 2) the transformation of generally more-toxic, higher-chlorinated congeners to less-toxic, less-chlorinated congeners (ATSDR, 2000).

The less-chlorinated PCBs also have a lower potential than do more highly-chlorinated PCBs for bioaccumulation. For example, 2-chlorobiphenyl and 2,2-dichlorobiphenyl display an approximately 450-fold decrease in the tendency to bioaccumulate in fish compared with tri- and tetra-chlorinated PCBs (Abramowicz and Olson, 1995). Furthermore, the PCB mixture becomes more susceptible to aerobic degradation, and by lowering the chlorination level of the mixture, the tendency of the mixture to bioaccumulate is also reduced.

Several approaches have been attempted to enhance the microbially-catalyzed reductive dechlorination of PCBs. Researchers have attempted to stimulate dechlorination by amending microcosms with carbon substrates (*e.g.*, fatty acids, glucose, methanol). Amendment of anaerobic bacterial consortia in sediments resulted in shortened lag times or increased initial rates of dechlorination, but the overall extent of PCB dechlorination was not significantly increased (Abramowicz and Olson, 1995). Amendment with glucose or methanol stimulated preferential dechlorination of highly-chlorinated (>5 chlorines) PCBs in lake sediments (Natarajan *et al*., 1998). Others have attempted to stimulate dechlorination by adding individual polychlorinated or polybrominated congeners to microcosms. The process is designed to selectively enhance populations of organisms that can use the supplied congener as an electron acceptor. In one instance, this strategy reduced hexa- through nona-chlorobiphenyls by 79% in sediments contaminated with Aroclor 1260; the resulting dechlorination products were predominately tri- to penta-chlorobiphenyls (Abramowicz and Olson, 1995). This approach may not be applicable to *in-situ* sediment remediation efforts due to the potential for release of halogenated biphenyls into the environment, but these results do suggest that PCB dechlorination can be stimulated.

Although PCBs in sediments can be biodegraded by aerobic and anaerobic bacteria, the rates of degradation are too slow, even under nutrient stimulation, to allow adequately rapid attenuation by MNR alone. Sinkkonen and Paasivirta (2000) estimated the degradation half-lives of PCDDs, PCDFs, and PCBs in air, soils, and sediments (Table 3-9). Estimated half-lives in sediment of different PCB congeners ranged from 26,000 hours for 2,4,4'-trichlorobiphenyl to 333,000 hours for 2,2',3,4,4',5,5'-heptachlorobiphenyl. The most toxic PCB congener (PCB 126) has an estimated half-life in sediment of 87,600 hours (10 years).

Table 3-9. Estimated Half-Lives (hours) for Selected PCBs, PCDDs, and PCDFs in Sediments

Compound	Half-Life	Compound	Half-Life
Polychlorinated Biphenyls (PCBs)			
2,4,4′-Trichloro-BP (PCB 28)	26,000	2,2′,4,4′5′-Penta-BP (PCB 138)	165,000
3,3′,4,4′-Tetra-BP (PCB 77)	87,600	2,2′,4,4′,5,5′- Hexa-BP (PCB 153)	165,000
2,3′,4,4′5-Penta-BP (PCB 118)	60,000	3,3′,4,4′,5,5′-Hexa-BP (PCB 169)	165,000
2,3′,4,4′,5- Penta-BP (PCB 126)	87,600	2,2′,3,4,4′5,5′-Hepta-BP (PCB 180)	333,000
Polychlorinated Dibenzo-*p*-Dioxins (PCDDs)			
2,3,7,8-Tetra-CDD	900,000	1,2,3,6,7,8- Hexa-CDD	550,000
1,2,3,7,8-Penta-CDD	1,000,000	1,2,3,7,8,9- Hexa-CDD	700,000
1,2,3,4,7,8-Hexa-CDD	2,400,000	Octachloro Dibenzodioxin	1,300,000
Polychlorinated Dibenzofurans (PCDFs)			
2,3,7,8-Tetra -CDF	550,000	1,2,3,4,6,7,8-Hepta-CDF	350,000
1,2,3,7,8-Penta-CDF	450,000	1,2,3,4,7,8,9- Hepta-CDF	200,000
2,3,4,7,8- Penta-CDF	550,000	Octachlorodibenzofuran	250,000

Compounds with dioxin-like toxicity (Table 3-4) are highlighted. Source: Sinkkonen and Paasivirta (2000)

3.3.3 PCDD and PCDF Biotransformation. PCDDs/PCDFs in sediments are primarily tightly adsorbed to organic particles, including BC. These adsorbed PCDDs/PCDFs are chemically stable and immobile and have low bioaccessibility to sediment-dwelling bacteria and fungi. The estimated half-lives of different PCDD/PCDF congeners in sediment range from 200,000 hours (22.8 years) for 1,2,3,4,7,8,9-heptachlorodibenzofuran to 2,400,000 hours (274 years) for 1,2,3,4,7,8-hexachlorodibenzodioxin (Table 3-9). The most toxic PCDDs (2,3,7,8-tetrachlorodibenzodioxin and 1,2,3,7,8-pentachlorodibenzodioxin) have half-lives in sediments of 900,000 to 1,000,000 hours (Table 3-9). An earlier estimate of the half-life of 2,3,7,8-tetrachlorodibenzodioxin was 12,000 to 144,00 hours based on oxidation (Ward and Matsumura, 1978), indicating the importance of mixed oxidation/reduction in mineralization of these compounds.

Several strains of sediment bacteria and fungi that are capable of oxidizing or dechlorinating most PCDD/PCDF congeners have been isolated. Species such as *Sphingomonas wittichii*, *Pseudomonas veronii, Cordyceps sinensis,* and *Dehalococcoides* spp. are capable of enzymatically degrading PCDDs, and *S. wittichii* has been used successfully to bioremediate contaminated fly ash (Simon, 2006; Johnson, 2008). Biodegradation pathways for PCDDs/PCDFs are similar to those discussed above for PCBs. There are several pathways of aerobic oxidation and anaerobic reductive dechlorination of PCDD/PCDFs by bacteria and fungi. Sediment bacteria and fungi use several enzymatic mechanisms to biodegrade PCDD/PCDFs (Chan, 2008). These pathways include oxidative degradation by dioxygenase-containing aerobic bacteria, bacterial and fungal cytochrome-P450 enzyme systems, fungal lipnolytic enzymes, reductive dechlorination by anaerobic bacteria, and direct ether ring cleavage by fungi containing esterase-like enzymes.

The aerobic bacterium, *Burkholderia* sp., is able to biodegrade dibenzofurans and dibenzodioxins by biphenyl dioxygenase enzymes (Kasuga *et al.*, 1997; Seeger *et al.*, 2001). Dioxins and dibenzofurans are attacked at the quasi-*ortho* position (the benzene carbons to which the oxygen[s] are attached) and the immediate adjacent carbons. The angular attack by biphenyl dioxygenases is the main route of dibenzodioxin oxidation. Later dioxygenation leading to dihydrodiols is the major oxidative reaction for dibenzofuran. The major biodegradation product of dibenzodioxin is a trihydroxylated diphenyl ether. The major biodegradation product of dibenzofuran is a dihydrodiol. These metabolites are degraded further to catechols with a substantial decrease in toxicity. Other oxidative degradation products include chlorophthalates or salicylates and chlorophenols (Nam *et al*., 2006). Some aerobic sediment bacterial species can biodegrade PCDDs with up to six chlorine atoms (Yamazoe *et al.*, 2004; Nam *et al*., 2006). The rate of these aerobic bacterial mediated reactions decreases sharply with increasing chlorination of the dibenzodioxin and dibenzofuran molecules.

Reductive dechlorination appears to be the main pathway of microbial PCDD/PCDF biodegradation in anoxic sediment layers (Adriaens and Grbic-Galic, 1994; Barkovskii and Adriaens, 1996; Bunge *et al.*, 2003; Johnson, 2008). The more highly-chlorinated congeners (octachloro-DD and octachloro-DF) are dechlorinated most rapidly, and the dechlorination rate appears to decrease with decreasing levels of chlorination (Gaus *et al.*, 2002). Thus, vertical PCDD/PCDF profiles in sediment cores often exhibit a decrease in concentrations of highly-chlorinated congeners with depth in the sediment core. Reductive dechlorination of PCDDs/PCDFs has been reported to be very slow under normal environmental conditions (Deriziotis, 2004).

White rot fungi (*Phanerochaete* spp.) also are able to biodegrade PCDDs/PCDFs under aerobic conditions (Gold *et al.*, 1994; Takada *et al.*, 1996). Biodegradation is initiated by extracellular peroxidase catalized oxidation reactions that generate quinone intermediates. Quinones are reduced enzymatically to peroxides. Several cycles of oxidation and reduction or oxidation, reduction, and methylation successively remove more chlorines from the dioxin and dibenzofuran molecules. A lignin peroxidase is responsible for cleaving the C-O-C bonds. The dechlorinated molecules are converted to 1,2,4,5-tetrahydroxybenzene and 1,2,4-trihydroxybenzene that are subject to ring opening and further degradation. The rate of biodegradation by the fungal enzymes increases with increasing chlorination of the PCDDs/PCDFs.

Given the very high toxicity of some PCDDs/PCDFs to animals, including humans, and their extreme stability and low degradation rates in sediments, natural attenuation, managed by MNR, may not be a sufficiently rapid remediation strategy unless the PCDD/PCDF-contaminated sediments can be effectively sequestered by irreversible sorption and/or burial. MNR then would be used to ensure that the toxic chemicals are not leaching from the buried deposit. Rigorous MNR would be required because many aquatic animals are able to metabolize PCDDs/PCDFs, producing reactive oxidation products that are highly toxic and possibly carcinogenic in the aquatic food web and the animals, including man, who depend on it. Although PCDD/PCDF metabolism in animals is ecotoxicologically important, it does not contribute to appreciable reduction in total mass loadings of PCDDs/PCDFs in sedimentary environments.

3.4 Assessing Contaminant Transformation

An integral part of an MNR evaluation is consideration of both: 1) the nature and extent of HOC contamination in sediments and their source(s) (particularly for sediments that contain similar suites of HOCs introduced from multiple sources), and 2) the rate and extent of contaminant transformation and mineralization. For example, PAHs often are introduced from multiple sources, *e.g.*, MGP and aluminum smelter wastes, creosote, petroleum residues, urban runoff, and aerial deposition of PAHs from combustion exhaust. Early in the MNR evaluation, attempts to understand the potential for long-term recovery and risk reduction of PAH-contaminated sediment sites were facilitated by the identification of sources and interpreting concentration distributions and changes over time. A chemical forensic approach known as chemical fingerprinting employs high-resolution analytical methods and interpretative techniques to identify and differentiate unique chemical characteristics of organic mixtures from different sources. This approach is a critical tool in MNR for attributing particular chemical fingerprints to different sources and for indentifying and characterizing weathering processes in environmental samples. Hydrocarbon fingerprinting methods have evolved rapidly in the last few years. Several publications describe these methods (*e.g.*, Stout *et al*., 2001a, 2003a, 2003b; Fabbri *et al*., 2003; Christensen *et al.*, 2004; Burns *et al.*, 2006; Wang *et al.*, 2006; Arey *et al.*, 2007; Ebrahimi *et al.*, 2007; Malmquist *et al.*, 2007; Wang and Stout, 2007).

A universal characteristic of chemical fingerprinting methods is that they provide significantly greater chemical detail than standard analytical (*e.g.*, EPA SW-846) methods. Greater chemical information permits sources to be differentiated and chemical weathering processes to be more accurately quantified (Douglas *et al*., 2004). This is particularly useful for urban watersheds where pervasive and persistent background chemical sources may create a chemical concentration threshold in sediments. Chemical fingerprinting plays an important role in MNR by providing the chemical detail necessary to:

- Identify or confirm chemical sources in sediments;
- Monitor chemical concentration changes and transformation processes due to weathering;
- Determine the kinetics of various weathering processes; and
- Establish sediment ambient or background conditions.

Using chemical fingerprinting as part of the MNR evaluation requires that analytical strategies and goals for field investigations be developed carefully. It is necessary to balance costs with project goals because chemical fingerprinting methods tend to be more detailed and costly than conventional analytical methods. For example, a site assessment could be optimized by applying higher-cost fingerprinting methods to a small sample set and using lower-cost conventional analytical tools to make a broad characterization of the full extent and distribution of chemicals of concern. The U.S. Navy has demonstrated the benefit of combining low-cost, rapid sediment characterization techniques (*e.g.*, immunoassay screening) with chemical fingerprinting methods to identify contaminant sources in sediments (Stout *et al.*, 2003b).

Chemical fingerprinting can be more powerful when coupled with information about both spatial concentration gradients and temporal variations relative to known, or suspected, sources where data are acquired through the collection of sediment core samples to provide historic records of contaminant deposition and transformation (Brenner *et al.*, 2001). Spatial and temporal trends (*e.g.*, sediment age and/or contaminant age in sediment) can impact the distribution and weathering of chemicals in the environment. Chemical fingerprinting can be combined with historical information, spatial distributions, and temporal distributions to better differentiate sources, historical depositional events, and weathering trends, the combination of which will ultimately determine the expected rate of sediment restoration via MNR.

3.4.1 Analytical Methods Used in Support of Fingerprinting. The most common methods for the analysis of regulated semivolatile organic compounds (SVOCs) in sediments are modifications to EPA SW-846 Method 8015 and Method 8270 (Table 3-10) (EPA, 1997b, 2007a,b). Modifications are required because the original EPA methods provide insufficient information to differentiate hydrocarbon source or weathering patterns in samples. For example, the target contaminant list (TCL) for EPA Method 8270 includes only 16 unalkylated PAHs (Table 3-1), which is an insufficient number to distinguish unique sources, particularly petrogenic mixtures, or different degrees of weathering in sediments (Douglas and Uhler, 1993). An appropriately-modified EPA Method 8270 (8270M) can simultaneously generate with much greater sensitivity (~1 ng/g [parts per billion: ppb] is generally needed for fingerprinting analyses) the required regulatory data (*i.e.*, TCL PAH concentrations) plus additional SVOCs for chemical fingerprinting (Table 3-1). Douglas *et al.* (2004) reported MDLs for PAHs in sediments on the order of 0.5 ng/g dry wt, which is more than 1,000 times lower than the 660 ng/g sensitivity specified by EPA Method 8270. Such modifications are permitted within EPA SW-846 methods provided the fundamental SW-846 performance criteria are maintained or exceeded (EPA, 2007b).

Table 3-10. Analytical Methods Frequently Used for Fingerprinting of Semivolatile Hydrocarbons in Sediment

Measurement Method	Target Compounds	Utility for Fingerprinting of Contaminants
Modified EPA Method 8015	Total extractable hydrocarbons (THC) Total aliphatic and aromatic hydrocarbons C8 to C44 normal and branched-chain hydrocarbons Distinguishing resolved vs. unresolved compounds in a chromatogram	THC Quantification Develop diagnostic source indices Develop diagnostic weathering indices Establish background characteristics and THC concentrations
Modified EPA Method 8270	Priority pollutant PAHs Alkyl homologues of priority pollutant PAHs S-, N-, O-containing heterocyclic aromatics Petroleum biomarkers PCB congeners	Quantitate >50 semivolatile hydrocarbons Develop diagnostic source indices Develop diagnostic weathering indices Establish background characteristics and PAH concentrations

Source: Stout *et al*., 2002

The advantage of greater chemical detail, *i.e.*, using a more extensive analyte list and markedly lower detection limits, is demonstrated in Figure 3-6. Here, the distribution and concentration of PAHs and related compounds in a heavy fuel oil #6 (from an oil-fired electric power plant) analyzed by standard EPA Method 8270 is compared to data from analysis by the modified EPA Method 8270 that includes a longer analyte (43 parent PAH and alkyl-congener groups). The larger number of target analytes included in the modified analytical method substantially improves the ability to distinguish PAH sources and recognize PAH weathering in sediments. It also shows that the standard method grossly underestimates the concentration of total PAHs.

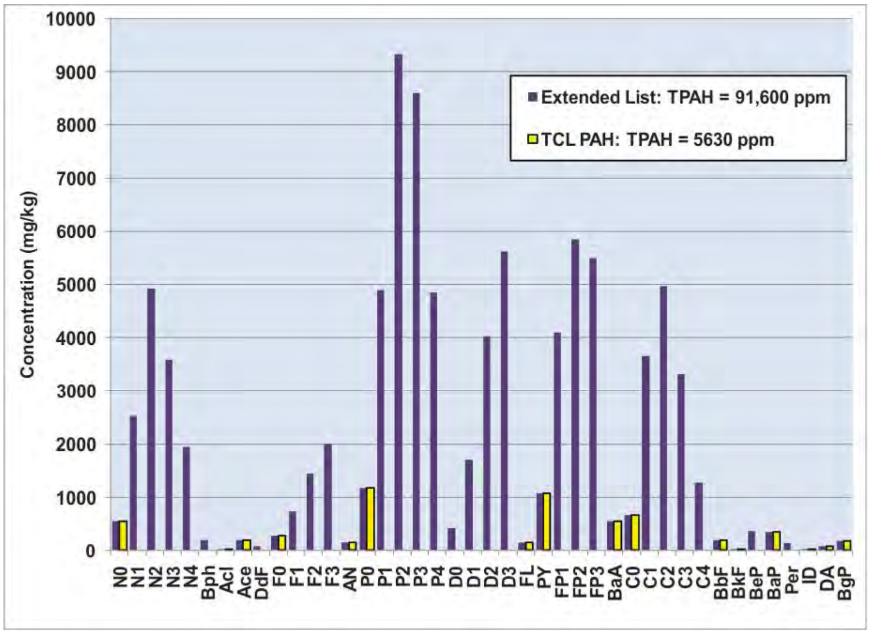


Figure 3-6. Comparison of PAH Composition and Concentration of a Heavy Fuel Oil #6 Based on Analysis of the 16 TCL PAHs by Standard EPA Method 8270 and Analysis of the Extended List of 43 Parent and Alkyl-PAHs by Modified EPA Method 8270 (PAH abbreviations [x-axis] are defined in Table 3-1.)

The analytical methods used in support of chemical fingerprinting generally include the following optimizations:

- Fingerprinting analyte lists for PCBs and PAHs tend to be more extensive than those obtained by standard SW-846 analyses (Plumb, 2004). PCB congener analyses typically include 50 to 110 individual and co-eluting congeners (NRC, 2001). PAH analyses often include both non-alkylated PAHs (commonly comprised of the 16 priority pollutant PAHs identified under the CWA) and their alkylated derivatives, representing more than 40 individual PAHs or congener groups.
- Analytical protocols are optimized for better chromatographic separation of individual compounds, thereby providing greater chemical specificity.
- Analytical protocols are optimized to achieve lower detection limits than required by standard SW-846 analyses (typically up to two or three orders of magnitude lower), thereby reducing or eliminating the ambiguous non-detects at elevated detection limits.
- Detailed quality assurance/quality control (QA/QC) protocols are used to ensure accurate and precise data sets that allow confident and defensible characterization of samples.
- Statistical or numerical data analysis approaches often are used to help minimize subjectivity in establishing the degree of chemical similarity or dissimilarity among samples.

3.4.2 Hydrocarbon Fingerprinting and Weathering Processes. PAHs that are present in the environment, from any source, are ultimately derived from the degradation and rearrangement of natural organic precursors of microbial, plant, and animal origin (Neff, 1979). Four types of PAH assemblages can be identified in water, soil, sediment, and tissues of organisms. As discussed in Section 3.1.2.1, PAH assemblages in environmental compartments are of petrogenic, pyrogenic, diagenic, or biogenic origins. Advanced fingerprinting methods can differentiate PAH assemblages from the four sources. The petrogenic and pyrogenic assemblages are of major environmental concern because the numbers and concentrations of PAHs in them are much larger than in diagenic and biogenic assemblages and much of the petrogenic and pyrogenic PAH mixtures are released to the environment by human activities. PAH source fingerprinting can identify multiple sources of pyrogenic and petrogenic PAH assemblages, differentiate pyrogenic and petrogenic PAH assemblages from one another, and differentiate these sources from diagenic and biogenic assemblages in environmental samples. PAH fingerprinting also can document the rate and extent of weathering of pyrogenic and petrogenic PAH assemblages.

“Urban background” PAHs in sediments are derived from numerous chronic, relatively low-flux, point and non-point sources. Characterization of these urban background PAHs and differentiation of the contribution of these PAHs from PAHs present at a site that originate from non-urban sources is particularly important in MNR studies and is a topic for further discussion in Section 3.4.2.3.

PAHs that are frequently analyzed as part of environmental investigations, particularly hydrocarbon fingerprinting studies, are listed in Table 3-1. The TCL PAHs (the 16 EPA priority pollutant PAHs) identified in Table 3-1 and shown graphically in Figure 3-6 usually are analyzed as part of remedial investigations; however, as shown later, the TCL PAHs alone usually are insufficient for satisfying the objectives of hydrocarbon fingerprinting.

As discussed above, PAHs are subject to physical, chemical, and biological weathering processes in sediments. Lower-molecular-weight, 2- and 3-ring PAHs are more susceptible than high-molecular-weight, 4- through 6-ring PAHs to loss from sediments by dissolution, volatilization, and biodegradation. Higher-molecular-weight PAHs are sensitive to photooxidation but are persistent in sediments, particularly in anoxic layers, because of their low solubilities, high affinities for sorption to sediment organic matter (particularly BC), resistance to degradation, and protection from photooxidation.

Weathering and degradation can reduce the concentrations, mobility, and bioavailability of PAHs in sediments. Weathering of higher-molecular-weight, 4- through 6-ring PAHs usually is slow and, in some cases, may not be measurable over reasonable time periods, particularly if the PAHs are sequestered in a fine-grained, low-permeability sediment layer. In general, hydrocarbon weathering is characterized by a progressive decrease in the proportion of lower-molecular-weight hydrocarbons and the persistence of higher-molecular-weight hydrocarbons (Brenner *et al.*, 2001; Stout *et al.*, 2001a; Bence *et al.*, 2007). These patterns of PAH loss from sediments may reduce or eliminate acute exposures to lower-molecular weight compounds (*e.g.*, naphthalene and phenanthrene and their alkyl homologues) that tend to be more mobile and bioavailable in the environment due to their higher solubility.

3.4.2.1 Hydrocarbon Source Fingerprinting. Sediments often contain hydrocarbons from a variety of sources. The ability to recognize different sources of hydrocarbons depends primarily on the interpretation of data acquired by two analytical methods identified in Table 3-10. An overview of the interpretation of these data is provided in this section. A more detailed and comprehensive discussion of hydrocarbon source characterization and fingerprinting is provided by Wang and Stout (2007).

Modified Method 8015 (8015M) provides a chromatographic fingerprint and concentrations of the total hydrocarbons in sediments. Method 8015M uses a solvent to extract organic material from the sediment sample, silica gel to remove most of the non-hydrocarbon organic material from the extract, and high resolution gas chromatography with flame ionization detection (GC/FID) to determine the total hydrocarbon concentration in the sample and to reveal a unique chromatographic pattern useful in fingerprinting activities. Method 8015M is useful for distinguishing distillate from residual range petroleum sources, and for comparing the relative abundances of easily recognized compounds such as normal alkanes (*n*-alkanes), selected isoprenoids (*e.g.*, pristane and phytane), and some PAHs.

Method 8015 has been used routinely as a first-level identification of both petroleum product type and weathering state (EPA, 2007a). The GC/FID method differentiates and quantifies different types of refined and residual petroleum in environmental samples, including total petroleum hydrocarbons (TPH)-gasoline range (GRH), TPH-diesel range (DRH), and TPH-residual (crude and heavy fuel oil) range (RRH). These types of hydrocarbon assemblages are based on quantification of the area under chromatographic peaks in a certain segment of the gas chromatogram corresponding to hydrocarbons of a defined carbon number and boiling point range. The area under the chromatogram (including both aromatic and aliphatic hydrocarbons) between C_6 and C_{10} is defined as GRH; the area under the chromatogram between C_{10} and C_{24} is defined as DRH; and the area under the chromatogram $>C_{24}$ is defined as RRH.

A GC/FID chromatographic trace or TPH fingerprint is produced as part of the TPH analysis. TPH is defined as the sum of the concentrations of the resolved compounds in the chromatogram in the carbon range of n-alkanes C_{10} to C_{40} plus the concentration of the unresolved complex mixture (UCM: the hump on the chromatogram composed of a complex mixture of unresolved hydrocarbons) between n-alkanes C_{10} and C_{40}. Due to evaporative losses of the more volatile hydrocarbons during the solvent extraction process for the TPH analysis, only the higher-molecular-weight, less volatile hydrocarbons ($> C_{10}$) are measured by this method. The UCM contains hundreds of individual compounds that cannot be resolved by conventional GC and appears as a broad unresolved “hump” above the baseline of the chromatogram. Often the TPH concentration is divided into distinct carbon ranges that are quantified using different types of fuel oils as standards. For example, the hydrocarbon concentration in the DRH range of n-alkanes usually is quantified using a commercial diesel distillate product. Although reported as DRH, the hydrocarbon source material need not be diesel fuel or even from a petrogenic source. All hydrocarbons from any source including pyrogenic sources in the effective carbon range of C_{10} to C_{24} are captured and reported as DRH. Another carbon range fraction typically reported is RRH and includes mixtures of heavy hydrocarbons, including heavy fuel oils, residual oils, and middle- and heavy-weight crude oils, represented by the hydrocarbon concentration range of *n*-alkanes C_{25} to C_{40}.

Source characterization begins with visual examination of the THC chromatogram. For instance, peak patterns and intensities in the THC fingerprint are useful for differentiating different fuels or refined oil types (*e.g.*, kerosene, diesel, or bunker oil), and for comparing the relative abundances of easily recognized compounds such as *n*-alkanes, selected isoprenoids (*e.g.*, pristane and phytane), and some PAHs (Stout and Wang, 2007). Different refined petroleum products (gasoline, diesel fuel, heavy fuels, and lubrication oils), crude and residual oils, and pyrogenic sources (coal tar and creosote) have distinctive THC chromatographic features that can be used to identify and distinguish these sources in sediments. The UCM or "hump" can be identified in chromatograms of weathered and sometimes fresh, middle- and heavy-weight refined, residual, and crude oils (Jones *et al.*, 1983; Gogou *et al.*, 2000; Frysinger *et al.*, 2003), but is not characteristic of most pyrogenic hydrocarbon mixtures (*e.g.*, coal tar). The UCM in petroleum-contaminated sediments contains a complex mixture of weathering-resistant and recalcitrant hydrocarbons that are persistent in sediments (Reddy *et al.*, 2002).

3.4.2.2 Differentiating Petrogenic from Pyrogenic PAH Signatures. Although fingerprints and concentration measurements of TPHs can be used to distinguish a variety of hydrocarbon sources, their use for ecological and human health risk assessments usually focuses on PAHs in sediments due to their toxic, mutagenic, and carcinogenic characteristics, and persistence in sediments. As discussed previously, the two major types of complex PAH assemblages in the environment are pyrogenic and petrogenic. Pyrogenic and petrogenic PAH assemblages can be distinguished easily on the basis of their alkyl PAH distributions (Giger and Blumer, 1974; Youngblood and Blumer, 1975; Lee *et al.*, 1977; Laflamme and Hites, 1978) and the relative concentrations of low- and high-molecular-weight PAHs present.

Crude oil (a petrogenic source) is refined, *i.e.*, distilled, to separate hydrocarbon fractions spanning different boiling point ranges (Gary and Handwerk, 1984) to produce light distillates (gasoline, kerosene, and jet fuel), middle distillates (diesel fuel #2, fuel oil #2, and fuel oil #4), and residual oils (lube oils, fuel oil #6, bunker C fuel, and paving asphalt). The PAH composition is unique among the discrete refined oil fractions, reflecting the distillation boiling point range for each refined petroleum product. Refined petrogenic products contain primarily PAHs that were present in the parent crude oil. Because distillation temperatures are relatively mild (<550^{o}C), only small amounts of new, highly-condensed PAHs are formed during catalytic cracking of the heavy distillate fractions. Figure 3-2 shows the PAH profiles (fraction of total PAHs represented by each PAH) of typical gasoline, diesel fuel, and crude oil.

Major pyrogenic PAH sources include fuel combustion exhaust emissions, combustion ash and other debris, and high-temperature combustion residues (tars and black carbon) from MGPs (associated with coal or petroleum coking) and steel and aluminum smelting, and commercial products from these items such as creosote and various tar products. Because of the high temperature of formation (≥700°C), pyrogenic PAH assemblages are dominated by the more thermally stable linear and unalkylated PAHs.

PAH assemblages in the environment contain parent PAHs and alkyl PAHs with one or more alkyl carbons bonded to aromatic carbons. The relative abundance of parent PAHs and their alkyl homologues in PAH assemblages in environmental samples is used frequently for identifying and characterizing hydrocarbon sources and interpreting the effects of natural weathering processes. Figure 3-2 shows the PAH profiles for three petrogenic samples (gasoline, diesel fuel, and crude oil), and Figure 3-6 shows the PAH concentrations in heavy fuel oil #6. Figure 3-3 illustrates the PAH profiles for two pyrogenic samples (coal tar and creosote). The petroleum samples are relatively enriched in the naphthalene homologous series PAHs (N0 - N4) and the phenanthrene series (P0 - P4). The gasoline and diesel fuel contain only traces of a few 4- through 6-ring PAHs, due to fractionation during the distillation process. The heavy fuel oil (Figure 3-6) contains relatively high concentrations of alkyl fluoranthenes/pyrenes and chrysenes. Alkyl-PAHs are more abundant than the parent PAHs in all of the petrogenic PAH assemblages (Figure 3-7).

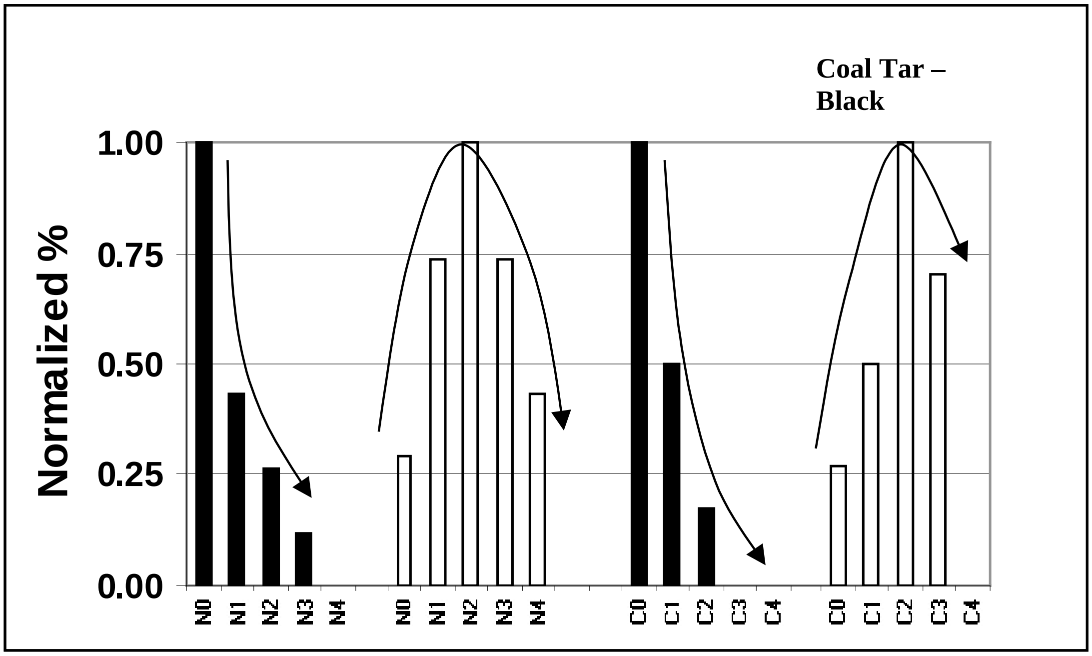


Figure 3-7. Profiles of the Naphthalene (*N*) and Chrysene (*C*) Distributions in Pyrogenic (Black) and Petrogenic (Gray) PAH Assemblages (from Neff *et al.*, 2005)

In contrast to the petroleum samples, the PAHs in the pyrogenic source material are enriched in higher-molecular-weight, 4- through 6-ring PAHs (Figure 3-3). Creosote, a distilled product of coal tar or petroleum, has a noticeably higher concentration of naphthalene than coal tar. The parent PAHs are more abundant than any of the corresponding alkyl homologues (Figure 3-7).

PAH concentrations usually are markedly different in petrogenic and pyrogenic source materials, and this difference can be useful in characterizing PAH sources and extent of weathering in environmental samples. The unweathered crude oil and distillate fuel samples in Figure 3-2 contain only 0.6% to 2.8% dry weight PAHs; the heavy fuel oil, a residual oil fraction, contains about 9% total PAHs. The pyrogenic coal tar and creosote samples in Figure 3-3 contain 27% and 20% dry weight PAHs, respectively. Some heavy coal tars from coal coaking at MGPs may contain more than 80% total PAHs (Neff, 1979). Even small quantities entering waterways can contribute significant quantities of PAHs to sediments because of the high relative percentage of PAHs in these pyrogenic source materials.

Environmental weathering often removes the parent PAHs more rapidly than their alkylated homologues from pyrogenic PAH assemblages. Therefore, the PAH profile of a weathered pyrogenic PAH assemblage may resemble the bell-shaped profile of a fresh petrogenic PAH assemblage. When fresh and weathered mixed petrogenic and pyrogenic PAH assemblages are encountered, a more in-depth analysis that extends beyond simple visual evaluation of TPH and PAH fingerprints may be necessary.

3.4.2.3 Understanding Urban Background Sediments. The characterization of urban background PAHs is important for source control and development of sediment remediation strategies. Understanding and characterizing the contaminant contribution at an MNR site that can be attributed to urban-industrial background in sediments is essential for recognizing and assessing the inputs and contributions to hydrocarbon contamination of sediments from point (including upland sites) and non-point sources (Stout *et al.*, 2004). Sediment remediation strategies, including MNR, must consider the potential for recontamination or concentration plateaus in surface sediments due to continuing inputs from persistent background PAHs from uncontrollable urban sources (air deposition, road runoff, asphalt leachate, etc.).

The urban background hydrocarbons present in sediments are derived and delivered from non-point sources and diffuse transport processes (*e.g.*, storm water runoff, surface runoff from asphalt roadways, direct atmospheric deposition, and small but persistent discharges) (Stout *et al.*, 2004). Urban background PAHs enter waterways from numerous chronic non-point pyrogenic and petrogenic sources and are added to PAHs from the targeted point sources that contaminated the site undergoing remediation. Pyrogenic PAHs usually are most abundant and sources include exhaust emissions (including BC) from internal combustion engines and burning of fossil fuels, wood, and other organic matter, rainout and dry fallout of particulate and vapor phase PAHs from the atmosphere, and PAHs associated with BC from wear of vehicle tires (Neff, 1979). Petrogenic urban background sources include road runoff containing lubricating and hydraulic oils, fuel oils from accidental spills, and leachate and wear from asphalt pavement.

These PAHs enter waterways via atmospheric deposition and in combined sewer overflows and storm water runoff. Although urban background sources contain both pyrogenic and petrogenic PAH signatures, the urban background PAH assemblage in urban fresh water and estuarine sediments usually is dominated by pyrogenic PAHs (Eganhouse *et al.*, 1982; Stout *et al.*, 2004; Brown and Peake, 2006; Stein *et al.*, 2006).

The pyrogenic PAHs in urban waterway sediments usually come primarily from deposition of particulate and vapor phase PAHs from the urban atmosphere. Simcik *et al.* (1999) reported that atmospheric deposition is the major source of PAHs to the sediments and water column particulate phase of Lake Michigan off Chicago. Most of the PAHs are from combustion sources: 48% from coal combustion, 26% from natural gas combustion, 14% from coke ovens, and 9% from gasoline and diesel vehicular emissions. Much of the petrogenic PAHs in urban runoff comes from storm water runoff from parking lots, highways, and gas stations (Smith *et al.*, 2000).

No single “representative” urban background fingerprint or hydrocarbon concentration exists since the total PAH concentration, relative age of the PAH contamination, and mixture of PAHs varies spatially (*i.e.*, across different urban watersheds) and also geologically. The residues of combustion byproducts from fossil fuels, however, have produced a modern urban background PAH signature in areas affected by hydrocarbon contamination. Background hydrocarbon assemblages tend to be dominated by: 1) a variably-shaped UCM in the residual (> C_{20}) range, and 2) a variable distribution of 4- to 6-ring TCL non-alkylated PAHs (Stout *et al.*, 2004). The mean TPH concentration in 280 sediment samples from nine well-studied urban waterways on the east and west coasts of the United States was 415 mg/kg (dry wt); the total TCL PAHs concentration was less than 20 mg/kg in 96% of the sediments studied. TPH and PAH fingerprints of a characteristic urban background sediment sample collected from the Wyckoff/Eagle Harbor Superfund Site (Bainbridge Island, Washington) are shown in Figure 3-8 (Stout *et al.*, 2001b). Notably, PAHs from each homologous series exhibit a skewed pyrogenic pattern despite the presence of a petroleum component, indicative of an urban source PAH signature of contamination.

Recognizing an urban background PAH signature in sediments is an important component of an MNR study. Doing so can help distinguish the urban background component of PAHs in sediments from hydrocarbons introduced from point sources. The potential for sediment recontamination due to the persistent influx of background PAHs should be addressed in any sediment remedy, including MNR (Brenner *et al.*, 2001).

3.4.2.4 Characterization of Hydrocarbon Weathering. Fingerprinting analyses can provide information about the state and rate of hydrocarbon weathering in addition to characterizing and differentiating hydrocarbon sources in sediment samples. Fingerprinting to characterize hydrocarbon sources is virtually indistinguishable from fingerprinting to characterize weathering processes. Both rely on detailed chemistry to identify and characterize unique chemical hydrocarbon patterns. For MNR, it is very valuable to estimate the rate of weathering loss due to all processes of individual and total PAHs from contaminated field sediments. However, because of the extreme variability in loss rates and the number of physical, chemical, and biological factors in the environment affecting loss rates, it usually is not possible to accurately estimate weathering rates of PAHs in sediments.

The effects of weathering processes (*i.e.*, dissolution, volatilization, photooxidation, and biodegradation) on concentrations and compositions of hydrocarbon assemblages in sediments have been studied in both natural (Connan, 1984; Palmer, 1993) and controlled laboratory conditions (Huesemann, 1995; McMillen *et al.*, 1995). PAH weathering processes and their effects on the composition and concentrations of PAHs from different sources in sediments were discussed above in Sections 3.2 and 3.3.

Most studies of hydrocarbon weathering in sediments have focused on biodegradation because, under oxidizing (aerobic) conditions for sediments at moderate temperatures (5 to 30°C), microbial biodegradation is the most rapid weathering process. All non-alkylated (parent) PAHs biodegrade aerobically, including the TCL PAHs (Douglas *et al.*, 1992; Prince and Drake, 1999; Nadalig *et al.*, 2000; LeBlanc and Brownawell, 2002). Some PAHs also degrade under anaerobic conditions that are associated with microbially-mediated sulfate reduction (Coates *et al.*, 1996, 1997; Rothermich *et al.*, 2002), nitrate reduction (Milhelcic and Luthy, 1991; Durant *et al.*, 1995), and methanogenesis (Sharak Genthner *et al.*, 1997). Sulfate-reducing conditions are particularly relevant for marine sediments due to high natural sulfate concentrations (~28 mM) in sea water. Nitrogen reduction and methanogenesis usually are more important in anoxic fresh water sediments where sulfate concentrations may be low. The relative rates of degradation of the different hydrocarbon classes in petroleum in sediments are discussed in Section 3.3.1.

Rates of PAH biodegradation vary widely depending on PAH source and form (see Section 3.3), molecular weight, structural configuration, oxygen concentration in and permeability of sediment, and, for anoxic sediments, electron acceptor availability (Bressler and Gray, 2003). Pyrogenic PAH assemblages, particularly if they are adsorbed to BC, weather more slowly than do petrogenic PAH assemblages, which are often associated with NAPL (oil, coal tar, or creosote). Generally, PAH biodegradation rates decrease with increasing numbers of aromatic rings, increasing molecular weight, and decreasing solubility (Prince *et al.*, 2003). Parent, non-alkylated PAHs usually degrade more rapidly than their alkylated derivatives, and biodegradation rates decrease with increasing alkylation (Elmendorf *et al.*, 1994; MacGillivray and Shiaris, 1994; Burns *et al.*, 1997; Prince *et al.*, 2003). Different alkyl congeners of some PAHs may biodegrade at different rates (Elmendorf *et al.*, 1994; Wang and Fingas, 1995; Mazeas and Budzinski, 2002). This tendency usually is attributed to steric hindrances of various methyl group positions.

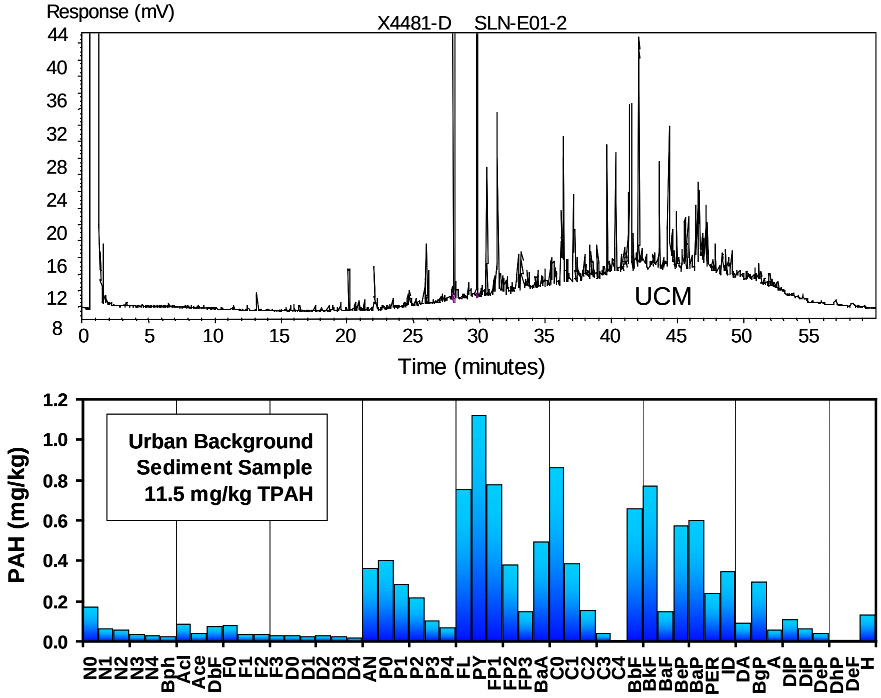


Figure 3-8. THC Fingerprint (top) and PAH Histogram (bottom) of a Sediment Sample Containing Hydrocarbons Attributed to Non-point Sources (from Stout *et al.*, 2001a)

Detailed composition data (individual and total PAHs and hydrocarbon biomarkers) are needed for fresh source samples (samples of the spilled crude oil, heavy fuel oil, coal tar, or creosote) and sediment samples that are collected periodically over several years at the contaminated sediment site in order to characterize chemical and biological weathering of PAH mixtures in sediments. Rates of biodegradation of PAHs in crude oil and some pyrogenic (*e.g.*, coal tar) NAPLs in sediment can be assessed by comparing mass reduction rates of individual and total PAHs to those of petroleum biomarker compounds. Petroleum biomarkers are non-polar organic compounds in the original source sample that are highly resistant to biodegradation or other weathering loss (Wang and Stout, 2007; Peters *et al.*, 2008). A C_{30}-hopane, 17α(H)hopane, or 21β(H)hopane is used frequently as a biomarker in crude and heavy fuel oils. If this biomarker is not analyzed or is not present in a source sample (*e.g.*, middle distillate fuel oils, coal tar, or creosote), a congener group of higher-molecular-weight PAHs, such as total C_0-C_4 chrysenes, can be used. Most light and middle distillates, such as gasoline and diesel fuel, do not contain any high-molecular-weight degradation-resistant PAHs or petroleum biomarkers, so it may not be possible to use biomarker measures of PAH depletion in sediments containing these hydrocarbon mixtures. Depletion (loss) of individual or total PAHs in oil-, coal tar-, or creosote-contaminated sediment can be estimated with the equation:

$$\%\ \text{loss of component X} = [1 - (C_x/C_{con})_w/(C_x/C_{con})_s] \times 100 \qquad \text{(Eq. 3.9)}$$

where: C_x = mass concentration of component x in oil
C_{con} = mass concentration of conserved species (biomarker) in oil
w = weathered sample
s = source or reference sample.

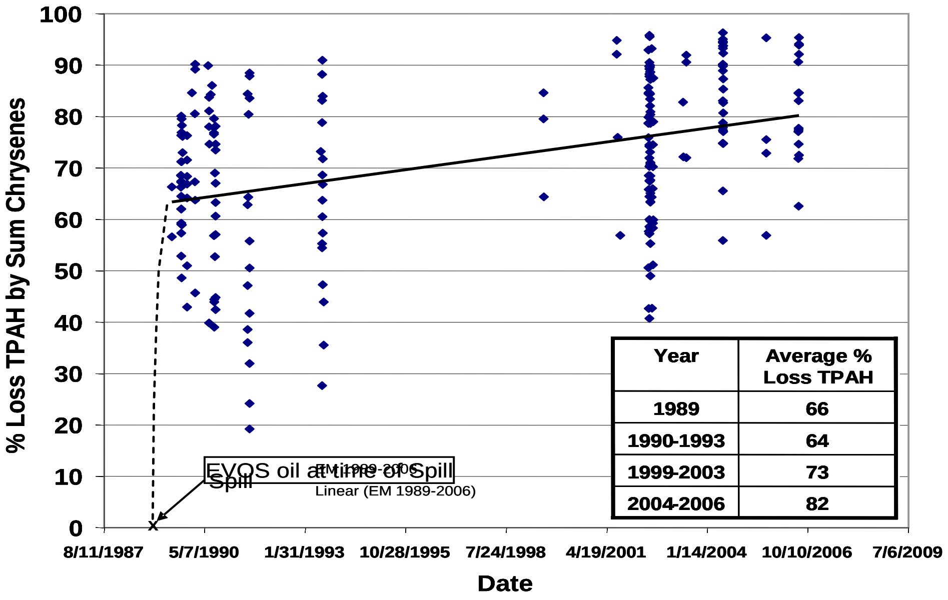
Atlas and Bragg (2007) used this approach to estimate the depletion of petrogenic PAHs from residues of the North Slope (Alaskan) crude oil buried in intertidal sediments after the *Exxon Valdez* oil spill. Source samples of unweathered crude oil from the tanker and approximately 200 oil-contaminated subsurface sediment samples were analyzed for individual and total PAHs and sterane/triterpane petroleum biomarkers by advanced analytical methods (Douglas *et al.*, 2004). Initial loss of PAHs from sediments was rapid, caused primarily by water-washing and volatilization. Total PAHs were depleted by an average of 66% in oil-contaminated sediment samples collected during the summer after the spill (Figure 3-9). However, depletion was extremely variable in the 4 years after the spill, with depletions ranging from less than 20% to more than 90%. Mean PAH depletion from buried oil residues in intertidal sediments increased from 64% to 66% in 1989 through 1993 to 73% in 1999 through 2003 and 82% in 2004 through 2006. PAH degradation was observed to be most rapid shortly after the spill, with the degradation rate observed to decrease substantially within the 10 years after the spill. However, PAH degradation was still occurring 17 years after the spill, but at a low rate. The weathered, spilled oil remaining in intertidal sediments 10 years or more after the spill was sequestered in fine sediment layers under boulder-cobble armor and was not readily bioaccessible for continued microbial biodegradation.

Stout *et al.* (2001b) provides examples of unweathered and weathered petrogenic and pyrogenic sources. Knowledge of specific PAH transformation processes permits the prediction of how weathering alters the PAH distribution in sediments. PAH weathering is expected to:

- Preferentially reduce the proportion of lower-molecular-weight (2- and 3-ring) PAHs, thereby increasing the proportion of higher-molecular-weight (4- to 6-ring) PAHs; and
- Preferentially reduce the proportion of non-alkylated PAHs relative to alkylated PAHs, thereby increasing the proportion of alkylated PAHs.

The weathering trends for petrogenic and pyrogenic PAH sources can reduce or eliminate acute exposures to lower-molecular-weight PAHs (*e.g.*, naphthalene, phenanthrene, and their alkyl homologues) that are more mobile in the environment than the higher-molecular-weight PAHs. Weathering of higher-molecular-weight (4- to 6-ring) PAHs often is slow as the relative concentrations (as percent of total PAHs [tPAHs]) of high-molecular-weight PAHs in the oil residues in sediments often increase during weathering, even though the total mass of oil residues and PAHs in sediment decreases with weathering. The rate of natural attenuation of high-molecular-weight PAHs in sediments from oil, coal tar, and creosote spills may not be sufficient (decades) to warrant long-term surveillance by MNR unless the sediments are buried and inaccessible to surface biological receptors.

3.4.2.5 **Summary of Hydrocarbon Fingerprinting and Weathering Processes**. Hydrocarbon characterization from the application of hydrocarbon fingerprinting (*i.e.*, forensics), particularly PAH fingerprinting, is essential for providing valuable site information regarding identification and differentiation of contaminant sources including urban/industrial background PAH levels and sources; the magnitude and extent of hydrocarbon weathering; the impact of weathering on the distribution of PAHs in sediments; and, ultimately, providing critical lines-of-evidence to evaluate the suitability of MNR.



Year	Average % Loss TPAH
1989	66
1990-1993	64
1999-2003	73
2004-2006	82

Figure 3-9. Percent Loss of Total PAHs from Weathered North Slope Crude Oil in Subsurface Sediments on the Shore at Sites Where Oil Has Persisted for 17 Years after the *Exxon Valdez* Oil Spill
(Based on sum of chrysenes as the hydrocarbon biomarker; average percent total PAH losses relative to original concentrations are given for four time intervals [from Atlas and Bragg, 2007].)

A thorough understanding of the sources of hydrocarbons in site sediments and the fate and transport of PAHs in sediments is needed for studies intended to monitor the recovery of ecological receptors at hydrocarbon-contaminated sediment sites. This is particularly true for unidentified sources that can persist after known sources are controlled. The pervasive example of one such persistent source is urban background that must be characterized and evaluated independently from known point sources. Obviously, unrecognized hydrocarbon sources could easily confound an MNR analysis by erroneously increasing unresolved surface sediment concentration trends and/or surface sediment chemical concentration plateaus, or contributing to recontamination after remedy implementation.

To illustrate this approach, a forensic case study from the Wyckoff/Eagle Harbor Superfund Site (Bainbridge Island, WA) is shown in Highlights 3-1 and 3-2. As part of a program to achieve a better understanding of the mechanisms contributing to the natural recovery of ecological resources at contaminated sediment sites, EPA conducted a study of sources and fate of hydrocarbon contamination at the Wyckoff/Eagle Harbor Superfund Site (Stout *et al*., 2001b; Brenner *et al*., 2001). Chemical forensic analyses were employed to identify hydrocarbon sources, including creosote, that were used as a wood preservative at the former Wyckoff facility.

The urban sediments in Eagle Harbor were contaminated with urban background and creosote. The relative contributions of different PAH sources were determined through fingerprinting techniques (as described above). The fingerprinting analysis became a much more powerful tool when coupled with PAH spatial concentration gradients and temporal relationships relative to known or suspected point sources identified through historical research. This study site demonstrates how a coupled spatial and temporal understanding of PAH contamination obtained through the characterization of sediment core profiles, combined with radiogenic isotopic age-dating (*e.g.*, ^{137}Cs or ^{210}Pb; Brenner *et* *al.*, 2001) permits an evaluation of the PAH signatures present in sediments deposited at different locations and time intervals, which may be used to better recognize the contribution of historical and modern sources to the MNR study area.

3.4.3 Chemical Fingerprinting of PCBs as Part of MNR. This section summarizes techniques for characterization of PCB source and weathering patterns through the use of chemical fingerprinting techniques as applied specifically to the analysis of PCBs. As with PAHs and other HOCs, the fate of PCBs in sediments is controlled by sorption, dissolution, volatilization, and biotransformation/ biodegradation processes. Weathering of PCBs in sediments by these processes was discussed earlier in Sections 3.2 and 3.3.2. The number and positions of chlorines on the biphenyl molecule and the oxidation/reduction condition of the PCB-contaminated sediments affect the rate of attenuation of complex PCB mixtures in sediments. Sorption is the dominant process influencing the fate of PCBs in sediments, and is of particular significance because strength of sorption influences the rate of biodegradation and other weathering processes by controlling the concentration of dissolved (bioavailable) PCBs in sediment pore water and PCB accessibility to sediment microbes (Hickey, 1999). The strength of sorption of PCB congeners to sediment organic matter (proportional to log K_{oc}: Table 3-6) increases with degree of chlorination of the biphenyl molecule.

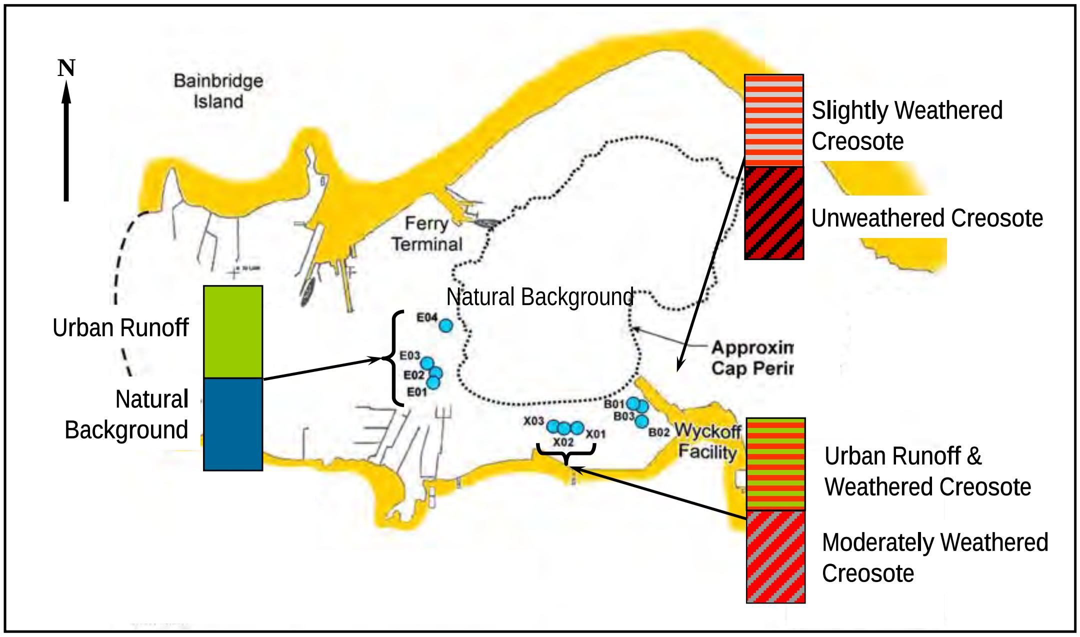
The primary factors affecting PCB biotransformation are the number and pattern of chlorine substituents and the redox state of the sediments. PCBs behave similarly to PAHs and PCDDs/PCDFs in aerobic sediments; low-molecular-weight PCBs (*e.g.*, ≤ 3 chlorines) are preferentially weathered and biodegraded. The ability of aerobic bacteria to degrade PCBs decreases with increased chlorination; congeners with five or more chlorines are relatively recalcitrant to aerobic biodegradation (Bedard *et al.*, 1986; Abramowicz, 1990; Abramowicz, 1995).

Under anaerobic conditions, the primary metabolic pathway is reductive dechlorination in which chlorine removal and substitution with hydrogen by bacteria results in a chemically reduced organic compound with fewer chlorines (Brown *et al.*, 1987; Mohn and Tiedje, 1992; Zanaroli *et al.*, 2006). Highly chlorinated PCB congeners are reductively dechlorinated with the accumulation of mono-, di-, and tri-chlorobiphenyls (Bedard and Quensen, 1995; Wiegel and Wu, 2000). Reductive dechlorination preferentially removes chlorines from the *meta* and *para* positions and replaces them with hydrogen atoms. Dechlorination results in a decrease in the toxicity of complex PCB mixtures in sediments (Section 3.3.2).

Forensic techniques may be used to identify different commercial PCB mixtures (*e.g.*, Aroclors) and their weathering state, and to differentiate the various complex physical, chemical, or biological processes that are altering the composition of mixtures over time. Johnson *et al.* (2002) provides a comprehensive discussion of environmental forensics for PCBs. Examples of PCB congener interpretations and fingerprinting analyses are included in this section to aid the reader in understanding the application of environmental forensics for PCB mixtures, which may also be relevant to other halogenated hydrocarbon compounds in the environment, such as PCDDs/PCDFs, that are susceptible to reductive dechlorination. EPA's NRMRL has been characterizing biological, chemical, and physical MNR processes at the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site since 2000.

Highlight 3-1. Hydrocarbon MNR Case Study – Creosote Impacted Sediments

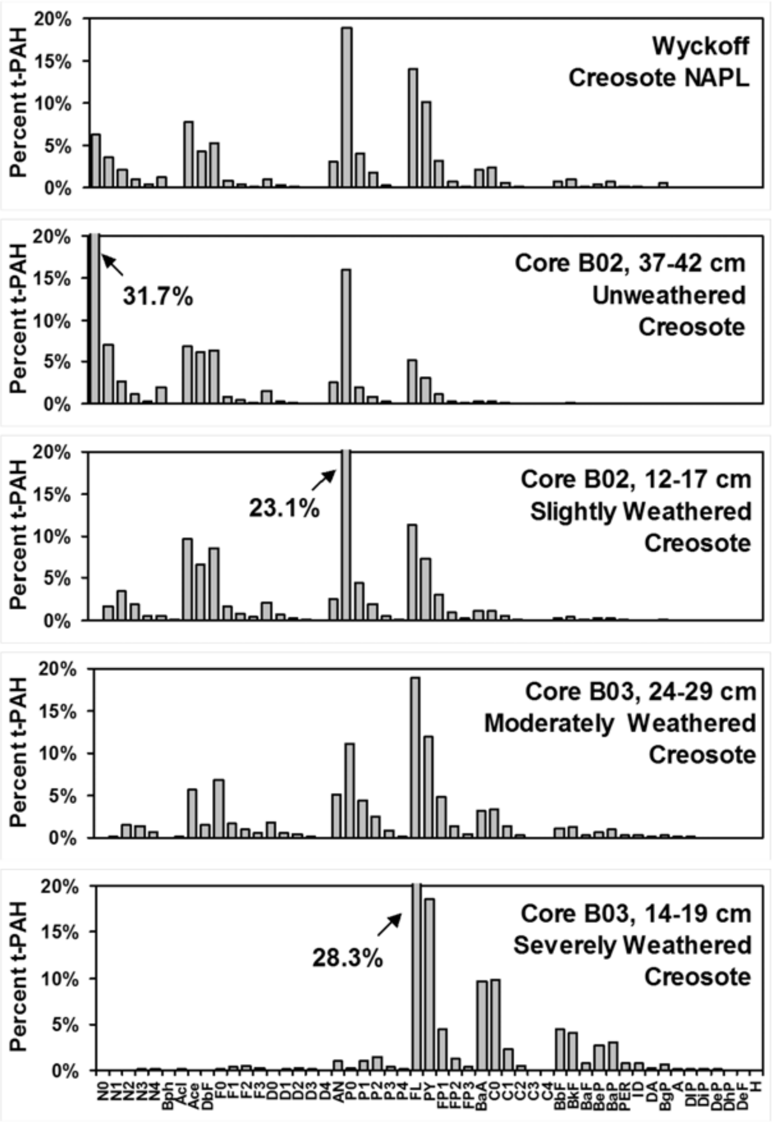
Eagle Harbor is a shallow marine embayment on Bainbridge Island, located approximately 10 miles due west of Seattle, WA. Sediment cores (<100 cm) were collected from 10 locations. Cores were age-dated with ^{210}Pb and ^{137}Cs (Brenner *et al.*, 2001), and chemical fingerprinting was used to characterize PAH sources and weathering processes (Stout *et al.*, 2001b). Fingerprinting revealed three primary hydrocarbon sources (urban background, natural background, and creosote), as well as various degrees of source weathering. Principal component analysis (PCA) was used to identify the spatial distribution of the natural background-, urban background-, and creosote-dominated samples; weathered PAH signatures; and source mixtures. Creosote signatures were mostly in sediments from the vicinity of the former creosoting operation. However, the absence of creosote near the center of the harbor was unexpected. In this area, surface sediments were dominated by urban background, attributed primarily to ferry terminal traffic on the north shore of the harbor (Brenner *et al.*, 2001). Natural background signatures were observed only in buried sediments where age-dated deposition preceded industrialization and urbanization of the area. Urban background and creosote signatures probably obscured the natural background signature at shallower depths.



Creosote, urban runoff, and natural background distributions in Eagle Harbor sediment cores (adapted from Brenner *et al.*, 2001). The vertical columns represent the tops and bottoms of vertically profiled sediment cores (~40 to ~70 cm deep).

Highlight 3-2. Creosote Weathering Trends in Eagle Harbor Sediments

This highlight shows selected examples that exhibited varying degrees of PAH weathering. Weathering not only changes the chemical fingerprint, but also can result in irreversible sorption to sediments. Eagle Harbor sediments with a dominant creosote chemical signature were examined to evaluate the extent of creosote weathering to determine the natural recovery potential of the creosote-impacted sediments. The shift from unweathered to more highly-weathered creosote was characterized by a progressive decrease in the percentage of low-molecular-weight (2- and 3-ring) PAHs. The severely weathered creosote sample contained a very low percentage of 2- and 3-ring PAHs, but exhibited a sharp increase in the proportion of fluoranthene and higher-molecular-weight PAHs. However, because of mass reduction in creosote during weathering, concentrations of all PAHs decreased in the sediment (Brenner *et al.*, 2001).



Normalized PAH histograms for sediments containing increasingly weathered creosote from Eagle Harbor (from Brenner *et al.*, 2001)

3.4.3.1 Properties of PCB Mixtures. As discussed in Section 3.1.2.2, a PCB molecule is composed of a biphenyl molecule with chlorines bonded to between one and 10 of the available benzene carbons (Figure 3-4). The possible 209 PCB congeners are distinguished by the number and position of the chlorine atoms on the biphenyl molecule (Table 3-3). The degree of chlorination (homologue groups) and physical properties of the seven most common Aroclors are summarized in Table 3-6, and congener profiles of five Aroclors are summarized in Figure 3-10. One of the most important considerations when evaluating PCBs in environmental samples is whether to measure Aroclors, homologue groups, or individual congeners. Detailed forensic analysis of PCB mixtures used to identify the source of the contamination by comparison with the original Aroclor mixture and extent of degradation (*e.g.*, dechlorination) in environmental samples typically will quantify 50 to 110 of the most environmentally relevant congeners.

The selection of which measure of PCBs should be a site-specific decision based on information about the sources of PCB contamination, concerns about congener-specific toxicity, the need to characterize PCB weathering processes, comparability between multiple data sets, and the cost of analyses (EPA, 2005a). The NRC's (2001) *A Risk Management Strategy for PCB-Contaminated Sediments* provides an overview of PCB analytical methods for Aroclor, congener, and homologue analyses. Aroclor-equivalent methods generate a single t-PCB concentration based on comparison of the sample chromatogram with those of the original Aroclor formulations. Even though t-PCB analyses are relatively inexpensive and may be useful for general assessment and screening of PCB concentrations in sediments, they provide little information on PCB sources and long-term fate.

At many sites, PCBs no longer resemble their original formulations due to weathering. PCB homologue and/or PCB congener analyses are necessary when more detailed information is required. For homologue and congener analyses, t-PCB concentrations are determined by summing congener or homologue concentrations. Summing congeners or homologues provides more accurate t-PCB concentration values than the Aroclor t-PCB method (NRC, 2001).

Congener analyses are necessary to identify sources and to evaluate congener distribution changes over time or distance from a source. Congener analysis is the most reliable approach for characterizing the PCB contamination in environmental samples that have undergone significant changes from the original source material or if the PCB mixtures in site sediments are derived from releases of multiple commercial PCB mixtures. Homologue methods are similar to the congener method except that they quantify entire homologue groups to decrease analytical and QA/QC times and costs. A dedicated PCB homologue analysis can be performed concurrently with a congener analysis if GC/low resolution mass spectrometry-SIM is used.

Congener analyte lists are based on the relative toxicity of the individual congeners and their relative abundance in commercial Aroclor mixtures and the environment. Because PCB congener behavior and transformation processes are well understood, characterization of PCB sources and weathering patterns can be obtained with a well selected set of approximately 50 to 100 congeners. Table 3-3 summarizes the complete PCB congener analyte list; most analyte lists are relatively consistent among laboratories, though they may differ by some congeners and the total number of congeners resolved. About 97% to 99% of the PCB congeners in Table 3-3 are targeted in most environmental samples and analyses. Eighteen congeners are targeted in the National Status and Trends (NS&T) and EPA Environmental Monitoring and Assessment Program methods (NRC, 2001). The sum of these 18 congeners typically makes up between 45% and 55% of the PCBs in many environmental samples (more if the congener distribution is predominantly higher in molecular weight than Aroclor 1254, and less if the distribution has a lower molecular weight than that of Aroclor 1248).

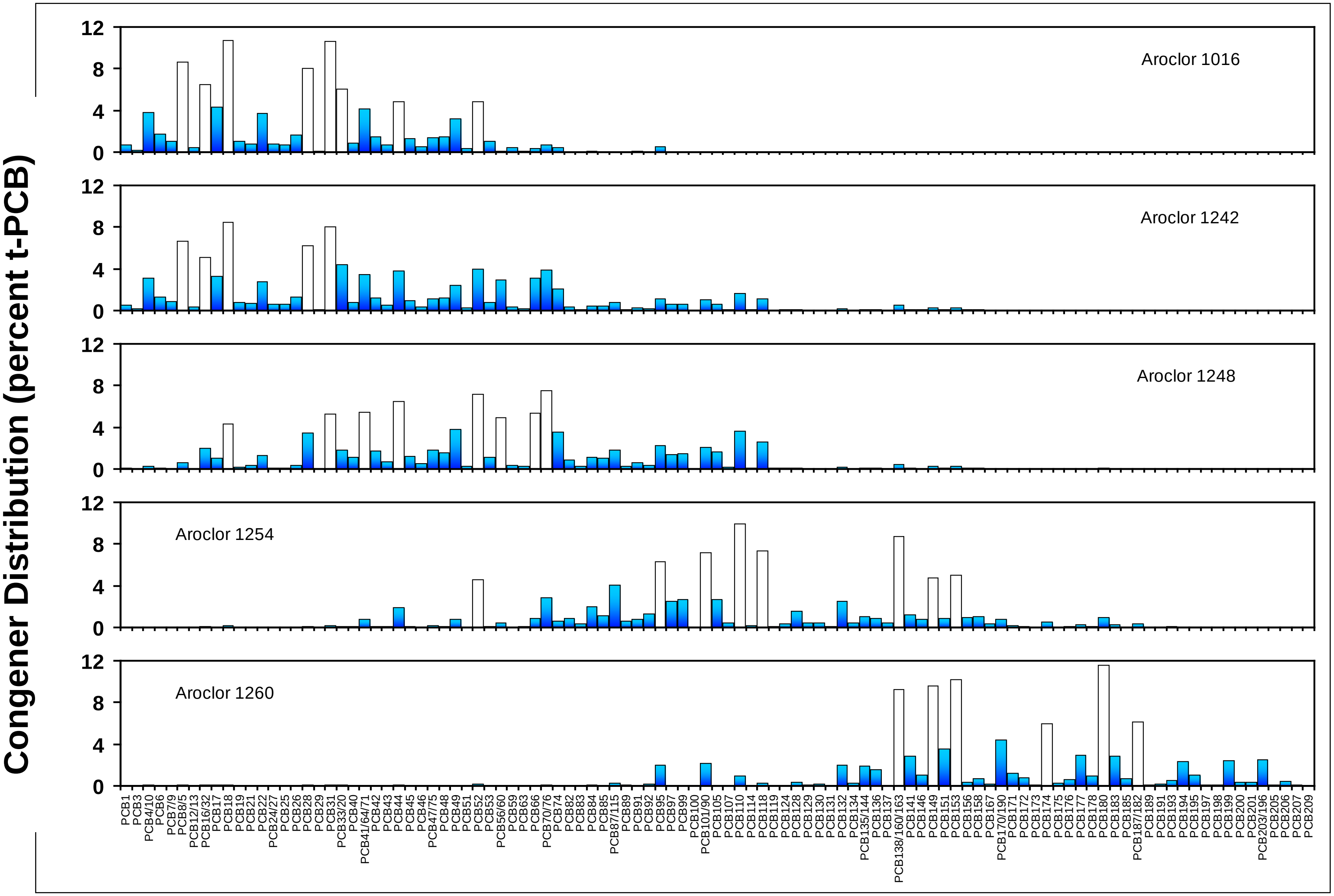


Figure 3-10. Congener Distribution Histograms for Five Common Aroclor Mixtures
(Data provided by Battelle [Duxbury, MA], 2011; Chromatography resolved 105 congeners or coeluted congener groups identified by IUPAC number.)

Selecting the most appropriate analytical method to characterize PCB-contaminated sediments, which can affect long-term project costs, is important to the level of interpretation possible with the data and for comparison across multiple data sets. Whereas analytical costs may be lower using the NS&T Aroclor method, this method often provides insufficient information for source identification and characterizing fate and transport that is possible through a more detailed fingerprinting approach. Hence, long-term costs may be higher if samples have to be reanalyzed, more samples are necessary, or if MDLs are high, resulting in higher assumed contaminant concentrations for samples below the MDL. Resolving Aroclor mixtures, distinguishing among various sources, and quantifying PCB weathering in sediments generally requires the specificity provided by congener or, to a lesser degree, homologue analyses. As is the case with other aspects of MNR, the level of sampling and type and degree of chemical analysis should be tailored to the risk and ecological importance of the PCB-contaminated site.

The second challenge is that most Aroclor mixtures begin to weather immediately upon release into the environment. Weathering can significantly alter congener distribution patterns making it difficult, and sometimes impossible, to identify the original source. The resulting congener distribution may not resemble any Aroclor, or it may resemble a more- or less-chlorinated Aroclor mixture depending on the type of weathering (Chiarenzelli *et al.*, 1997; Magar *et al.*, 2005a). The similarities between congener histograms from field samples and source patterns are usually determined by visual observation. However, they can also be evaluated by calculating the cosine theta similarity metric (cos θ) between the individual sample compositions compared to Aroclor source and alteration patterns (Magar *et al.*, 2005a; Johnson *et al.*, 2000, 2002; Davis, 1986). The cos θ metric calculates the cosine of the angle between two multivariate vectors, in this case the two matrices formed by the 50 to 100+ congeners included in the analysis for each sample. A cos θ value of 0 would indicate two completely dissimilar, orthogonal vectors. A cos θ value of 1.0 would indicate two identical vectors.

An example of sample source characterization for surface sediment samples collected from the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site is presented in Highlight 3-3. Field sampling and forensics analyses were used to characterize surface sediment congener distributions and relate those distributions to historically-released Aroclor mixtures.

3.4.3.2 Characterization of PCB Weathering. As discussed in Sections 3.2 and 3.3.2, PCB mixtures undergo several weathering processes following release to the environment including dissolution, volatilization, sorption to and desorption from dissolved and particulate organic matter, and aerobic and anaerobic biodegradation by water, soil, and sediment bacteria and fungi. The most important weathering mechanisms for PCB mixtures in sediments include oxidative and reductive biodegradation, sorption, and dissolution. These processes may be influenced by sedimentation, sediment organic carbon quality and concentration, sediment redox potential, and abiotic (bed transport) and biological (bioturbation) mixing of sediments. The significance of dissolution, photooxidation, and volatilization processes become greater in contaminated surface sediments that are resuspended and re-enter the water column or that are directly exposed to the atmosphere at low water levels (*e.g.*, intertidal marine sediments).

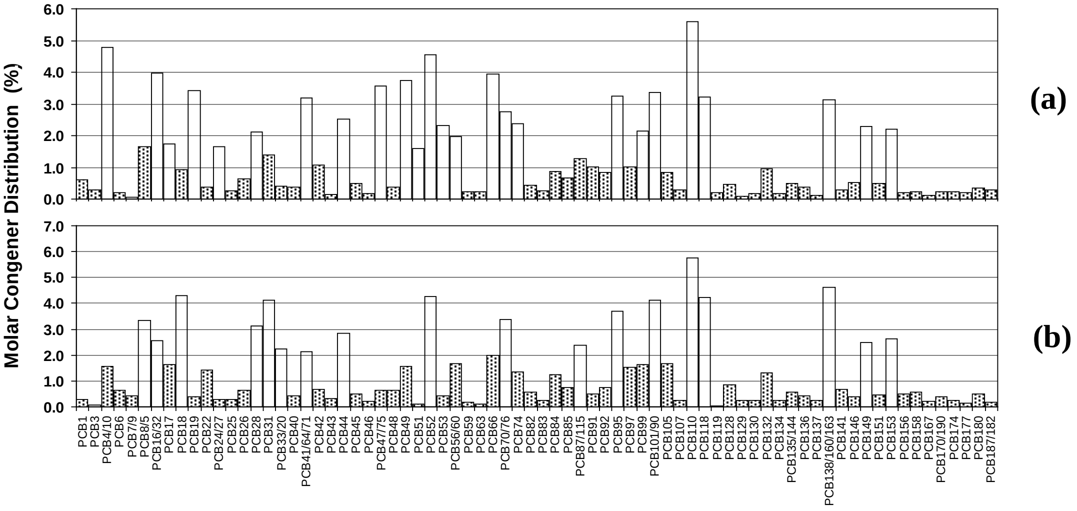
Evaporation, dissolution, and aerobic microbial degradation selectively remove the less-chlorinated PCB homologue groups from PCB mixtures in sediments. Photooxidation and anaerobic, bacterial reductive dechlorination selectively remove the more highly-chlorinated PCB homologue groups from sediments. Hydrophobicity, which is proportional to log K_{ow} and associated log K_{oc}, increases and vapor pressure and aqueous solubility decrease with increasing levels of PCB chlorination (Table 3-4). The most highly-chlorinated, most hydrophobic congeners are approximately 10,000 times more hydrophobic than their least chlorinated, most mobile counterparts. Thus, the strength of sorption to sediment organic matter increases and evaporation and dissolution decrease with increasing PCB chlorination, decreasing the mobility and bioavailability of the more highly-chlorinated PCB congeners.

Highlight 3-3. Characterization of Lake Hartwell Surface Sediments by Comparison with Known Aroclors and Aroclor Mixtures

At Lake Hartwell, SC, a search of historical records revealed that the former Sangamo-Weston plant used Aroclors 1016, 1242, and 1254 (Magar *et al.*, 2005a, and references therein). Congener distributions in surface sediment samples were characterized by comparing them with various mathematically-derived mixtures of these three Aroclors. The surface sediment congener distributions most strongly resembled a 50/50 mixture of Aroclors 1242 and 1254, particularly beginning from PCB26 (2,3′,5-TCB) (Magar *et al.*, 2005a).

A cosine θ similarity metric (cos θ) analysis was conducted to determine the similarity between surface sediment histograms and that of the 50/50 Aroclors 1242/1254 mixture. The cos θ values were near 1.0, suggesting similarity between field samples and the Aroclor mixture. The cos θ for the histograms shown in this highlight was 0.85, and the average cos θ value for 18 surface sediment samples (0 to 5 cm) was 0.648 ± 0.241. The similarity of the histograms was influenced by the degree of chlorination. For mono- through trichlorobiphenyl congeners, the average cos θ was 0.562 ± 0.105, compared to 0.875 ± 0.054 for tetra- through hexachlorobiphenyl congeners and 0.934 ± 0.045 for hepta- through decachlorobiphenyl congeners. The poorer correlation among the lower-chlorinated congeners could have been due to: 1) the onset of dechlorination in the upper 5 cm, resulting in the accumulation of lower-chlorinated congeners, 2) weathering during sediment transport, resulting in the loss of lower-chlorinated congeners, or 3) a combination of these phenomena. These factors, and the fact that the surface sediments did not resemble a single Aroclor, demonstrate the difficulties associated with comparing sample congener distributions with known Aroclor congener distributions.

At Lake Hartwell, deeper sediments exhibited a decreasing resemblance to Aroclors or Aroclor mixtures due, presumably, to their age and long exposure to dechlorination reactions. Surface sediments most closely resemble source patterns because they have undergone the least amount of dechlorination; however, they may experience aerobic degradation of the lower chlorinated congeners. Eventually, when these surface sediments are buried over time, they too will become anaerobic and will undergo dechlorination; with time, the congener distributions will look less and less like their sources.



PCB congener distributions in: (a) a Lake Hartwell surface sediment sample (1.6 mg/kg), and (b) a 50/50 distribution of Aroclors 1242 and 1254 (from Magar *et al.*, 2005a)

Evidence for PCB dechlorination can be obtained by comparing congener histograms for multiple samples that have been anaerobic for different lengths of time (Zanaroli *et al*., 2006). In laboratory studies, PCB-contaminated sediments containing inocula of different anaerobic bacteria are incubated under anaerobic conditions for long periods of time. The sediments are then sampled and analyzed periodically, enabling dechlorination rates and patterns to be monitored. In the field, dechlorination must be inferred by comparison of congener distributions from *in-situ* samples with known or inferred source distributions. Historical documents may provide information about the types and amounts of Aroclor mixtures used and released into the environment. Comparison of the congener distribution of historical sources may be inferred from record searches that reveal the types of Aroclor mixtures used in association with a source. Another strategy to surmise original PCB source and/or the specific Aroclor mixture responsible for a contaminated area is to compare surface sediment samples with progressively older, buried sediment samples (Bzdusek *et al*., 2006). Implicit in this second approach is the assumption that the surface sediments are characteristic of historical PCB sources, *i.e.*, when buried sediments once resided on the sediment surface, their congener distributions resembled the current surface sediment distributions.

Highlights 3-4 and 3-5 illustrate examples of PCB dechlorination in sediments from the Lake Hartwell site. In Highlight 3-4, congener shifts are compared visually and by subtracting the congener distribution in surface, less-altered PCBs from those in buried, extensively-dechlorinated PCB residuals. The result is a graph of the net dechlorination observed at a particular location in the lake. In Highlight 3-5, Lake Hartwell dechlorination was examined by plotting relative *ortho* and *meta* plus *para* chlorine concentrations per biphenyl molecule with sediment depth. The loss of *meta* plus *para* chlorines and the conservation of *ortho* chlorines provided very strong evidence of PCB dechlorination with sediment depth and age. Bzdusek *et al.* (2006) performed similar studies with Lake Harwell sediment cores and obtained similar results.

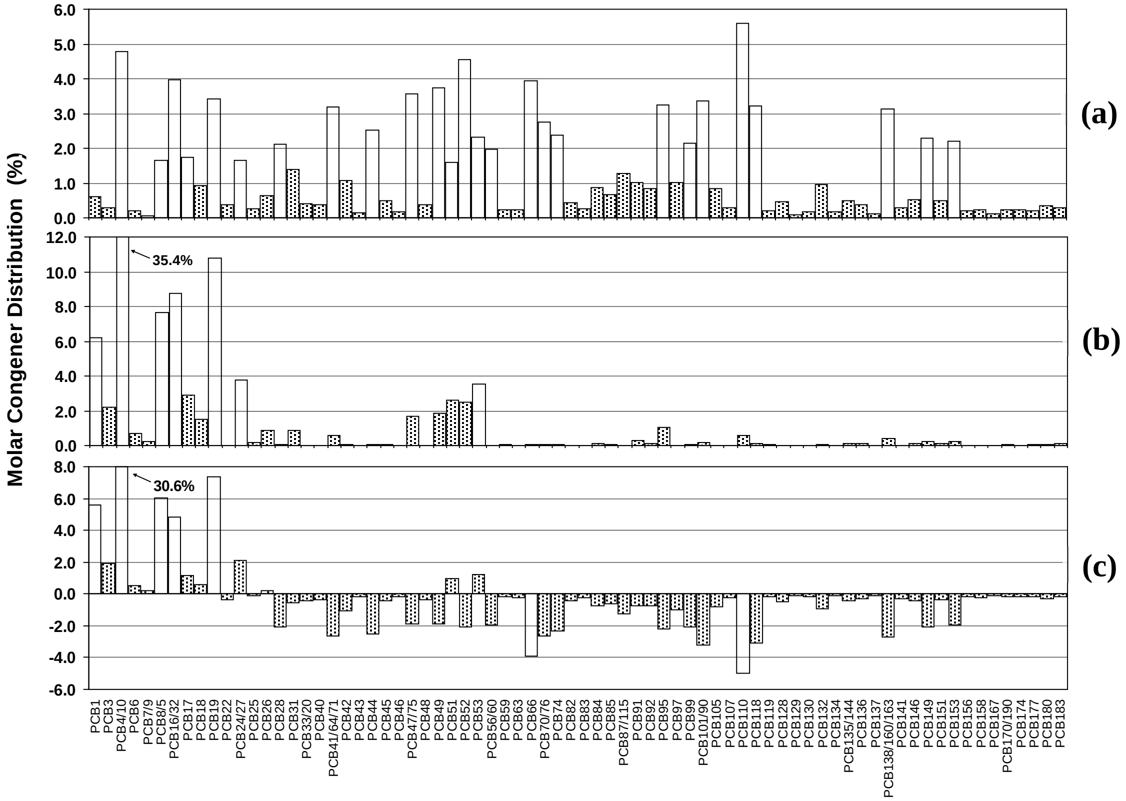
PCB dechlorination can be an important natural process leading to a reduction in toxicity of PCB-contaminated sediments and recovery of sediment-water ecosystems (as discussed above). However, the positive impact of dechlorination (*e.g.*, reduced mass and reduced toxicity) must be understood in the context of where in the sediment bed these reactions occur. Dechlorination is a progressive, anaerobic process. Most near-shore fresh water and marine sediments become anoxic at a depth of 0.5 to 10 cm below the sediment surface, depending on factors such as the concentration of biodegradable organic matter in the sediments, pore water flows, bioturbation, etc. Since reductive dechlorination is performed by obligate anaerobic bacteria, the extent of dechlorination, which usually reflects the time since deposition, increases with sediment depth so that surface sediments, which typically are aerobic and support benthic receptors and pose the greatest risk of environmental exposure, are likely to exhibit the least PCB dechlorination. The most highly-dechlorinated PCBs usually are in the deepest sediment layers deposited after the introduction of commercial PCBs. Consequently, whereas PCB dechlorination is likely to provide limited short-term risk reduction, it is a potentially beneficial process that, over time, can lead to the detoxification of buried sediments.

3.4.3.3 Multivariate Model Fingerprinting. Multivariate chemometric models, such as polytopic vector analysis (PVA), have been used frequently to characterize sources and alteration patterns of chlorinated organic compounds in complex environmental settings (Johnson *et al.*, 2000, 2002; Johnson and Quensen, 2000; Imamoglu *et al*., 2004; Barabas *et al*., 2004). The advantage of PVA is that it is a mathematical/statistical technique valued as an exploratory data analysis method that can be used to identify end-member fingerprints with minimal assumptions about contributing source patterns and/or alteration mechanisms. PVA provides estimated compositions of contributing PCB fingerprints directly from the analysis of the ambient data. PVA also provides estimates of the relative contribution of each end member in each sample. Only after the end-member patterns are resolved are they compared to

Highlight 3-4. Evaluating PCB Dechlorination by Comparing PCB Congener Histograms

Congener distributions for surface and buried sediment samples from Lake Hartwell sediment reveal a congener shift from higher- to lower-chlorinated congeners with sediment depth and age (Magar *et al.*, 2005a). Comparison of surface (a) and buried (b) sediment PCB profiles, represented in (c) as the histogram of the difference of surface and buried sediment samples, demonstrated concentration decreases in the tetra- through decachlorobiphenyl homologues, and corresponding increases in mono- through trichlorobiphenyls. Negative values in (c) represent a net concentration loss, while positive values represent a net concentration gain.

Though dechlorination is shown to be extensive, most occurred after burial. Surface sediments (a) exhibit the least dechlorination. Dechlorination can contribute to long-term risk reduction by reducing more toxic PCB congeners in buried sediment, particularly if there is a risk of sediment erosion and resuspension.



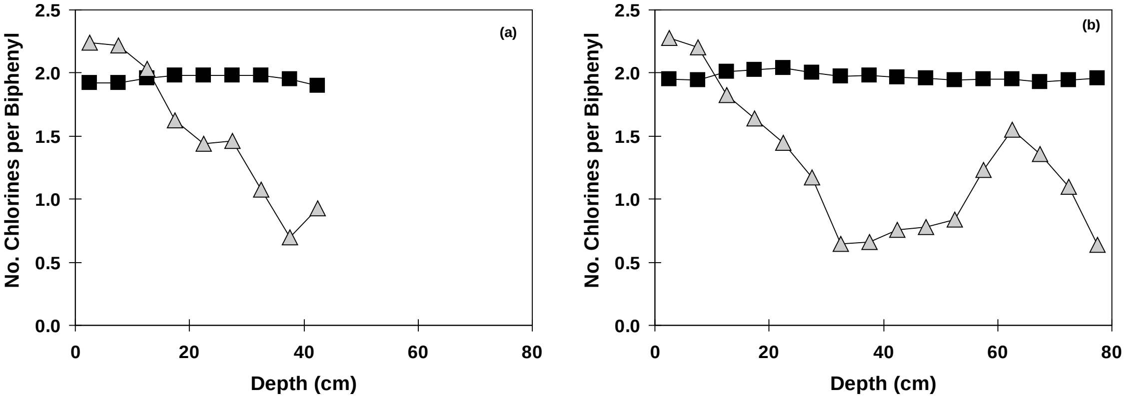
Congener distributions showing dechlorination characteristics for Lake Hartwell sediments (f**rom Magar *et al.*, 2005a)**

Highlight 3-5. Dechlorination of *Meta* and *Para* Chlorines and Conservation of *Ortho* Chlorines at Lake Hartwell (from Magar *et al.*, 2005b)

PCB dechlorination was measured in Lake Hartwell sediment cores by plotting *ortho* chlorines and *meta* plus *para* chlorines per biphenyl molecule (*i.e.*, moles chlorine/mole PCBs) with sediment depth. The loss of *meta* plus *para* chlorines and the conservation of *ortho* chlorines with sediment depth showed that the PCBs underwent reductive dechlorination after burial. Notably, *ortho* chlorines were remarkably well conserved for more than five decades, since the first appearance of PCBs (ca. 1950 to 1955).

Dechlorination rates were determined by plotting the numbers of *meta* plus *para* chlorines per biphenyl with sediment age. The average dechlorination rate was 0.094 ± 0.063 mol Cl/mol PCBs/year, and the time required per chlorine removal ranged from 4.3 to 43.5 years, with an average of 16.4 ± 11.6 years.

Though dechlorination tended to be very extensive in buried Lake Hartwell sediments, it was not always consistent from core to core or at various depth intervals within a single core, as shown below. The reason for this variability in dechlorination extent could not be determined, but it did not appear to correlate with such factors as PCB concentration, total organic carbon, or age.



Number of *ortho* (■) and *meta* plus *para* (△) chlorines per biphenyl molecule with sediment depth for two Lake Hartwell sediment cores (from Magar *et al.*, 2005b)

literature-reported source and alteration patterns (*e.g.*, Aroclor compositions, PCB dechlorination patterns, and other weathering patterns).

PVA is particularly useful for large data sets. Comparison of paired samples, such as those shown in Highlight 3-3, would be difficult to perform for every sample pair in a large data set. PVA makes it possible to: 1) determine dominant sources and alteration patterns in a large data set, 2) calculate the distribution of end members in each sediment sample, and 3) model the distribution of end members in multiple sediment cores. PVA methods are described in detail by Johnson *et al.* (2002) in *Introduction to Environmental Forensics* and summarized by Johnson and Ehrlich (2002). The reader is referred to Johnson *et al.* (2000) and Magar *et al.* (2005a) for examples demonstrating the use of PVA for identification of PCB source and alteration patterns.

The discussion above describes a single multivariate fingerprinting method, PVA. While PVA is a valuable, proven method for resolving certain complex source mixtures, it is not the only mathematical tool available for such analyses. PCA is another method that has often been employed to distinguish different sources in less complex sediment mixtures (Johnson *et al.*, 2002). Three other methods described by Johnson *et al.* (2002) for use with complex source mixtures are target transformation factor analysis, source apportionment by factors with explicit restrictions, and positive matrix factorization. Because different methods are better suited for different data situations, practitioners are encouraged to consider each of these methods when evaluating data sets.

3.4.3.4 Summary of PCB Fingerprinting for MNR. PCB dechlorination and weathering can affect the concentrations and distributions of PCB congeners in sediments. Many factors can influence the rate and extent of PCB dechlorination and other weathering processes such as PCB concentrations, the presence of co-contaminants, redox conditions, and sediment age. Several fingerprinting techniques and detailed PCB congener analysis methods can be used together to better understand surface sediment sources and dechlorination processes. Evidence of dechlorination can be observed in the net loss of chlorines with depth, the preferential loss of *meta* and *para* chlorines, and dechlorination patterns characteristic of patterns reported in the literature by others.

Contaminant weathering and biotransformation processes in sediments can collectively contribute to reduced exposure and the recovery of sediment-water ecosystems at contaminated sediment sites. At PCB-contaminated sediment sites, dechlorination, leading to reduced mass and reduced toxicity, may be an important component of natural recovery. However, dechlorination typically occurs slowly and mainly in buried, anaerobic sediments and it increases with sediment depth and age. Thus, dechlorination of biologically active, near-surface sediments rarely is complete and residual mono- through tri-chlorobiphenyl PCB congeners commonly persist. Whether dechlorination provides sufficient risk reduction to justify MNR must be assessed on a site-specific basis, depending on the nature of the sediment environment as it relates to promoting or restricting dechlorination processes, the formation of dechlorination intermediates and end products, and the presence or absence of ecological receptors. In fact, the greatest potential for natural dechlorination processes to provide long-term benefits (*i.e.*, ecosystem recovery) is likely to be found at sediment sites that exhibit anaerobic conditions and limited benthic resources.

3.4.4 Assessing Natural Attenuation of PCDDs/PCDFs in Sediments. The characteristics of PCDDs/PCDFs and their weathering, including biodegradation, in the environment were discussed in Sections 3.1.2.3 and 3.3.3. PCDDs/PCDFs are unintended byproducts of manufacture of certain commercial chlorinated hydrocarbons (pentachlorophenol, Aroclor, and 2,4,5-trichlorophenoxy acetic acid contain trace impurities of mixed PCDDs/PCDFs), chlorine bleaching of wood pulp in paper manufacture, and combustion of organic material in the presence of chlorine. There are 75 possible PCDD congeners and 135 possible PCDF congeners. The tetrachloro-DDs/DFs contain the most congeners (Safe, 1991). Fifteen congeners containing chlorines in the 2-, 3-, 7-, and 8-positions are extremely toxic (Table 3-4) and are of major concern in sediments contaminated with chlorinated HOCs. However, the most highly-chlorinated congeners, octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran, are so insoluble and bind so strongly to sediment organic matter (log $K_{ow} > 8.0$: Table 3-6) that they are not bioavailable or toxic to aquatic organisms (Berends *et al.*, 1997) and do not biomagnify in aquatic-terrestrial food chains (Broman *et al.*, 1992).

The fingerprinting methods described above for PCBs (Section 3.4.3) can be used to determine possible sources of PCDDs/PCDFs in environmental samples (O'Keefe *et al*., 1996). Most of the PCDDs/PCDFs in sediments, however, are from diffuse, non-point sources (*e.g.*, atmospheric deposition of combustion products), and their homologue and congener compositions, relative concentrations, and weathering patterns have not been well characterized.

Brzuzy and Hites (1996) compared the homologue profiles of globally-averaged PCDD/PCDF atmospheric deposition to typical single-source incinerator emissions. The most abundant homologue in deposited mixtures was octachlorodibenzofuran, followed by heptachlorodibenzofuran. Incinerator emissions contained nearly equal amounts of dibenzodioxin homologue groups with five, six, and seven chlorines and dibenzofuran homologue groups with seven or eight chlorines. The differences could have been caused by degradation of all dibenzodioxins and the less-chlorinated dibenzofurans in the atmosphere by photooxidation or in sediments by biodegradation, or to the presence of one or more additional major sources of PCDD/PCDF emissions with substantially different homologue distributions than the incinerator emissions.

O'Keefe *et al.* (1996) used PCA to compare concentrations of PCDDs and PCDFs in sediments from two interconnected lakes in New York, Lake Champlain and Lake George. Two different PCDD/PCDF congener profiles were present in surface sediments from Lake George. Sediments near residential areas and power boat marinas had the highest levels of PCDDs/PCDFs, dominated by hepta- and octa-CDDs and tetra- and octa-CDFs. However, the PCDD/PCDF profiles in the sediments resembled those in sediments from remote lakes where atmospheric deposition was the most likely source of contamination, suggesting that the dioxins/furans in Lake George sediments were not from boating activities. Lake Champlain sediments also contained two PCDD/PCDF congener profiles, but these were different from those in Lake George sediments. The most heavily-contaminated samples contained high concentrations of octa-CDD. Some of these high samples also contained elevated concentrations of several tetra-CDDs, primarily highly toxic 2,3,7,8-tetrachlorodibenzodioxin. The likely source of these PCDDs/PCDFs is the bleached kraft pulp and paper mills on the shores of Lake Champlain.

Gaus *et al.* (2002) evaluated congener profiles of PCDDs in Queensland, Australia sediments. There was an increase in the relative concentrations of less-chlorinated PCDDs and a decrease in the relative concentrations of the more highly-chlorinated PCDDs with depth and time of deposition in sediment cores. Sequential reductive dechlorination of OCDD to TCDDs in anoxic sediment layers was the most likely cause of these changes. Because this process is slow relative to the rate of sediment deposition, the most abundant PCDDs at all depths in sediment were the heptachloro- and hexachloro-dibenzodioxins. Tetrachlorodibenzodioxin congeners (the most-toxic congeners: Table 3-4) were most abundant in the deeper sediment layers. The most toxic congener, 2,3,7,8-tetrachlorodibenodioxin, however, was not present in the Queensland sediments or in sediments from the Mississippi River; Osaka Bay, Japan; and Hong Kong, China. Gaus *et al.* (2002) hypothesized that sediments from all of these locations contained PCDD/PCDF assemblages from multiple, poorly-characterized sources, including releases of contaminated commercial chlorinated hydrocarbons and incineration.

3.5 Assessing Sorption/Sequestration

The only HOCs in fresh water, estuarine sediments, and marine sediments that are of ecological importance are those in forms and locations that can interact with ecological receptors causing sublethal and lethal responses that may disrupt local biological populations and ecological communities. The HOC must be in a form that is bioavailable to ecological receptors, including sediment microbes (see Section 3.2.1). The most bioavailable form of most HOCs is the dissolved species. The HOC must also be in a location where potential receptors can come in contact with it or with HOCs dissolving (partitioning) from the adsorbed, or otherwise sequestered, HOC inventory in sediments. Therefore, sorption, sequestration, and burial govern the relative bioavailability and hazard of HOCs in sediments.

As discussed in Section 3.3.2, sorption and sequestration of HOCs in sediments vary widely depending on the hydrophobicity (driven by compound polarity and functional group characteristics) of the HOC (proportional to log K_{ow}) and surficial sediment properties. The physical form and chemical milieu in which the HOC or HOC mixture was introduced into sediments is an important determinant of the subsequent *in-situ* behavior of the HOC. Petrogenic and some pyrogenic PAHs often are still associated with a NAPL phase in sediments. Pyrogenic PAHs often enter water bodies and are deposited in sediments tightly bound to soot particles from the combustion source. Mixed petrogenic/pyrogenic PAHs associated with coal tars and creosote are often associated with highly viscous or solid particles in sediments. The petroleum PAHs often partition from the oil NAPL phase more easily than the pyrogenic PAHs partition from the organic particle or NAPL phase. Therefore, it is important, as an early phase of MNR, to determine the physical/chemical forms and sources of PAHs in site sediments and their association with the sediment matrix (Neff *et al.*, 2005).

PCB and PCDD/PCDF mixtures may also be present in sediments in NAPL or adsorbed to organic phases (coatings on particles, BC, and colloids) as discussed in Sections 3.2.4 and 3.2.7. Most PCDDs/PCDFs that enter sediments are from combustion sources and are introduced to aquatic systems adsorbed to soot particles; they partition similarly to pyrogenic PAHs. In contrast, PCBs usually are introduced to aquatic systems from releases of oily commercial mixtures (*e.g.*, Aroclor) and may partition in sediments more similar to petrogenic PAHs (Section 3.2.8).

Sources of PAH, PCB, and PCDD/PCDF mixtures in sediments sometimes can be identified by fingerprinting techniques (Sections 3.4.2.1, 3.4.3, and 3.4.4). Different mathematical relationships can be used to estimate partitioning from NAPL phases (oil, coal tar, and creosote) or sorbed phases into the dissolved (bioavailable) phase in water. Organic particle/colloid–water partitioning has been studied more thoroughly and should be used for an initial assessment of sediment-water partitioning of HOCs from all sources.

Equilibrium partitioning models provide only a first estimate of actual partitioning behavior due to high variability in sorption/desorption and sequestration of different HOCs in sediments with different geochemistry and concentrations and quality of organic matter. Because BC adsorbs PAHs and PCDDs/PCDFs much more effectively than predicted by conventional sediment organic matter/water partition coefficients (K_{oc}), some of the variability in predicted sorption behavior of these chemicals can be reduced by correcting or accounting for the fraction of BC in site sediments (Accardi-Dey and Gschwend, 2002; Hawthorne *et al.*, 2007b).

In order to make site- and HOC-specific predictions of aqueous phase HOC concentrations, more accurate, site-specific data can be obtained by determining log K_{oc} empirically in sediment samples from cores collected at several locations at the study site. Hawthorne *et al.* (2005, 2006, 2007b) outline an approach to measuring log K_{oc} for PAHs in sediments from the vicinity of former MGP sites. Sediment samples are collected and processed quickly according to EPA (2001b) recommendations. Wet sediments are centrifuged at moderate speed to separate sediment solids from pore water. Colloids are precipitated from the water phase by alum flocculation. Target analytes (PAHs, PCBs, or PCDDs/PCDFs) are extracted and analyzed from all three phases by GC/MS. If soot carbon concentration is measured in an aliquot of the dry sediment, the distribution of particulate-phase HOCs between soot and natural organic carbon can be estimated (Cornelissen and Gustafsson, 2005; Cornelissen *et al.*, 2005). An example of data generated by this protocol is summarized in Table 3-7, where partition coefficients to soot (K_{sc} values) are greater than K_{oc} values by at least an order of magnitude, illustrating the importance of considering BC (in this case, soot) material in sediments as HOC sorbent materials.

4.0 FATE OF INORGANIC CONTAMINANTS IN SEDIMENTS

4.1 Relevance of Metals Behavior for MNR

An understanding of the biogeochemical processes in sediment is of particular importance for evaluating the effectiveness of MNR for metals-contaminated marine, estuarine, and fresh water sediments. Many environmental variables govern the chemical state of metals in sediment, which in turn affect their mobility, bioavailability, and toxicity, making natural recovery of metals-contaminated sediments difficult to predict. Much of the current understanding of the role of chemical processes in controlling risk is focused on the geochemical transformations resulting from changes in pH and redox potential that can profoundly affect speciation, solubility, and, consequently, bioavailability of metals and organometallic species. For any site where MNR is implemented, determination of metal speciation is of critical importance for estimates of bioavailability and risk. For some metals, the free metal (or aquo ion) may be the most toxic form to organisms; however, for other metals, such as mercury, biologically transformed species (*e.g.*, methyl mercury) pose the greatest risk. The redistribution of a contaminant from soluble to insoluble species through the formation of independent solid phases, precipitates, co-precipitates, or adsorption onto sediments may reduce the bioaccessibility of the contaminant. For example, formation of relatively insoluble metal sulfides under reducing conditions may effectively reduce the risk posed by metal contaminants if reducing conditions are maintained. Environmental variables that influence metal mobility and bioavailability in sediments include pore water pH, alkalinity, major ion composition/concentration, sediment grain size, sediment mineralogy, redox conditions, and the amount of sulfides and organic carbon present in the sediments. Furthermore, the resident biological community affects many chemical processes in sedimentary environments. Sediment dwelling organisms impact the physical/chemical properties of surface layers of the sediment through mixing of surface sediments with deeper layers and facilitate transport of oxic surface water into deeper layers in sediments where conditions are often sub-oxic or anoxic.

The success of MNR as a risk reduction approach typically is dependent on understanding the dynamics of the contaminated environment and the fate, mobility, and bioavailability of the contaminant under the geochemical conditions in that specific sedimentary environment. The natural processes of interest for MNR may include a variety of processes that, under favorable conditions, act without human intervention to reduce the mass, mobility, or concentration of bioavailable/toxic forms of contaminants in the sediment bed. Natural processes that result in metal sequestration, immobilization, stabilization, or reduced bioavailability may include physical, biological, and chemical mechanisms such as redox and sorption. This section focuses specifically on: 1) chemical processes of metals in sediments, 2) behavior of specific metals in sediments, 3) sediment sampling and analytical considerations, and 4) analytical approaches to metal speciation in sediments.

4.2 Biogeochemical Processes that Affect Metal Behavior

The distributions and concentrations of metals in sediments will depend on a large number of factors, with the most important being the conditions related to the aqueous phase (*e.g.*, ionic strength, specific inorganic co-contaminants, alkalinity, pH, and DOC), but also on the types and abundance of metal-binding phases present in the sediments, such as particulate sulfide (acid volatile sulfides [AVS]), oxides of iron and manganese, clay minerals, and organic matter (Besser *et al.*, 2003; Lee *et al.*, 2004; Simpson *et al.*, 2004; Simpson and Batley, 2007). These factors affecting metal speciation (*i.e.*, aqueous phase concentration) and, by extension, bioavailability, are discussed in detail in this section.

4.2.1 Ionic Strength, Hardness, Alkalinity, and Temperature. The ionic strength of surface and interstitial pore water will influence the bioavailability of metals and metal compounds. The dissolved salts in waters having a high ionic strength may compete for biological uptake with charged metal species or may influence the thermodynamic equilibria by altering the ratios of metal species in solution (Stumm and Morgan, 1981). This phenomenon is most relevant to marine and estuarine environments (*e.g.*, Riba *et al.*, 2003). Ultimately, the concentration of the various organic and inorganic cations and anions, which collectively contribute to the overall ionic strength, influence the distribution of metal species in the aqueous phase.

Hardness, mainly determined by calcium (Ca^{2+}) and magnesium (Mg^{2+}) in most natural waters, affects metal behavior and bioavailability by competing with metals for binding with DOM, anions, and biological membranes (*e.g.*, gills) (Hodson *et al.*, 1978; Pagenkopf, 1983; Benson and Birge, 1985; Lauren and McDonald, 1986). Increased concentration of hardness ions can, therefore, interfere with an organism's ability to take up potentially toxic trace metals due in part to the common divalent characteristics of hardness cations and common metal contaminants. Natural seawater (salinity 35 g dissolved salt/L) contains approximately 420 mg/L calcium and 1288 mg/L magnesium and, consequently, is extremely hard. The metals most affected by hardness include common divalent metal contaminants (*e.g.*, cadmium, chromium, cobalt, copper, manganese, nickel, and zinc), but insufficient data exist for the development of hardness-based toxicity equations for some metals (*e.g.*, cobalt, lead, manganese) (*e.g.*, Chapman *et al.*, 1980; Pagenkopf, 1983; Bradley and Sprague, 1985; Stubblefield *et al.*, 1991; Diamond *et al.*, 1992). Although hardness historically has been considered an independent factor in determining the bioavailability and toxicity of metal and metalloid contaminants, modern predictive approaches used for toxicity estimates (*e.g.*, the Biotic Ligand Model; see EPA, 2007c) typically consider hardness in conjunction with other factors, such as pH, alkalinity, and DOC.

Alkalinity refers to the acid neutralizing capacity of the sampled water. For a water body containing dissolved carbonate and no other strong bases, the alkalinity will be approximately equal to the sum of dissolved bicarbonate, carbonate, and hydroxide ion (see Stumm and Morgan [1996] for extended definition and formal calculations of alkalinity). Alkalinity affects bioavailability in a manner analogous to hardness, but involves the carbonate anion instead of the Ca^{2+} and Mg^{2+} cations. Increased alkalinity will reduce metal bioavailability through the formation of metal carbonate complexes. For some metals (*e.g.*, copper and lead), it has been found that in addition to hardness, alkalinity also may have an influence on bioavailability (Shaw and Brown, 1974; Andrew, 1976; Davies, 1976; Nelson *et al.*, 1986); however, the mechanism by which alkalinity governs metal speciation and, consequently bioavailability, was not elucidated. For a regional site manager, alkalinity may be used as an initial indicator of several factors that govern metal speciation, including the formation of carbonate complexes, carbonate precipitates, and hydroxide precipitates; the sorption of trace metals onto the formation of a bulk carbonate/hydroxide solid phase; or a combination of these processes.

Temperature exerts an important effect on metal speciation because most chemical reaction rates are highly sensitive to temperature changes (Elder, 1989). Equilibration rates of metals between dissolved and sorbed phases in sediment increase with increasing pore water pH and temperature (Simpson *et al.*, 2004). Temperature may also affect quantities of metal uptake by an organism because biological process rates in unacclimated organisms typically double with every 10°C temperature increment (Luoma, 1983; Prosi, 1989). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma, 1983). Temperature also has an indirect influence on metal cycling through its effect on organisms and the biogeochemical processes involving trace metals that they mediate.

4.2.2 pH and Eh. pH and Eh are important factors governing metal speciation, solubility, and sorption/desorption to mineral and/or organic surfaces, which, in turn, affect metal transport and bioavailability in aquatic systems. The system pH influences the solubility of oxyhydroxide, carbonate, phosphate, and sulfide minerals and adsorption-desorption processes. The pore water of marine and estuarine sediments, like the overlying seawater, is strongly buffered, and pH changes typically are not as significant as in fresh water sediments. The buffer capacity of the sediment solid phase is even greater than that of seawater, but reactions involving solid phases can be slow (Simpson and Batley, 2007). Addition of dissolved cationic metals to sediment tends to release hydrogen ions (H^+) to solution via electrostatic exchange or proton displacement reactions as a result of surface complexation, increasing acidity, and reducing pore water pH. Although mineral solubility is a function of pH, most metal hydroxide minerals have very low solubility under pH conditions typical of natural waters (pH 6 to 8). The solubility of metal hydroxide minerals usually increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes. Furthermore, increased solution acidity results in increased free metal ion concentration in solution due to competition with protons for exchange sites or electrostatic repulsion from the increased net positive charge of mineral surfaces.

A key factor determining the speciation and biogeochemistry of multi-valent trace metals (*e.g.*, arsenic and chromium) in sediment is the Eh of the system. System redox influences both the oxidation state of the contaminant (*e.g.*, Cr[III] versus Cr[VI]) and the stability of various mineral phases that affects solid-phase partitioning of the contaminant (*e.g.*, iron oxides versus iron sulfides). A redox reaction occurs when electrons are transferred from an electron donor (the reductant) to an electron acceptor (the oxidant). The redox condition of any environment can be described either as reducing, where the tendency is for electron-deficient species (*e.g.*, oxides of Fe[III] or Mn[IV]) to gain electrons, or oxidizing, where electron-rich species (*e.g.*, reduced organic carbon) tend to lose electrons. Biogeochemical processes often facilitate the transfer of electrons between chemical constituents, resulting in oxidation and reduction. Different important oxidation/reduction reactions occur at different Eh values; the critical MnO_2/Mn^{2+} and Fe_2O_3/Fe^{2+} redox reactions occur at about +10 to +50 mV, and the SO_4^{2-}/H_2S and CO_2/CH_4 reactions occur at about –70 to +50 mV, depending on pH (Stumm and Morgan, 1996; Drever, 1997). Field measurements of *in-situ* redox potential should be regarded with some caution as typical methods that rely on a platinum working electrode do not necessarily reflect the distribution of redox species for a given redox couple (EPA, 2002b). Whereas pH-buffering processes may occur rapidly, electron transfer processes are often kinetically slow and the actual concentrations of reduced/oxidized species of a given element in a specific environment may vary greatly from predictions based solely on thermodynamic considerations. In sedimentary environments, pH and Eh control the solubility and concentration of the major metal species through the dissolution of redox-active mineral oxides (*e.g.*, Fe/Mn oxides) and desorption of those elements associated within or adsorbed onto the structural matrix of these oxides (Kimball and Wetherbee, 1989; Van Cappellen and Wang, 1996).

4.2.3 Sediment Diagenesis and Establishment of Vertical Redox Profile. In surficial sediments, a major process that dictates the chemical speciation and biogeochemistry of trace elements is microbial respiration of organic matter, which, in turn, controls the redox potential of the sediments and concomitantly influences pH and alkalinity. In surficial sediments, this is referred to as early diagenesis.[1] In early diagenesis, fresh sediment in the uppermost layer is transformed by a suite of biogeochemical reactions, all of which combine to lower the free energy of the system (Sundby, 2006). Microbial processes drive organic matter oxidation in sediments through the utilization of a series of terminal electron acceptors (TEAs) (Figure 4-1). The TEAs are utilized in the order of decreasing free energy yield with the major components (in order) being O_2, NO_3^- and NO_2^-, $MnO_2(s)$, $FeOOH(s)$ or $Fe(OH)_3(s)$, and SO_4^{2-} (Stumm and Morgan, 1996). Once all of the TEAs are consumed, oxidation of organic matter occurs by methanogenesis (*e.g.*, $CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$ or $CH_3COOH \rightarrow CH_4 +$

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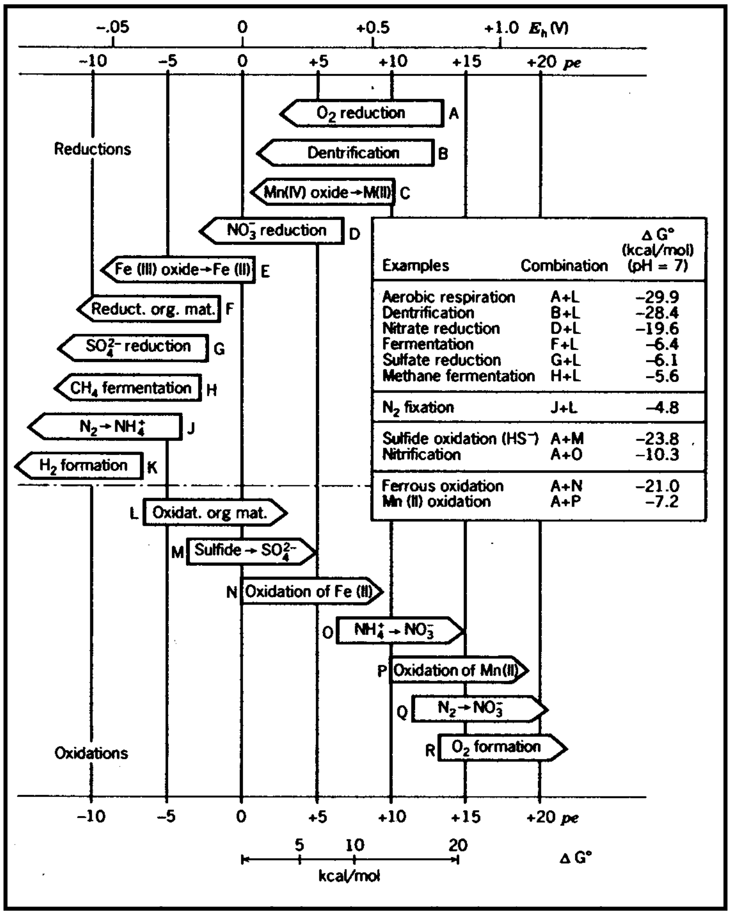
[1] Diagenesis is the process of chemical and physical change in deposited sediment during its conversion to rock.

CO_2). This preference of TEAs results in a vertical layering of redox conditions in near surface sediments (Figure 4-2) (Froelich *et al.*, 1979). This figure represents a typical marine system; however, the spatial scale of this vertical distribution may change depending on the actual fluxes of the different TEAs into the sediment layer. The vertical concentration distributions of several TEAs in sediments utilized by microorganisms in the oxidization of organic matter to carbon dioxide are depicted in Figure 4-2. The preference in the use of oxidants by microorganisms results in a layering of reduction zones, each layer driven by a different class of microorganism. As illustrated, there is often considerable overlap of the reduction zones, which can be exacerbated by bioturbation, resulting in a smearing of the redox zones. In open ocean sediments, the abundance of organic matter delivered to sediments is typically low and early diagenesis rarely proceeds beyond nitrate reduction into sub-oxic diagenesis. In coastal areas where the delivery of organic matter can be high, sulfate reduction is usually the dominant oxidant pathway due to the abundance of sulfate in marine systems. In fresh water sediments, the spatial scale of the vertical stratification of redox strata may be compressed relative to marine sediments, with the redox transitions from nitrate reduction to sulfate reduction occurring within the uppermost 4 cm (Wersin *et al.*, 1991). The vertical distribution of TEAs shown in Figure 4-2 may vary for different sites, including changes in overall depth and the degree of overlap between TEA distributions. In addition, depending on depth of surface water and flux of degradable organic carbon, the transition from oxidizing to reducing conditions may occur within the water column, at or some depth below the sediment-water interface. Methane production is not normally seen in marine systems, but is more common in fresh water systems where sulfate levels are far less abundant. This layering can directly affect bioavailability of metals by controlling the redox state of the metal and indirectly by providing a barrier to diffusive transport due to the oxidative precipitation of insoluble iron and manganese phases near the sediment-water interface (Stumm and Morgan, 1996).

4.2.4 Iron and Manganese Oxides. The iron/manganese oxide component of sediments is an important, even controlling, repository for a wide variety of metals in the majority of systems. Iron hydrous oxide particles have diameters ranging from tens of nanometers to hundreds of microns depending on the physical and chemical conditions where the oxides were formed and degree of atomic substitution (Cornell and Schwertmann, 1996). These small dimensions give them a large surface area per unit mass and a strong propensity to adsorb as surface films on larger, clay-sized particles. During initial weathering, estuarine mixing, or groundwater upwelling, iron and manganese often precipitate near the sediment-water interface as the reduced forms encounter oxic conditions. Conversely, as oxidized forms of iron and manganese oxides encounter reducing conditions, a combination of biotic and abiotic processes acts on these minerals, causing reductive dissolution and/or the transformation to new mixed-valence oxide phases. For iron oxides, this process can be observed in the transformation of crystalline ferric oxides (commonly found as hematite, goethite, ferrihydrite, and/or amorphorous phases) to mixed valence magnetite and/or green rust minerals to ferrous minerals depending on the specific geochemical conditions at each site. For manganese oxides, oxidation of buried Mn(II) minerals results in a vertically dynamic distribution of Mn(IV) and Mn(III) minerals. For manganese oxides, upward diffusion of reduced phases results in oxidation/precipitation of Mn(III) and Mn(IV) oxides. As these oxides are buried, they are reduced to Mn(II) and/or Mn(III) species (Anschutz *et al.*, 2005). Oxidation and aging of Mn(II) minerals is also the result of microbiological (enzymatic) transformation (Tebo *et al.*, 2004). In redox active sediments (*e.g.*, at the sediment-water interface), the action of a multi-copper enzyme was observed to facilitate the transformation of reduced manganese to manganese oxide similar to birnessite (Tebo *et al*., 2004). Biogenic Mn(IV) oxides are significant adsorbents for trace metals governing the *in-situ* speciation and bioavailability of metals cations such as Cu, Cd, Co, Ni, Zn, Sn, Ca, Hg, Se, and Pb (Fuller and Harvey, 2000; Tebo *et al.*, 2004).

In high-alkalinity waters with sufficient dissolved carbonates, ferrous iron may precipitate as carbonate solids (*e.g.*, $FeCO_3$, siderite), whereas in sedimentary environments with elevated phosphate, the formation of iron phosphate minerals (*e.g.*, $Fe_3[PO_4]_2$, vivianite) may occur. In some cases, the presence of minerals such as siderite are inferred on the basis of equilibrium considerations and not direct spectroscopic evidence (Wersin *et al.*, 1991). During ferric oxide reduction, dissimilatory iron reducing bacteria have been shown to use ferrihydrite as a TEA, transforming the ferric hydroxide to mixed-valence Fe(II)/Fe(III) oxides including magnetite (Fe_3O_4) and green rust (fougerite, a clay-like mineral) (Behrends and Van Cappellen, 2007; Glasauer *et al.*, 2003). During the iron oxide mineral transformations, the sequestration of inorganic contaminants may occur via adsorption, surface complexation, or co-precipitation processes, all of which may operate separately or concurrently depending on specific site conditions.



Examples	Combination	ΔG° (kcal/mol) (pH = 7)
Aerobic respiration	A+L	–29.9
Dentrification	B+L	–28.4
Nitrate reduction	D+L	–19.6
Fermentation	F+L	–6.4
Sulfate reduction	G+L	–6.1
Methane fermentation	H+L	–5.6
N_2 fixation	J+L	–4.8
Sulfide oxidation (HS^-)	A+M	–23.8
Nitrification	A+O	–10.3
Ferrous oxidation	A+N	–21.0
Mn (II) oxidation	A+P	–7.2

Figure 4-1. Sequence of Microbially Mediated Reduction-Oxidation Reactions (Source: *Aquatic Chemistry,* W.S. Stumm and J.J. Morgan, 1981, reprinted with permission by John Wiley and Sons, Inc., New York City, p. 460)

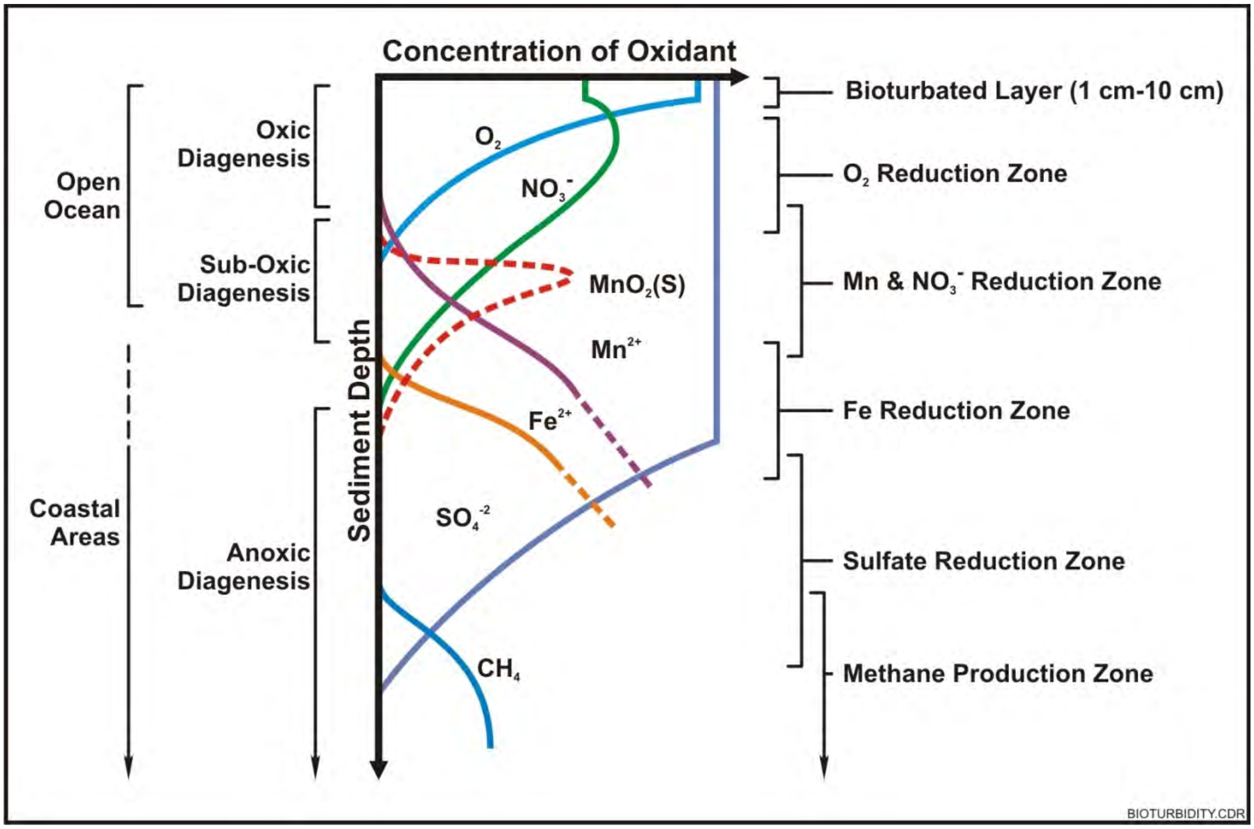


Figure 4-2. Typical Redox Zones in Surficial Sediments in a Marine System Mediated by Biological Reactions (Adapted from Froelich *et al.*, 1979.)

Both ferric and manganese oxides display prominent pH-dependent, variable-charge surface electrostatic properties. The different iron and manganese oxides have different surface pKa values: when the pH equals the surface pKa, the surface is considered to have a net zero charge, also known as the pH at the point of zero charge (pHpzc). When the pH is less than the pKa, the surface has a net positive charge, and when the pH is greater than the pKa, the surface has a net negative charge. Surface pKa values for manganese oxides are typically lower than for iron oxides with reported values of pHpzc for different manganese oxides ranging from 2.7 (δ-birnessite [Scott and Morgan, 1995]) to 4.6 for hollandite (McKenzie, 1989) to 6.2 for naturally occurring manganese oxide-containing sediments (Amirbahman *et al.*, 2006). In contrast, the pHpzc for common Fe(III) oxide minerals ranges from 8 to 9. As such, Fe(III) oxides are typically good sorbents for metals and metalloids from circumneutral to slightly acidic pH, whereas Mn(IV) oxides are good sorbents for metal cations from slightly acidic to basic pH.

4.2.5 Natural Organic Matter and Low Molecular Weight Organic Acids. Nearly all contaminant metals, particularly those that exist as cations and/or cationic hydrolysis species, may form complexes with organic ligands, which are ubiquitous features of sedimentary environments. NOM in sediments exists in a dynamic equilibrium between dissolved phases and non-aqueous phases (usually adsorbed onto clay or oxide surfaces, or suspended colloidal particles). DOM, usually an operationally defined pool of NOM that passes a 0.45-μm cutoff filter, contains functional groups predominantly comprised of oxygen-, nitrogen-, or sulfur-containing moieties, which are able to form complexes with dissolved metals. Four classes of humic substances can be differentiated based on molecular weight and solubility behavior: humin, humic acid, fulvic acid, and low-molecular-weight organic acids (Jonasson, 1977; Aiken *et al.*, 1985). Of these, only humin is virtually insoluble. Humic and fulvic acids are heterogeneous, polydisperse, electrolytic macromolecules with a strong tendency to adsorb to particles, surfaces, and complex metals and to bind organic molecules. Humic acids are higher molecular weight and more aromatic in character than are fulvic acids and, therefore, typically are not dissolved in sediment pore waters where the pH is usually less than 9. At pH values above 9, humic acids can become more important in the binding, adsorption, and precipitation of metals via coagulation. Fulvic acids have lower molecular weights compared to humic acids. Accordingly, they are more water soluble and are characterized by a lower C:O ratio, indicative of a greater number of carboxylate functional groups and, therefore, a greater metal-binding capacity than humic acids on a per-carbon basis. For example, the average C:O ratio of humic acids is between 0.47 and 0.57 as compared to between 0.64 and 0.74 for fulvic acids (Sparks, 2003). Even lower in molecular weight and more water soluble are the low-molecular-weight organic acids. These tend to be comprised of simple mono- and di-carboxylic acids such as acetate, lactate, oxalate, malonate, lactate, phthalate, salycilate, and many others. Nearly all forms of NOM are found to co-occur with metals. Even the most rigorous attempts to isolate NOM substances will result in NOM containing some metals as well as metal oxides, which are often quantified as "ash-content" during elemental analysis. This indicates that many metals are irreversibly bound to NOM and not likely to be accessible for biotic uptake.

In addition to direct metal complexation, NOM in sediments will form coatings on sediment particles (clays, oxides, etc.) and will act as new reactive surfaces having a high affinity for trace metals. Small particles, with large reactive surface area to mass ratios, have the capacity to adsorb trace metal contaminants and may adsorb metal contaminants from the dissolved phase. It has been observed that NOM coatings of iron oxide particles can govern the formation and growth of these particles and determine the ultimate morphology and reactivity of iron oxide particles in the natural environment (Perret *et al.*, 2000). These carbon-iron particulates were further observed to contain significant quantities of other elements and may, thus, be a significant ternary phase for the partitioning of trace metals in sedimentary environments where iron and carbon, two environmentally ubiquitous elements, co-occur (Perret *et al.*, 2000). Furthermore, as DOM forms metal complexes, the metal ions act as bridges, binding together several DOM molecules, gradually increasing the molecular size of the complexes, and eventually creating discreet colloid-sized particles. These particles can flocculate, deposit on the sediment surface, and become buried within the sediment. Irrespective of the precise mechanism, metal contaminants bound to particulates still may have a significant toxic effect on some benthic communities through the ingestion of the particulates.

4.2.6 Solubility Controls by Precipitation and Dissolution: The Formation of Insoluble Complexes, Sediment Resuspension, and Oxidation. Precipitation of insoluble metal phases is a significant process facilitating the sequestration of toxic metal contaminants in sediments (Porter *et al.*, 2004). Solids precipitation may lead to metal sequestration via three principle routes: 1) precipitation of a pure-phase mineral when sufficient metals and ligands are present, 2) co-precipitation in the case where the formation of a solid phase captures a metal contaminant within the mineral matrix, and 3) the sorption of a metal contaminant onto surfaces of a freshly precipitated solid-phase sorbent material. Commonly-occurring solid phases in sedimentary environments include hydroxide, carbonate, phosphate, and sulfide minerals, although this list is not exhaustive. Geochemical conditions of the sediment environment must meet certain criteria in order for these solid phases to form. For example, high alkalinity waters, or waters of karst bedrock environments, are characterized by elevated levels of dissolved carbonates, conditions where precipitation of carbonate minerals may occur.

Eutrophic conditions, especially in areas impacted by agriculture or animal husbandry, commonly contain high levels of phosphate. In these areas, precipitation of phosphate minerals in sediments (*e.g.*, $Fe_3[PO_4]_2$ [vivanite] or $Pb_5[PO_4]_3OH$ [hydroxypyromorphite]) may occur (Porter *et al.*, 2004; Scheckel and Ryan, 2004). In areas where metal contaminants are predominantly present as relatively soluble minerals (*e.g.*, $PbSO_4$ [anglesite]), amendments can be made (*e.g.*, phosphate, sulfide, or lime) in order to facilitate the formation of insoluble and relatively stable mineral phases (*e.g.*, anglesite transformation to pyromorphite via phosphate addition; Porter *et al*., 2004). However, consideration must be given to temporal changes in redox status, which may cause oxidation (*e.g.*, dissolution of sulfide precipitates) or reduction (*e.g.*, dissolution of iron/manganese oxide geosorbents) and lead to the mobilization of the sequestered contaminant of concern.

Sediments that receive large amounts of organic carbon from photosynthesis (autochthonous) in overlying waters or transport from terrigenous plant debris (allochthonous) are often highly anoxic. Low redox potential in this type of environment can promote microbial iron and sulfate reduction and, consequently, sulfide mineral deposition (*e.g.*, Kanaya and Kikuchi, 2004). During diagenesis, potentially toxic metals such as arsenic, cadmium, copper, mercury, lead, and zinc may co-precipitate with insoluble sulfides (*e.g.*, mackinawite or pyrite), form discrete sulfide phases (*e.g.*, PbS [galena], CdS [hawleyite or greenokite], or HgS [cinnabar or metacinnabar]), or adsorb to the surfaces of freshly precipitated sulfide phases (*e.g.*, arsenite adsorption onto FeS [mackinawite] or FeS_2 [pyrite]) and through each of these processes become increasingly unavailable to benthos (Morse, 1994; EPA, 2005c). Pyritization (*i.e.*, formation of insoluble sulfide mineral phases) and/or depyritization (*i.e.*, oxidation and solubilization of sulfide mineral phases) of trace metals are important processes in controlling bioavailability of many trace metals, especially in estuarine and marine environments (Morse, 1994). The importance of sulfide phases is underscored by their very low solubilities relative to carbonate or phosphate minerals (Table 4-1). Although sulfides have been identified as a main factor for decreasing the solubility of some metals in sub-oxic sediments, toxicity might not be seen even if the sulfide pool becomes exhausted. This implies the importance of other binding phases (*e.g.*, organic ligands and particulate and/or colloidal iron or manganese oxides [Müller and Sigg, 1990]) that also contribute to the reduction of metal dissolution and bioavailability (see Section 4.3). Understanding of fundamental geochemical conditions, such as those outlined in this section (*e.g.*, alkalinity, pH, redox, etc.), should be used to guide regional assessments for the potential of solid-phase precipitation as a viable MNR process.

The solubility and toxicity of chromium, cobalt, and selenium are not influenced by the amount of sulfide in the sediment layer to the same extent as are other metals, such as those illustrated in Table 4-1. The fate, mobility, and toxicity of these metals are influenced more strongly by the presence of organic material and iron and manganese oxyhydroxides and the redox state of the sediment. For example, Berry *et al.* (2004) showed that chromium solubility may be observed to correspond to sulfide concentration even though chromium does not form stable sulfides, presumably due to the rapid reduction of chromate to insoluble Cr(III) precipitates. The solubility of chromium in sediment pore water is affected by sediment redox potential; chromium tends to precipitate as chromic hydroxide ($Cr[OH]_3$) (solubility product, 6.3×10^{-31}) in sub-oxic sediments, where sulfide minerals concurrently increase in abundance.

Arsenic is unusual because its reactivity and fate have been observed to differ in marine (high sulfate) versus fresh water (low sulfate) sediments. Arsenic is adsorbed mainly to iron and manganese hydroxides in oxidized sediment layers; as redox potential declines, it is released from the Fe/Mn oxides and, in high sulfide environments, may precipitate as orpiment (As_2S_3) or realgar (AsS) or as inclusions in other metal sulfide solid phases, such as pyrite (Porter *et al.*, 2004). In fresh water sediments with low sulfate concentrations, arsenate released during reductive dissolution of Fe/Mn oxides may be reduced to arsenite and become mobilized or bind to sediment organic matter. At low Eh and low sulfate concentrations, arsenite may precipitate as arsenolite (As_2O_3), which is soluble (equilibrium concentration of H_3AsO_3 is reported to be $10^{-0.68}$ M in equilibrium with arsenolite; Yue and Donahoe, 2009) and may diffuse upward into the overlying water column (Porter *et al.*, 2004).

Table 4-1. Solubility Products for Selected Metal Sulfide, Carbonate, Phosphate, and (Hydr)Oxides

Sulfide	**log$_{10}$ K$_{sp}$**	**Carbonate**	**log$_{10}$ K$_{sp}$**	**Phosphate**(e)	**log$_{10}$ K$_{sp}$**	**(Hydr)Oxides**	**log$_{10}$ K$_{sp}$**
MnS (alabanite)	12.84(a)	$MnCO_3$	9.3(c)	$MnHPO_4$	5.74(a)	$Mn(OH)_2$	12.8(c)
FeS (mackinawite)	18.80(d)	$FeCO_3$	10.7(c)	$Fe_3(PO_4)_2$	36.0(c)	Fe_2O_3	40.63(b)
NiS (millerite)	20.97(d)	$NiCO_3$	6.9(c)	$Ni_3(PO_4)_2$	31.30(b)	$Ni(OH)_2$	17.20(b)
ZnS (wurtzite)	22.50(a)	$ZnCO_3$	10.0(c)	$Zn_3(PO_4)_2$	36.70(b)	$Zn(OH)_2$	15.55(b)
PbS (galena)	27.51(a)	$Pb_3(CO_3)_2(OH)_2$	45.46(b)	$Pb_3(PO_4)_2$	43.5(c)	PbO	15.09(b)
HgS (metacinnabar)	51.66(a)	$HgCO_3$	16.1(c)	n/a		$Hg(OH)_2$	25.40(b)
CuS (covellite)	36.10(a)	$Cu_2(OH)_2CO_3$	33.8(c)	$Cu_3(PO_4)_2$	35.12(b)	$Cu(OH)_2$	19.36(b)
CdS (greenockite)	27.07(a)	$CdCO_3$	13.7(c)	$Cd_3(PO_4)_2$	32.60(b)	$Cd(OH)_2$	14.27(b)
Ag_2S (acanthite)	49.02(a)	Ag_2CO_3	11.1(c)	Ag_3PO_4	17.6(c)	AgOH	7.70(b)

(a) From Lindsay, 1979
(b) From Benjamin, 2002
(c) From Morel and Hering, 1993
(d) From Van den Hoop *et al.*, 1997
(e) n/a indicates no record of insoluble phosphate mineral

4.2.7 Spatial and Temporal Stability of Sedimentary Redox Boundaries. The sequestration of toxic metals through precipitation, co-precipitation, or adsorption processes is reversible. Through dissolution of the solid phase, precipitated or adsorbed metals are released into the dissolved phase. This is commonly caused by shifts in redox potential. Shifts in pH can cause surface electrostatic conditions to change dramatically, resulting in the release of adsorbed species. Of critical importance to effective natural attenuation of sequestered metals is the knowledge of how both natural (*e.g.*, tidal or bioturbation) and anthropogenic (*e.g.*, dredging) forces can induce shifts in Eh and/or pH, and how those shifts affect metal speciation in sediments. For example, a shift from reducing to oxidizing conditions can lead to the oxidative dissolution of Cr(III) minerals, or release trace metals associated with the oxidation of sulfide minerals. Alternatively, a shift from oxidizing to reducing conditions can lead to the desorption of metals adsorbed to Fe(III)/Mn(IV) oxides. Resuspension of sediments (*e.g.*, in the event of storms, tidal surges, or dredging) could result in a potential increase in dissolved concentrations of metals in the surface water, primarily related to environmental conditions promoting the shift of trace metals from the particulate state to the dissolved state. However, the kinetics of oxidation/reduction processes are often slow relative to time-scales of resuspension events, and the dissolution process may require days to years before release of solid-bound metals are detected. Van Den Berg *et al.* (2001b), for example, collected data on metal remobilization during a large-scale experimental dredging project and found that dredging activities did not notably influence dissolved concentrations of trace metals in the water column for the studied site. These observations could be related to a relatively slow oxidation of metal sulfides or to rapid resequestration of liberated trace metals by freshly formed manganese and/or iron (hydr)oxides.

Spatial and temporal stability of sediment redox boundaries and processes can be disrupted, altered, or generally affected by the introduction of water containing a unique geochemical composition, such as salt water intrusion in a fresh water coastal lake or groundwater upwelling in a precipitation-fed bog (Whitmire and Hamilton, 2008). Groundwater discharge can introduce a seasonal flux of electron donor/acceptors or nutrient cations into lacustrine or riverine systems (Sebestyen and Schneider, 2004; EPA, 2005d). For example, high-iron groundwater upwelling into a fresh water lake system may result in iron oxide precipitation at the oxic-anoxic boundary, or salt water intrusion into a fresh water coastal lake/marsh can produce drastic changes in the predominant microbiological processes that govern the oxidation state of sedimentary redox-active metals. Salt water intrusion into a fresh water system represents a significant perturbation to the system. Anaerobic Fe/Mn reducers and/or methanogens can comprise the majority of microbial community structure in the absence of sulfate reducers, and the introduction of sulfate from sea water can promote SRB activity. Competition by SRBs for labile organic substrate can inhibit the activity of methanogens and/or Fe/Mn reducers (Canavan *et al*., 2006). This shift in anaerobic community structure has implications for the fate of mercury in contaminated sediments.

Several studies have reported dynamic seasonal and spatial (horizontal and vertical) behavior of sulfide minerals in natural systems (Koretsky *et al.*, 2003; Roychoudhury, 2007). Three interconnected factors may help to explain the observed patterns reported in the literature regarding the spatial and temporal variation in sedimentary redox conditions: 1) diagenetic processes (biotic and abiotic reactions that alter the chemical form of many of the inorganic and organic constituents of the sediment), variations in temperature, and oxygen and organic carbon content influencing the local flora that, in turn, influence sedimentary redox processes via rhizosphere processes, 2) the stability of the reduced metal precipitates and/or complexes with respect to oxidation, and 3) bioturbation.

In response to the activity of local flora, redox boundaries in shallow sediments may shift on seasonal and even diurnal time scales. In shallow waters and wetlands, the metabolic activity of algae (periphyton) living on the surface of sediments or attached vascular plants (marsh grasses) may produce a diurnal vertical shift of the sediment redox potential discontinuity depth (defined as the depth in sediment where Eh is 0). The surface layer of sediment becomes reducing during the night when algae at the sediment-water interface and/or marsh plants are respiring, decreasing ambient oxygen concentrations.

The surface layer is oxidized during the day when the algae and marsh grasses are photosynthesizing, producing a net increase in oxygen concentration. This process is of particular importance to mercury-contaminated sediments where transformation of inorganic mercury to methyl mercury (a potent neurotoxin) during reducing episodes may promote the release of mercury to the overlying water column and bioaccumulation of methyl mercury (Bloom *et al.*, 1998). The transient nature of sulfides depends on the particular metal sulfide. The oxidation of iron monosulfides in sediments cannot be taken as indicative of the oxidation of other metal sulfides that may be more stable (Table 4-1; Peterson *et al.*, 1996). Simpson *et al.* (1998) demonstrated that, although FeS and MnS are labile and rapidly oxidizable, CdS, CuS, PbS, and ZnS are kinetically stable for several hours.

Seasonal variation in flow rates or storms that induce an influx of oxygenated (sea) water can result in rapid oxidation of anoxic sediment and, thereby, release significant proportions of associated metals (Koretsky *et al.*, 2003; EPA, 2005c). Although considerable site-to-site variability exists due to climatic differences, in general, reducing conditions conducive to the formation of metal sulfides tend to be more prominent at the end of the summer and during fall and revert to more oxidizing conditions in the winter and spring (Howard and Evans, 1993; Van Den Hoop *et al.*, 1997; Grabowski *et al.*, 2001; Roychoudhury, 2006). Sediments tend toward anoxic conditions during summer months due to diminished fresh water inputs, higher water temperatures, an increased rate of particulate organic matter (*e.g.*, phytoplankton and detritus) deposition, and increased biological activity, which leads to increased oxygen consumption, general hypoxia, and more reducing conditions closer to the sediment-water interface (Kraus and Bragin, 1988; Koretsky *et al.*, 2006). Microbial degradation of organic matter in sediments depletes sediment oxygen and increases sediment sulfide concentration via sulfate reduction (Figure 4-3).

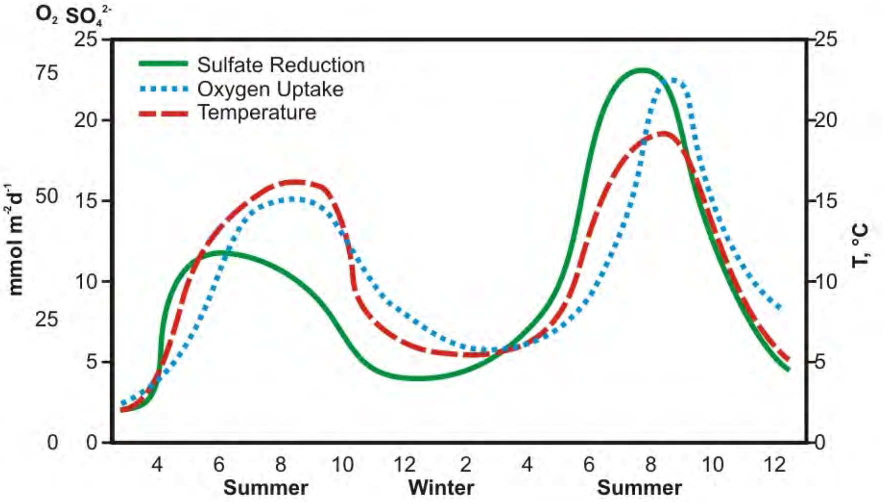


Figure 4-3. Seasonal Variations of Sediment Oxygen Uptake Rate (Oxygen Consumption), Sulfate Reduction Rate (Sulfide Production) in the Whole Sediment Column, and Sediment Temperature (Adapted from Jørgensen, 1977.)

In addition to temporal shifts in sediment redox potential, a vertical redox gradient is created from microbial respiratory processes (as illustrated in Figures 4-1 and 4-2). Most often, metal sulfide concentration increases with increasing sediment depth and is linked to the redox gradient present in the sediment (EPA, 2005c). This increase may occur over a small sediment distance (less than 1 cm) (Van Den Berg *et al.*, 1998, 2001a, 2001b). The observed vertical gradient in sediment metal sulfide concentration is caused mainly by the oxidation of sulfides near the sediment/overlying water interface. A factor that may contribute to this oxidation is sediment bioturbation (De Witt *et al.*, 1996), which may carry oxygen to deeper sediment layers due to the burrowing activity of benthic organisms and govern vertical trends of Fe(III) minerals and/or sulfate (Kostka *et al.*, 2002; Hyun *et al.*, 2007). The effect of bioturbation on a broader scale is to push the sub-oxic zone of sediments, especially in tidal or littoral zones, to great depths; the spatial distribution of aerobic decomposers, Fe/Mn reducers, and sulfate reducers may exhibit considerable overlap (Koretsky *et al.*, 2005). Since the oxidation process is often relatively slow, the rate of conversion of insoluble metal sulfide to dissolved metal in the pore water occurs slowly but still may be of significance to metal bioavailability in environments that are not dynamic. On the other hand, any surficial layer of metal sulfide that becomes dissolved in the pore water as a result of metal sulfide oxidation will not simply build up in the pore water and remain there. Rather, it will be subject to diffusion from the pore water into the overlying water as it is produced. Given that the sediment-water interface is quite thin, this diffusive flux will tend to offset any increase in pore water metal levels that occur as a result of the oxidation process. Furthermore, pore water metal concentrations will not necessarily be entirely available to benthic organisms since any metal that is present in the pore water has the potential to form non-bioavailable metal complexes with other pore water ligands on DOC, thereby further reducing the potential for toxicity.

4.3 Biogeochemical Process Affecting Speciation and Bioavailability of Metals in Water and Sediment

All sediments contain metals. The metals in fresh water and marine sediments originate from both natural and anthropogenic sources and are present in different physical and chemical forms (Gleyzes *et al.*, 2002; Canavan *et al.*, 2007). The two major pathways available for metal incorporation from sediments into higher trophic level aquatic species are: 1) ingestion of metal-enriched sediment, suspended particles, and metal-contaminated food, and 2) direct uptake of solution-phase (*i.e.*, strictly dissolved) species (Luoma, 1989; Simpson and Batley, 2007). Consequently, knowledge of geochemical reactions of metals in both water and sediment is necessary to understand controls on metal bioavailability in natural water (Luoma, 1989). Bioavailability studies indicate that aquatic organisms bioaccumulate free metal ions (*i.e.*, hydrated metals ions or aquo ions) from solution quite efficiently; similarly, terrestrial species bioaccumulate dissolved metals more efficiently than via direct particulate matter ingestion (Luoma, 1983; Newman and Jagoe, 1994). Consequently, geologic and/or environmental conditions that enhance dissolved metal concentrations (*e.g.*, lower pH) result in greater metal bioavailability. Indirect controls, such as larger particle or sediment size, also can result in greater bioavailability of metals by reducing effective surface area available for adsorption of increasing dissolved metal concentrations. Metal assimilation from ingested particulate matter may be of significance in some situations because metals are highly concentrated in this form (Luoma, 1989).

Sediments are composed of inorganic detrital particles derived from weathering of crustal rocks and *in-situ* precipitation of oxide minerals in upwelling groundwater plumes (*e.g.*, ferrous iron containing groundwater). They typically contain a variety of metals, mostly in a stable mineral lattice. Heavy minerals and many clay minerals are rich in one or more metals. Most of the metals in these solid, stable forms in coastal sediments are derived from natural chemical weathering, physical erosion, and surface runoff from land. However, anthropogenic inputs from such sources as mine tailings, dredge material, and oil well drilling muds may be locally important. The metals that are present in solid sediment particles are classified as residual or detrital metals; residual metals may represent up to about 90% of the total metals in some sediments (Loring, 1982). These residual metals are not bioavailable. Residual metals in sediment tend to be extremely persistent; therefore, it is important in MNR of metals-contaminated sediments to differentiate between residual and potentially more mobile, bioavailable metal fractions in sediments.

The detrital metals in sediments are present as precipitates from the overlying water or sediment pore water, or they are adsorbed to or complexed with various sediment components and may be bioavailable. In oxidized sediments, metals may be adsorbed to clay particles or to iron, manganese, and aluminum oxide coatings on clay particles or associated with particulate organic matter. During shifts in redox potentials, metals may be released from sorbed phases into sediment pore water as aqueous and, therefore, bioavailable forms. As the concentration of oxygen in sediment decreases, usually because of microbial respiratory utilization of organic matter, the iron, manganese, and aluminum oxy-hydroxide coatings begin to dissolve, releasing adsorbed metals. In oxygen-deficient and sulfur-rich sediments, many metals react with sulfide produced by SRB to form insoluble metal sulfides. Microbial degradation of organic matter may also release metals that were intercalated within the DOM macromolecular framework. Certain bacteria are able to methylate some metals, such as mercury, arsenic, and lead, to organic species that are more bioavailable and have high potential to bioaccumulate compared to non-methylated forms.

The chemical species (or forms) of metals in sediments (*e.g.*, aquo ions, hydrolysis species, dissolved complexes, adsorbed species, pure-phase precipitated solids, and trace-metal co-precipitated solids) profoundly affect the bioavailability and toxicity of the metals to aquatic/marine plants and animals (Nelson and Donkin, 1985). Each metal has unique physical and chemical properties that influence their speciation in sediments and pore water and, thus, their relative bioavailability to aquatic receptors. Metals in forms sequestered from the aqueous phase generally are not bioavailable to sediment-dwelling organisms. Metals in solution or colloidal suspension in sediment pore water, or that are readily desorbed (leached) into the aqueous phase by small changes in oxygen concentration, pH, or redox potential, are much more bioavailable. The free or aquo ions (*e.g.*, $Cu[H_2O]_4^{2+}$) are considered the most bioavailable forms of most metals, with mercury being a notable exception (Newman and Jagoe, 1994; Riba *et al.*, 2003; Bartacek *et al.*, 2008; Keung *et al.*, 2008).

As discussed in Section 4.2, fluctuations in redox status, due to natural or anthropogenic forces, can exert a profound effect on metal speciation and bioavailability. However, where thermodynamic considerations might predict drastic changes in chemical speciation, the kinetics of these changes may not lead to observed toxic effects corresponding to thermodynamic calculations. Kinetics of redox processes are specific for each metal, and, as such, rates of metal redox changes must be considered on a site-specific basis depending on the particular metal contaminant at the given site. For example, Sundelin and Eriksson (2001) provide evidence of minimal bioavailability of certain metals (*e.g.*, cadmium, zinc, and copper) after oxygenation and subsequent remobilization of bulk sedimentary metal sulfides. In this study, it was demonstrated that after long-term oxygenation of sediment cores (3 to 7 months), cadmium, zinc, and copper remained relatively unavailable to a benthic organism (*Monoporeia affinis*, a benthic amphipod) compared to the lead and mercury co-contaminants, although the solubility products of the different sulfide minerals would predict greater stability of mercury sulfide.

Long-term stability suggests that other ligands (in addition to sulfide) are important for metal bioavailability. Buykx *et al.* (2000), using a modification of the Tessier sequential extraction protocol, demonstrated that aeration of sediments for 3 weeks had little effect on the distribution of extractable nickel, copper, and lead across the operationally-defined pools typical of the Tessier sequential extraction method. Zinc and cadmium were observed to be released as sulfide levels decreased, but subsequently were bound as carbonates or adsorbed to other binding phases. These results should be taken with a cautionary note as all operationally-defined protocols are limited in their ability to translate to *in-situ* metal speciation. However, these results are consistent with the findings of Mahony *et al.* (1996) and DiToro *et al.* (2001) regarding metal binding to other geosorbents (*e.g.*, organic carbon and metal oxides/hydroxides) in sediments, where adsorption (*e.g.*, onto iron and manganese hydrous oxides occurring in sediment) can influence the distribution and bioavailability of metals. For example, Zhuang *et al.* (1994) investigated the effect of aeration on cadmium bioavailability in sediments in a series of lab aeration experiments in batch reactors during periods of approximately 1 month. During aeration, the concentration of metal ions associated with sulfide minerals and pyrite decreased. At the same time, increases were noted in the concentrations of hydrous iron and manganese oxides and these materials became increasingly more important in the binding of cadmium. Following aeration, more than 50% of the cadmium was associated with the extractable iron and manganese components and approximately 2% of the cadmium released during the oxidation of sulfide minerals entered into the liquid phase. However, in the case of highly contaminated sediments, a 2% release still may be significant.

4.3.1 Metal Speciation: Adsorption, Complexation, and Solubility. Adsorption, which occurs when dissolved metals are attached to surfaces of solid-phase precipitates or suspended particulate material (notably oxides of iron, manganese, and/or aluminum; clay; and/or organic matter), is principally governed by a combination of: 1) pH/Eh, 2) the pH-dependent electrostatic characteristics of the individual mineral phases present within a given specific sedimentary environment (Campbell and Stokes, 1985; Cusimano *et al.*, 1986), 3) the different affinity for adsorption of metal cations and anions present in solution, and 4) the availability of particulate surfaces and the total dissolved metal content (Bourg, 1988; Elder, 1989). Particle size and total surface area available for adsorption are important factors in adsorption processes and can affect metal behavior and subsequent bioavailability (Luoma, 1989). Small particles with large surface area-to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface area-to-mass ratios. Reduced adsorption results in more metals remaining in the dissolved phase, which can increase metal bioavailability. The sorptive capacity of sediment particles is less in marine than in fresh water sediments because of the high ionic strength of sea water.

The “adsorption edge”, defined as the pH range over which the rapid change in sorption capacity occurs, is unique to each metal. For example, metals have different hydrolysis constants (a function of pH) as well as different complexation constants with other common dissolved constituents (*e.g.*, carbonate, chloride, and phosphate) collectively governing the macroscopic affinity of metal contaminants for surface complexation or ion-exchange adsorption. For sites with complex mixtures of metal contaminants, adsorption of different metals occurs over a large pH range. Cadmium and zinc tend to have adsorption edges at higher pH values than do iron and copper, and, consequently, they are likely to be more mobile and more widely dispersed at typical environmentally-relevant pH values. Adsorption edges also vary with the concentration of the complexing agent; increasing concentrations of the complexing agent increase the pH of the adsorption edge (Bourg, 1988). Major cations such as Mg^{+2} and Ca^{+2} also compete for adsorption sites with other metals and can reduce the amount of metal adsorption (Salomons, 1995).

To illustrate how solution phase speciation and complexation can affect solubility, adsorption, and, by extension, bioavailability, an example of mercury speciation (Figures 4-4 and 4-5) and adsorption onto a simple, low-activity, 1:1 clay mineral (kaolinite) is discussed below. Several studies have shown that in the absence of complexing ligands or surficial columbic effects, the $Hg(OH)_2^0$ complex is the predominant sorptive species owing to the inherent solubility of the other charged species, Hg^{2+} and $HgOH^+$ (Sakar *et al.*, 1999, 2000; Kim *et al.*, 2004). In the absence of overwhelming electrostatic repulsive interactions between charged surfaces and ionic mercury species, a typical pH-sorption edge for mercury occurs at a pH between 3.5 and 4, roughly corresponding to the pKa of the hydrated mercury species (pH 3.2, Figure 4-4) (Sakar *et al.*, 1999). This observation alone indicates that simple electrostatic attraction between a negatively charged surface and positively charged ions is not the process governing the sorption of inorganic mercury from aqueous solution.

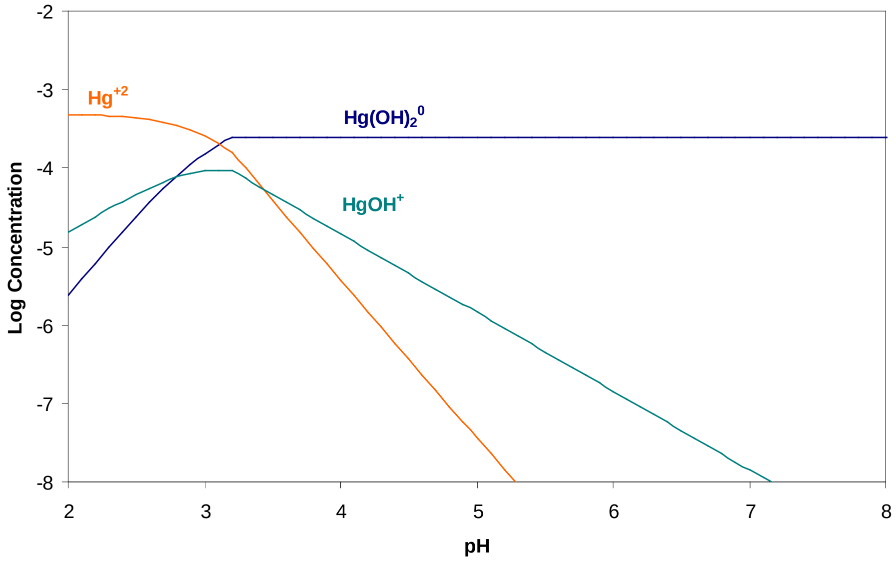


Figure 4-4. Mercury Speciation Plot, $Hg_{tot} = 10^{-3}$ M
(Mercury speciation was modeled using MINTEQ ver. 2.53.)

In the presence of a simple electrolyte, sodium chloride, experimental and model studies indicate that mercury complexation with chloride results in the formation of Hg-Cl complexes with greater intrinsic solubility than the hydrolysis species ($Hg[OH]_x^{+[2-x]}$) (Sakar *et al.*, 2000). Using 0.01-M NaCl as the background electrolyte, the pH absorption edge shifts to a pH of 7, an observation explained by the higher solubility of the dominant solution species $HgCl_2^0$, $HgCl^+$, HgClOH, and $HgCl_3^-$ that dominate at pH values up to 7.5 (Figure 4-5). Above pH 7.5, the dominant mercury species is $Hg(OH)_2^0$, which is the mercury hydrolysis species with the highest observed tendency for sorption in the absence of additional background salts. The observation of diminishing mercury sorption and the increasing pH of the mercury adsorption edge with an increasing chloride concentration has been attributed to the formation of Hg-Cl complexes, which are more stable in the aqueous phase and less prone to sorption, resulting in a greater aqueous phase pool of mercury for biotic processing in sediments containing dissolved chloride.

4.3.2 Metal-Solid Partitioning. The partitioning of metals between sediment and interstitial pore water is affected strongly by the presence/absence of reactive geosorbents (*e.g.*, organo-clays and oxides), the affinity of dissolved metals species for those sorbents, the chemical and phase speciation of the sediment-bound metals (*e.g.*, bound to sulfides, organic matter, or iron hydroxides), the pH and redox conditions, and the physical forces acting on the sediment (*e.g.*, bioturbation and tide-induced sediment resuspension) (Calmano *et al.*, 1993; Warnken *et al.*, 2001; Atkinson *et al.*, 2007). Particle size affects the accessibility and relative surface area of the different metal-binding phases. High pore water DOC concentrations may lead to an increase in pore water metal concentrations (although not necessarily in biologically available forms) (Besser *et al.*, 2003). Sulfides characteristically possess reactive surfaces important in controlling pore water concentrations of B-type metals, those metals in the iron, cobalt, nickel, copper and zinc groups (*e.g.*, silver, gold, cadmium, and mercury). Metal binding by POC and iron hydroxide phases is pH-dependent, with the adsorption edge typically being in the pH range of 5 to 7 (Lion *et al.*, 1982; Millward and Moore, 1982; Stumm and Morgan, 1996). Additionally, sediment-water partition coefficient (K_d) values typically decrease substantially as pH decreases, although the effect of pH on metal adsorption can vary widely across metals depending on the columbic and solubility

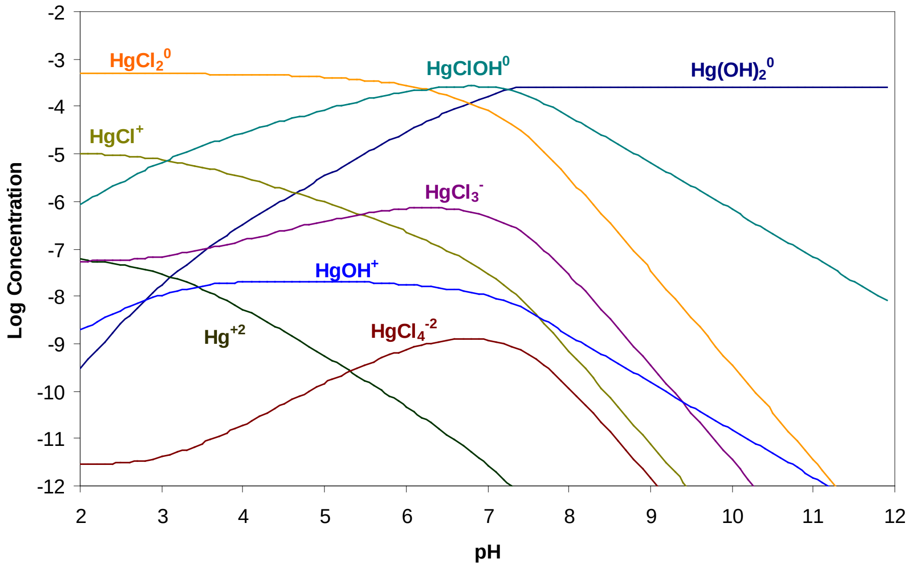


Figure 4-5. Mercury Speciation Plot in a Solution of Sodium Chloride (Mercury speciation was modeled using MINTEQ ver. 2.53.)

characteristics of the hydrolysis species (Stumm and Morgan, 1996; Tessier *et al.*, 1996; Trivedi and Axe, 2001). In spiked-sediment experiments, Simpson *et al.* (2004) found that metals in pore water equilibrated faster in sediments having high concentrations of metal-binding sites (*e.g.*, particulate sulfide, organic matter, and iron hydroxide phases) and large surface areas (*e.g.*, fine, silt/clay sediments) versus in sandy sediments having low binding capacities. Additionally, these authors found that equilibration rates were faster at higher pH values and at higher temperatures.

Commonly occurring iron(III) oxides (*e.g.*, hematite, goethite, and ferrihydrite) have surface pKa values ranging from 8 to 9, whereas manganese oxides have surface pKa values less than 5 (see Section 4.2). Therefore, at circumneutral pH values common in interstitial pore water of sedimentary environments, manganese oxides tend to sorb metal cations, rather than oxyanions, with high affinity. Ferric hydroxide is able to adsorb trace metals predominantly as cations (Cr^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+}) in neutral to high pH levels, and predominantly as anions (SeO_4^{-2}, CrO_4^{-2}, and AsO_4^{-3}) in neutral to mildly acidic pH levels (Patoczka *et al.*, 1998). Thus, sorption behavior is related to pH, and each metal ion has its own optimum pH range for adsorption (Farley *et al.*, 1985). Under circumneutral pH conditions, trace metals tend to bind directly to the OH groups of iron and manganese oxides and hydroxides, whereas binding to organic matter coatings of oxide particles is observed under more acidic (pH < 5) conditions (Tessier *et al.*, 1996). The unusually high adsorption and scavenging capacities of manganese oxide/hydroxide minerals provides one of the main controls of dissolved inorganic contaminant concentrations in aquatic sediments where manganese minerals are present (Young and Harvey, 1992; Dong *et al.*, 2000; Amirbahman *et al.*, 2006).

Manganese hydrous oxides are some of the strongest oxidants naturally found in the environment (Tebo *et al.*, 2004) and, as such, participate in a wide variety of redox reactions including oxidation of Se(IV) to Se(VI), Cr(III) to Cr(VI), and As(III) to As(V), thereby influencing toxic metal availability by oxidative precipitation (*e.g.*, arsenic) or solubilization (*e.g.*, chromium) (Huang, 1991; Manceau and Charlet, 1992; Scott and Morgan, 1995; Amirbahman *et al.*, 2006). Interaction of metals with even small amounts of manganese oxides has been reported to decrease the dissolved metal concentration by several orders of magnitude (Wei and Murray, 1991; Fuller and Harvey, 2000; Kay *et al.*, 2001). Manganese oxide minerals can adsorb or incorporate substantial amounts of metals such as copper, cobalt, cadmium, zinc, nickel, strontium, lead, calcium, iron, radium, mercury, arsenic, and selenium (Dong *et al.*, 2000; Foster *et al.*, 2003; Nicholson and Eley, 1997; O'Reilly and Hochella, 2003; Webb *et al.*, 2006).

4.3.3 Metal-Organic Matter Interactions: Relevance to Bioavailability. Oxygen-containing functional groups (*e.g.*, alcohols, phenols, and carboxylic acids) prefer to complex hard metals, such as Al(III) and Fe(III). Nitrogen-containing functional groups (*e.g.*, amines and aniline compounds) and sulfur-containing functional groups (*e.g.*, thiols) tend to bind with soft metals, such as Hg(II) and Cu(II). The formation of metal-DOM complexes can profoundly affect metal fate, transport, and bioavailability in sediments by increasing metal solubility through surface complexation-dissolution processes, promoting metal agglomeration and particle nucleation resulting in decreased solubility, or promoting metal sorption by facilitating the formation of ternary mineral-NOM-metal complexes. The amount of metal that can be complexed by DOM-associated organic ligands is metal dependent. Analytical techniques have been developed within the past two decades to demonstrate that the ligands responsible for complexing several metals (*e.g.*, copper, nickel, zinc, cobalt, lead, and iron) in marine and fresh water systems are organic in nature, not inorganic as was often previously assumed (Capodaglio *et al.*, 1990; Donat and Bruland, 1990; Xue and Sigg, 1993; Miller and Bruland, 1994; Rue and Bruland, 1995; Wells *et al.*, 1998; Ellwood and Van Den Berg, 2001). In many cases, organic ligands are responsible for binding the majority, in some cases close to 100%, of dissolved metals present in aqueous systems.

The interaction of metals with DOM in aquatic systems has been described by several conceptual models, illustrating a range of processes in contrasting environments. One model is of metal complexing ligands of low concentration, but with high metal-binding specificity and affinity having their origin in the evolution of biological systems (Bruland *et al.*, 1991). Organic ligands with multiple binding sites on a single discrete molecule with high metal binding affinity are referred to as chelating agents. Examples of chelating agents of these types include phytochelatins and siderophores, which are minor components of the overall organic carbon pool in the environment but whose environmental significance is underscored by high metal-binding constants and each chelating agent typically demonstrating a strong affinity for a specific metal. This type of interaction often is used to define metal-organic interactions in open ocean surface waters but has not been demonstrated in metal-organic associations occurring in sediments and interstitial pore waters. This is likely the consequence of the abundance of molecularly-uncharacterized organic substances in sediments that have undergone significant diagenetic alteration. Thus, specific siderophores or chelatins would be expected also to have experienced molecular transformations and, thus, not be readily identified by common isolation techniques. However, the metal binding properties of DOM for a range of metals has been modeled using a two-domain model with both high-affinity and low-affinity binding sites. The high-affinity sites are analogous to metal-chelate associations, indicating that high-affinity metal binding domains within DOM may be biogenic in origin. Metals bound within the macro-molecular framework of DOM typically are considered less bioavailable, as they are not readily accessible for uptake by microorganisms. Addition of humic material has been shown to reduce toxic effects of copper and cadmium in sediments, and adsorption of the metals onto the humic material was invoked to explain the diminished toxicity (Nadella *et al*., 2009).

Another conceptual model of trace metal complexation by organic ligands in aquatic systems has been described in which metals are associated with and trapped within colloidal aggregates. Metal availability is governed by steric constraints and mass transport limitations (Honeyman and Santschi, 1984; Mackey and Zirino, 1994; Santschi *et al.*, 1997). This model has been used to describe metal speciation in pore waters as well as the interaction of trace metals with organic matter coated on the surface of particles in sediments. While there are a paucity of studies, evidence exists that the physical form or physical speciation of many trace metals in interstitial water of sediments and in overlying water consists of colloidal particles and further that associated trace metals have a dynamic cycling between water and sediments (Guo *et al.*, 2000; Santschi *et al.*, 1997; Shank *et al.*, 2004a, 2004b; Skrabal *et al.*, 1997, 2000, 2006). It also is well recognized that organic matter coats the surface of sedimentary particles and serves as a binding site for the adsorption of trace metals (Hunter, 1980; Santschi *et al.*, 1997). This process likely is most important in surficial sediments during early diagenesis and probably does not play a significant role in deeper sediments where the abundance of NOM is usually observed to decline with depth.

4.4 Metal Specific Behavior

The total concentration of metals in sediment typically is not a reliable indicator of sediment toxicity because of the effect of sediment chemistry on metals speciation and bioavailability (Apitz *et al.*, 2005a; Berry *et al.*, 1999, 2004; Boothman *et al.*, 2001). Redox chemistry and pH strongly influence the solubility and availability of metals, particularly those with multiple valence states. Solubility and mobility of some metals (*e.g.*, chromium) decrease under anaerobic/low-redox conditions, while they increase for others (*e.g.*, arsenic). The pH and Eh of sediment pore waters can differ from the overlying aquatic environment and, in general, determine the redox state of the metal. Table 4-2 shows the dominant phases of metals in oxic and anoxic sediments. In this table, it can be seen that the speciation of divalent metals is influenced strongly by labile sulfides in sediments containing high total sulfur concentrations (marine, estuarine, and some fresh water sediments). In most cases, interactions between metal contaminants and reduced sulfur result in the formation of insoluble, non-bioavailable, metal sulfide precipitates. While chromium does not form an insoluble sulfide precipitate, its solubility and bioavailability still are influenced by sulfides and Fe(II) due to their acting as electron donors to catalyze the reduction of soluble Cr(VI) to insoluble Cr(III).

Table 4-2. Dominant Adsorbed or Complexed Phases of Metals in Oxic and Anoxic Sediments (from Brown and Neff, 1993)

Metal	Associations in Oxic Sediments	Associations in Anoxic Sediments
Arsenic	Fe/MnOx = AsO_4^{-3}	As_2SO_3, AsS, FeAsS
Cadmium	Fe/MnOx, OM/S, $-CO_3$	CdS
Chromium	OM, FeOx	OM, $Cr(OH)_3$
Copper	OM, Fe/MnOx	Cu_2S, CuS, FeCuS
Lead	Fe/MnOx	PbS
Mercury	OM	HgS,OM
Nickel	Fe/MnOx	OM, NiS, organic thiols
Tin$^{(a)}$	TBT-Cl-OH-CO_3	TBT-S, -OH, $-CO_3$
Zinc	Fe/MnOx, OM	ZnOM/S

(a) Only butyltins are considered.
Fe/MnOx = = AsO_4^{-3} = indicates arsenate – oxide sorption complex
CO_3 = carbonates
FeOx = iron oxyhydroxides
Fe/MnOx = iron and manganese oxyhydroxides
OM = organic matter
S = sulfides (dominant species given)
TBT-Cl, -OH, $-CO_3$, and –S = tributyltin chloride, hydroxide, carbonate, and sulfide

For divalent metal cations, including silver, cadmium, copper, nickel, lead, and zinc, the presence of reduced sulfur is a useful predictor of anoxic sediment toxicity (Ankley *et al.*, 1991; Berry *et al.*, 1999; Boothman *et al.*, 2001). Sulfide reacts with divalent metals to form highly insoluble compounds that are not bioavailable (Allen *et al.*, 1993; Ankley *et al.*, 1991; Berry *et al.*, 1999; Di Toro *et al.*, 1992; EPA, 2005b). It follows in theory (Di Toro *et al.*, 1992) that divalent transition metals do not cause toxicity in anoxic sediments until the reservoir of sulfide is exhausted. This concept is known as the simultaneously extracted metal (SEM)/AVS theory and is discussed in Section 4.6. Sulfide also reacts with mercury to form highly insoluble compounds. However, because mercury presents unique problems, particularly under anaerobic conditions where it can be methylated, mercury is not included in the standard SEM analysis and, if expected to be present, the sediments may require direct toxicity testing for the presence of methylated forms (discussed in detail later in this section).

The geochemistry of divalent metals often present in trace quantities relative to more abundant iron and manganese minerals (*e.g.*, cadmium, copper, lead, mercury, nickel, and zinc) is unique because, in the presence of excess sulfides, divalent metals will displace the iron and manganese moieties of aqueous FeS and MnS to form more insoluble metal sulfides. This renders the metals unavailable for uptake by biota. In aerobic sediments, these divalent metals will associate with negatively charged surface sites on either permanently- or variably-charged minerals, such as alumino-silicates or iron/manganese oxyhydroxides, respectively. It stands to reason that for most divalent metals, redox chemistry (*e.g.*, the reductive precipitation of a sulfide mineral or the precipitation of insoluble Cr[III] phases) plays a much larger role in MNR than sediment burial. If redox chemistry sufficiently reduces metal toxicity, additional measures intended to promote reduced toxicity and recovery of ecological receptors may not be required. However, under such conditions, it would be imperative to examine the long-term spatial and temporal stability of the anaerobic environment to ensure the long-term stability of the metal-complex precipitate as the reversion to aerobic conditions could result in mineral oxidative dissolution and subsequent release of toxic metals.

4.4.1 Arsenic. Arsenic has four oxidation states (V, III, 0, and –III) and is highly redox sensitive in the environment. In oxic environments, As(V) is the most stable form, while As(III) is predicted to form in moderately reducing conditions. As(III) can be reduced to As(0) under highly reducing conditions, although it is rarely seen in the natural environment. At low pH values, arsenic forms the covalent compound AsS (realgar), which has low solubility in water. The redox reactions of arsenic tend to be slow and are mediated by microorganisms and algae (Meng *et al.*, 2003; Rhine *et al.*, 2005). Inorganic arsenic species tend to predominate in the environment, although there are a number of methylated organic compounds that have been identified, with the mono- and dimethyl arsenicals being the most commonly observed species in aqueous systems (Anderson and Bruland, 1991).

Solid-phase arsenic speciation in sediments is one determinant of arsenic's potential mobility. Arsenic in more labile phases can be mobilized readily by changing redox conditions or other chemical changes, while arsenic that has become sequestered in mineral phases is unlikely to be mobilized by typical biogeochemical processes in sediments. Sequential extraction techniques for assessing the solid-phase speciation and mobility of arsenic in sediments (see Section 4.6.1) tend to be different from those often used for the transition metals (Hudson-Edwards *et al.*, 2004; Haus *et al.*, 2008). A major focus of methods developed for the solid phase speciation of arsenic is determination of As(III) and As(V) since commonly-employed extraction techniques focus on cationic metals and arsenic species are anionic (Keon *et al.*, 2001; Georgiadis *et al.*, 2006).

Arsenic behavior in sediments is driven by two major processes: 1) interaction with the redox cycling of iron during early diagenesis in surficial sediments, and 2) interaction with reduced sulfur and the formation of solid phases that are more recalcitrant and reduce arsenic mobility. The interaction with reduced sulfur tends to occur in deeper sediments where reduced sulfur is more abundant, but can vary considerably depending on the total concentrations of reduced sulfur in the sediments. Arsenic often is found associated with iron mineral phases through adsorption to their surfaces. When Fe(III) (oxyhydr)oxides are reductively dissolved, arsenic can be released to sediment pore waters. In anoxic sulfide-rich sediments, arsenic, as As(III), may be adsorbed to iron sulfide phases as an FeAsS-like precipitate (Bostick *et al.*, 2004). The chemical nature of the arsenic surface complexes on iron sulfides has been shown to transform on a time scale of weeks into an As_2S_3 (arsenolite) solid phase (Bostick *et al.*, 2004). Thus, sulfide-rich sediments have been identified as potential semi-permanent sinks for arsenic. In settings where reactive forms of iron exceed available sulfur, the formation of pyrite and/or greigite may impede the formation of arsenic-sulfide minerals (Wilkin and Ford, 2004; Toevs *et al.*, 2008). In more acidic sediment systems or marine systems undergoing sulfate reduction, precipitation of arsenic-sulfide minerals may dominate (*e.g.*, Neff, 2002; O'Day *et al.*, 2004).

In fresh water systems low in sulfur, arsenic is complexed primarily to iron oxides. In one study in fresh water having sediments low in sulfate and high in iron, the fate and transport of arsenic was coupled intimately to sedimentary iron redox dynamics (Root *et al.*, 2007). At the sediment-water interface, arsenic was found primarily as As(V) adsorbed to ferric oxides. Just below the sediment-water interface (~4 cm), As(V) was reduced to As(III) and arsenite was found to be complexed to iron oxides as bidentate-binuclear inner-sphere complexes. Below the oxic/anoxic transition zone (~10 cm), iron oxides were found to be transformed to mixed-valence Fe(II)/Fe(III) green rust and the release of arsenic at greater depths was concurrent with the reductive dissolution of solid iron phases (Root *et al*., 2007). In general, arsenic is more mobile in sediments that undergo regular fluctuations in redox status, and is more stable (less bioavailable) in sediments where the water level and redox status are more stable (O'Day *et al.*, 2004; Haus *et al.*, 2008). In fresh water sediments with low sulfate concentrations, arsenate released from Fe/Mn oxides during redox decline is reduced to arsenite and binds to sediment organic matter when NOM is available. At low Eh values, much of the arsenite may be present as arsenolite, which is slightly soluble and may diffuse upward into the overlying water column. Thus, arsenic is generally more bioavailable in fresh water than in marine sediments.

Most studies evaluating arsenic behavior in sediments have been relatively short investigations of 2 years or less. Many of the above processes have been elucidated from these studies. Longer-term observations of arsenic dynamics in contaminated sediments, although less common, underscore the importance of such observations for the application of MNR to arsenic-contaminated sediments. In one study, Senn *et al.* (2007) explored the long-term (>30 year) fate of arsenic in a dimictic eutrophic lake. Arsenic was added to this lake in the 1960s to control harmful aquatic macrophytes, with application principally to the littoral zone (Senn *et al.*, 2007). This lake experiences bottom-water anoxia during the spring-summer-winter months, during which time arsenic is reduced from As(V) to As(III), and concentrations were observed to increase in the water column along with concentrations of dissolved iron. As iron concentrations increased, the water column became super-saturated with respect to iron-bearing minerals and the arsenic ultimately was found to adsorb to these iron particulates and settle to the hypolimnetic sediments. Unexpectedly, the epilimnetic sediments from the littoral zone, which were oxic throughout the year, were observed to be a strong net source of arsenic to the water column. This observation was attributed to the high concentration of allochthonous organic carbon in these near-shore sediments, which resulted in anoxia just beneath the sediment-water interface. Upward diffusion of solubilized arsenic was found to enter the water column, adsorb to particulate iron (*e.g.*, hydrous iron oxides), and settle to the hypolimnetic sediments (Senn *et al.*, 2007). A prominent diffusive flux of arsenic from the epilimnetic sediments characterized by oxic conditions of the sediment-water interface indicates the importance of the relative kinetics of concomitantly-operative processes, such as reductive dissolution, diffusive/advective flux, ferric oxide precipitation, and arsenic adsorption, on the evolution of pore water geochemistry (Şengör *et al.*, 2007). This case study serves as an example that long-term monitoring of contaminated sediments selected for MNR is required to critically evaluate the results of system biology, geochemistry, and hydrology on long-term contaminant fate.

4.4.2 Cadmium. In anoxic environments, a majority of particulate cadmium is complexed by insoluble organic matter or bound to sulfide minerals (Kersten, 1988). In studies of cadmium speciation in anoxic marine and estuarine sediments, nearly all measured cadmium has been found to be present as cadmium sulfide (Lee and Kittrick, 1984; O'Day *et al.*, 2000). Greenockite (CdS) has extremely low solubility under reducing conditions, thereby decreasing cadmium bioavailability. Oxidation of reduced sediment or exposure to an acidic environment results in transformation of insoluble sulfide-bound cadmium into more mobile and potentially bioavailable hydroxide, carbonate, and exchangeable forms (Kersten, 1988).

As anoxic sediments containing cadmium are exposed to oxic waters, as much as 50% of the cadmium sulfide was found to be oxidized within a 90-day period in one study (Carroll *et al.*, 2002). Cadmium in oxidized sediments may be associated primarily with the carbonate plus Fe/Mn oxide fractions of the sediment (Rosental *et al.*, 1986). Most of the remainder is associated with the organic/sulfide fraction. Only about 1% is in the completely non-bioavailable residual fraction, indicating that cadmium associated with oxidized sediments is likely to be moderately mobile and bioavailable (Samant *et al.*, 1990).

4.4.3 Chromium. Elevated concentrations of chromium in soils, sediments, and groundwater usually result from anthropogenic inputs associated with the use of chromium in electroplating, tanning, pigments, corrosion inhibition, wood preservation, and other industrial processes (Papp, 1994; Johnson *et al.*, 2006). Chromium has two oxidation states in aquatic systems, chromate (Cr[VI]) and trivalent chromium (Cr[III]). Cr(VI) is fairly soluble and can be toxic to aquatic organisms and plants and carcinogenic to humans; Cr(III) is fairly insoluble and tends to be much less toxic and is even essential in animal and human nutrition (Katz and Salem, 1994; Nriagu and Nieboer, 1988; Berry *et al.*, 2004; EPA, 2002b, 2005a; Costa, 2003). An exception to Cr(III) insolubility can result if metal chelating agents produced by indigenous organisms are present that can dissolve amorphous chromium hydroxides and bind with Cr(III) (Carbonaro *et al.*, 2008).

Processes or environments that promote Cr(VI) reduction are of great interest because they represent conditions that should lead to minimal chromium toxicity. Hence, the reduction of Cr(VI) to Cr(III) can be considered a clean-up strategy without changing the total chromium content of a soil (James, 2001). Moreover, it has been hypothesized that sediments that are anoxic, as evidenced by the presence of AVS, should contain no Cr(VI) and also have minimal or no toxicity (Berry *et al.*, 2004; Rifkin *et al.*, 2004).

The reduction of Cr(VI) in aquatic sediments is linked intimately to the biogeochemical cycling of iron, sulfur, and DOM as facilitated by microbial activity (Buerge and Hug, 1998, 1999; Guha, 2004; Lee *et al.*, 2008) (see Figure 4-6). Cr(VI) is reduced readily to Cr(III) by various chemical and biochemical processes in anoxic or even moderately sub-oxic sediments (Morse and Rickard, 2004; Morse, 1994; Berry *et al.*, 2004; Magar *et al.*, 2008). If present, Cr(VI) observed in sediments usually is bound tightly to sediment organic matter and iron oxide coatings on clay particles, or is co-precipitated with iron sulfides (Schropp *et al.*, 1990; Olazabal *et al.*, 1997; Shtiza *et al.*, 2008). Chromium is not known to form sulfides, carbonates, or phosphates (Mayer, 1988); thus, most of the chromium in these sediments likely either is bound to organic matter or is present as the stable trivalent hydroxide.

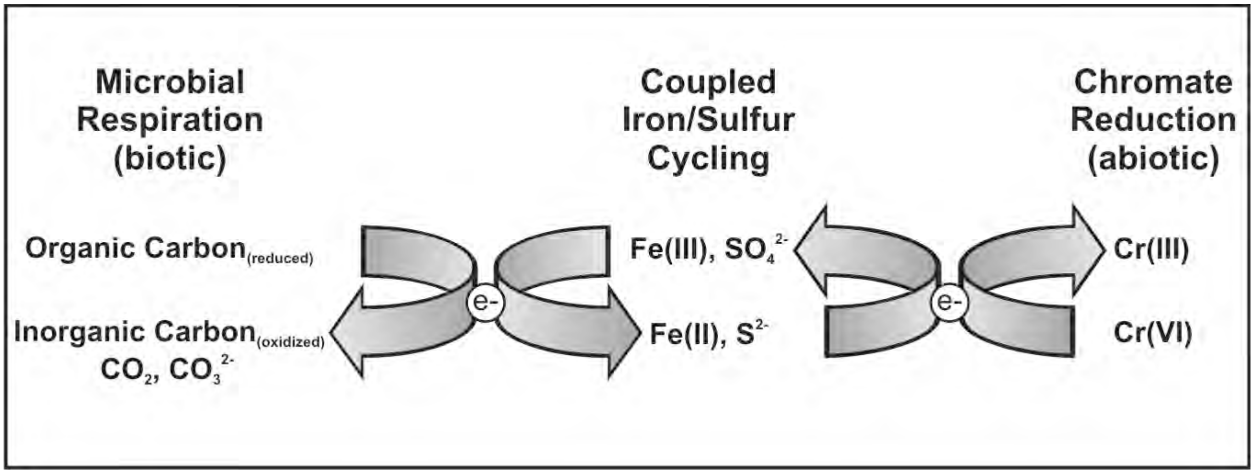


Figure 4-6. Oxidation/Reduction Cycling of Iron and Sulfur is Driven by Microbial Respiration, and Can Lead to Cr(VI) Reduction and Attenuation as Insoluble Cr(III) Precipitates

4.4.4 Copper. In sediments containing high concentrations of organic matter, copper is associated primarily with the organic/sulfide fraction or extractable organic matter (Luoma, 1985). Much of the remainder of the copper in oxidized sediments is associated with the reducible iron and manganese oxides (Prohic and Kniewald, 1987). In anoxic sediments, copper may undergo a variety of reactions with different inorganic and organic sulfur species to form a variety of soluble and insoluble complexes (Shea and Helz, 1988). Polysulfide complexes with Cu(I) are soluble, so the dominant form of copper in solution in the pore water of anoxic sediment layers is $CuS(S_5)^{-2}$. The dominant forms of copper in the solid phase of sediment include chalcocite (Cu_2S), covellite (CuS), and possibly chalcopyrite ($CuFeS_2$) (Shea and Helz, 1988). These sulfides have low solubility and bioavailability.

4.4.5 Mercury. Mercury sources to the environment are quite varied and include both natural (*e.g.*, volcanic activity, soil degassing, and forest fires) and anthropogenic processes (*e.g.*, burning of fossil fuels and medical waste, cement manufacturing, mining, and a variety of industrial processes) (United Nations Environmental Programme [UNEP], 2002; Pacyna *et al.*, 2006; Selin *et al.*, 2007). These sources enter the aquatic environment primarily through atmospheric deposition and municipal and industrial discharges. Recent estimates place the annual amounts of mercury released into the air by human activities at between 50% and 75% of the total yearly input to the atmosphere from all sources (EPA, 1997a). Once introduced to the aquatic environment, mercury quickly partitions to solid phases and settles to sediments (Santschi, 1988). Most sedimentary mercury in natural aquatic environments is associated with humic and other organic materials as well as oxide and sulfide minerals (Ravichandran, 2004; Merritt and Amirbahman, 2007). Several studies have shown that mercury is less bioavailable in sediment that is rich in organic matter (Luoma, 1989). Mercury reacts strongly with free sulfide to form insoluble sulfide mineral precipitates (HgS, cinnabar, and metacinnabar) or is bound as surface complexes with organic matter containing sulfur (Ravichandran, 2004). Vertical profiles of mercury in fresh water sediments indicate sulfide controls on mercury speciation, where zones of sulfide mineral precipitation act as a net sink for mercury (Merritt and Amirbahman, 2007). Mercury also forms a number of soluble polysulfide complexes that enhance the solubility of HgS in pore waters of sediments (Benoit *et al.*, 1997).

Microbial methylation of mercury in water and sediments leads to the formation of monomethyl mercury (MeHg), which is the toxic form of mercury that bioaccumulates through the food chain (Wiener *et al.*, 2003). Methyl mercury species are more readily assimilated and retained by aquatic organisms than are inorganic forms of mercury (Mason *et al.*, 1995, 1996). Most mercury methylation takes place in suboxic sediment layers (Gagnon *et al.*, 1996; Gilmour *et al.*, 1998) and is considered to be performed primarily by sediment-dwelling, SRB (Goulet *et al.*, 2007). The relationship between SRB activity and mercury methylation may be a consequence of the marine and estuarine environments where many of these observations have been made. There is evidence that iron-reducing bacteria (*Geobacter* sp.) also may be able to methylate mercury (Fleming *et al.*, 2006).

In general, factors that promote SRB activity also are influential in the production of MeHg (Goulet *et al.*, 2007). These parameters include the total mercury concentration in water or sediment, oxic/anoxic conditions, temperature, and concentrations of DOM, sulfate, and sulfide. High temperatures generally stimulate bacterial activity. In waters low in sulfate, increasing sulfate can stimulate methylation. In all waters, the sulfate-reduction process and the subsequent build-up of sulfide appears to limit the production of MeHg, perhaps by limiting the fraction of Hg^{2+} that is available for methylation (Benoit *et al.*, 1997; Marvin-DiPasquale *et al.*, 2005).

Dissolved MeHg in sediment pore waters can comprise a significant portion of the total dissolved mercury present (Gagnon *et al.*, 1996; Bloom *et al.*, 1998; Choe *et al.*, 2004). Although much of the dissolved MeHg in sediment pore waters actually is complexed to DOM or exists in association with colloidal organic matter, it should be considered potentially bioavailable to sediment-dwelling organisms. Movement of MeHg from anoxic pore water into the overlying water column occurs through sediment-water exchange processes, which can be enhanced by benthic fauna (Gill *et al.*, 1999; Choe *et al.*, 2004).

Several pathways exist for the removal (detoxification) of MeHg in water and sediment. Oxidative bacterial demethylation of MeHg can occur under both anaerobic and aerobic conditions (Marvin-DiPasquale and Agee, 2003; Marvin-DiPasquale *et al.*, 2003). Sunlight also can degrade MeHg via photolysis. In addition, bacteria may reduce Hg(II) to Hg(0), thereby eliminating the precursor of MeHg and generating a form of mercury (Hg^o) that degasses to the atmosphere. Because of rapid interconversions between inorganic and organic mercury species in oxidized and reduced layers of fresh water and marine sediments, MeHg typically comprises ≤1% of the total mercury in sediments (Berman and Bartha, 1986; Choe *et al.*, 2004). Implications of the above-described studies suggest a management strategy for a mercury-contaminated site in which primary sources and hot spots of mercury are removed, followed by monitoring of aged mercury present at reduced concentrations in the remaining part of the site.

4.4.6 **Nickel.** In oxidized sediments, much of the potentially bioavailable nickel is complexed to iron and manganese oxides (Luther *et al.*, 1986). Nickel forms weak coordination complexes with oxygen donors such as carboxylate, hydroxyl, and other oxy-ligands (*e.g.*, humic and fulvic acids, clays, and metal oxides) (Wood, 1987). It also becomes tightly bound to anionic groups of bacterial polysaccharides (Wood, 1987). Nickel forms stable, insoluble complexes with sulfides and organic thiols in anoxic sediment layers (Wood, 1987). However, most of the nickel (often more than 90%) in relatively uncontaminated sediments is in the residual fraction, associated primarily with oxide minerals such as magnetite and silicates (Loring, 1982). In the presence of clay minerals, short-term nickel sorption results in the formation of a nickel-aluminum layered double hydroxide phase (Ford *et al.*, 1999; Scheckel *et al.*, 2000). The formation of a layered nickel-aluminum double hydroxide phase has been observed following reaction of aqueous nickel with clay minerals (*e.g.*, Ford *et al.*, 1999). The chemical stability of this association increased with time and was consistent with the ultimate incorporation of nickel into a new phyllosilicate mineral (Peltier *et al.*, 2006). Thus, the bioavailability of nickel due to interactions with clays, oxides, and NOM in sediments usually is low.

4.4.7 Silver. Silver introduction into aquatic systems originates principally from industrial processes utilizing silver (*e.g.*, photofinishing and electroplating) via wastewater discharge; more recent sources include use of silver nanoparticles as antimicrobial agents (Sañudo-Wilhelmy and Flegal, 1992; Flegal *et al.*, 1996; Bothner *et al.*, 2002; Squire *et al.*, 2002; Blaser *et al.*, 2008). Silver is particle reactive and is quickly delivered to sediments via adsorption onto suspended matter or incorporation into biological matter (Santschi, 1988; Connell *et al.*, 1991; Sañudo-Wilhelmy and Flegal, 1992; Benoit *et al.*, 1994; Wen *et al.*, 1997). Measurements of silver in sediments, therefore, can be used to delineate zones impacted by wastewater discharges into the aquatic environment and assess changes in environmental quality associated with these discharges. Interstitial pore water profiles suggest that silver is released at the sediment-water interface during early diagenesis in near surface sediments (Rivera-Duarte and Flegal, 1997). In anoxic sediments, silver likely is sequestered in sulfide (Ag_2S) or selenide (AgSe or Ag_2Se) solid phases as evidenced by coincident increases in silver and selenium at depth in sediments and association with AVS in sediments (Gobeil, 1999; Crusius and Thomson, 2003). Exposure of anoxic sediments to oxygenated conditions can lead to a mobilization of silver (Crusius and Thomson, 2003). Numerous studies have shown that free ionic silver (Ag^+) or neutrally complexed forms of silver (*e.g.*, $AgCl_2^0$) are toxic to aquatic biota, while most other complexed forms of silver are far less toxic (Nebeker, 1982; Nebeker *et al.*, 1984; EPA, 1987a; Rodgers *et al.*, 1997; Reinfelder and Chang, 1999; Guadagnolo *et al.*, 2000). MNR may be a viable option for silver as suggested by long-term monitoring efforts in San Francisco Bay and elsewhere that show decreases in silver in water, sediments, and biota on time scales of decades (Bothner *et al.*, 1998; Squire *et al.*, 2002; Flegal *et al.*, 2005). The potential effectiveness of MNR for silver contamination would need to be evaluated on a site-by-site basis to determine if the rate of silver reduction is sufficient to achieve the remedial goals in a relevant period of time.

4.4.8 Zinc. Zinc speciation and bioavailability are influenced by biological transformations during the aging process (Webb *et al.*, 2000). Adsorption of zinc to oxide particles, such as iron oxides, is the dominant short-term sink for zinc. As these particles age, especially in anoxic or sub-oxic environments, zinc becomes associated with sulfides (Webb *et al.*, 2000). In slightly basic, anoxic marsh sediment environments, zinc is effectively immobilized and is not bioavailable (Gambrell *et al.*, 1991), presumably through the formation of insoluble zinc sulfide precipitates. Substantial amounts of zinc are released to solution if this sediment is oxidized or exposed to an acidic environment. Very high abundances of soluble zinc are present under well-oxidized conditions at pH 5 to pH 6.5. Conversely, low abundances of soluble zinc are present at pH 8 under all redox conditions and at pH 5 to 6.5 under moderately and strongly reducing conditions (Gambrell *et al.*, 1991). At the sediment-water interface, soluble zinc can be diminished significantly by sorption onto ferric oxide mineral phases. As the redox potential declines and reduction of ferric oxides commences, zinc can be incorporated into magnetite (Fe_3O_4) or siderite ($FeCO_3$) (Cooper *et al.*, 2000). In polluted river environments, most zinc is scavenged by non-detrital carbonate minerals, organic matter, and oxide minerals and is less mobile than cadmium (and perhaps less mobile than lead) (Prusty *et al.*, 1994). Elevated chloride content decreases adsorption of zinc to sediment (Bourg, 1988).

4.5 Sediment Sampling for Metals: Methods for Collection and Analytical Considerations

Mineralization of organic matter by benthic microorganisms in sedimentary environments results in the depletion of oxygen, utilization of alternate TEAs, and ultimately a vertical redox gradient within the sediment profile. Metal concentrations and speciation that develop under reducing conditions will be sensitive to exposure to oxygen in air; thus, collection of sediments for metals analysis must aim to preserve *in-situ* conditions prior to analysis. Changes in sedimentary geochemical properties, most notably through the diffusion of oxygen into anoxic sediments, may alter the distribution of mineral phases in sediment samples (*e.g.*, conversion of iron sulfides to iron oxides) such that an assessment of *in-situ* conditions would be impossible. Therefore, maintaining the integrity of sediments collected for metals analysis is a primary concern when monitoring a site for natural recovery of metal contaminants.

This section will briefly discuss the issues and approaches for air-sensitive collection of whole sediments and interstitial pore water, evaluation of sediment-water exchange, and analysis of metals in sediments and pore water.

For a complete discussion of the advantages and disadvantages of various types of sediment collection devices, the reader is directed to *Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual* (EPA, 2001b). The scope of this discussion is sediment collection and analysis relating specifically to the aims and objectives of sampling for MNR of metals-impacted sedimentary environments.

4.5.1 Collection of Sediments and Interstitial Water. It is recommended that the collection of sediments for metals analysis as part of assessing the viability of MNR for a contaminated site be conducted in a manner that maintains the original conditions of the sediments as much as possible for the purposes of understanding *in-situ* geochemistry. Primary factors that dictate sample integrity include: 1) preserving the original redox conditions, and 2) avoiding contamination of the sample during sediment acquisition.

Nearly all sediment sampling devices can be sorted into three categories: 1) dredge samplers, 2) grab samplers, and 3) core samplers. The former two devices have use in the collection of sediments to evaluate depositional rates and sediment thickness or the collection of benthic organisms. For sediment collection aimed at the preservation of *in-situ* geochemical conditions, the core sampling devices are preferred. Core samplers are preferred because they maintain the integrity of the sediment profile and are much less destructive than either dredge or grab samplers. Grab samplers can be used reliably for physicochemical characterization and toxicity testing provided the samplers are closed when the sediment sample is retrieved, are relatively full of sediment, and do not appear to have lost the superficial fines.

The materials used for sediment sampling should be chosen such that they minimize sources of contamination. If sediment samples are to be analyzed for trace concentrations of metals, the sampler, if constructed of metal, should be coated with an inert non-sorptive coating, such as Teflon® or Kynar®, to prevent contamination. Often, polypropylene sleeves with rubber caps on either end are used to avoid sample contamination from the coring device. Samples of sediment in the core sampler or grab sampler should be sub-sampled with a pre-cleaned plastic or Kynar®-coated scoop or mini-corer. This technique avoids obtaining a sample that is in contact with the walls of the sampling device. Additionally, whether using a grab or a core-type sampler, all materials should be pre-cleaned prior to filling with the sample. Containers used to transport or store the sample should be purged with an inert gas (*e.g.*, nitrogen) prior to and after filling, and the containers should be filled completely if the sample will not be frozen prior to analysis. Samples should be processed in a glovebox or similar apparatus under an inert, oxygen-free environment.

During collection of interstitial waters, the priority is to recover and stabilize the samples such that oxidation and/or volatilization are prevented. Many interstitial pore waters have long residence times and are assumed to be at thermodynamic equilibrium with the sediments. In many cases, the pore waters are in equilibrium with a partial pressure of CO_2 greater than that of the ambient atmosphere. As such, considerable off-gassing may occur from the moment of collection with accompanying increases in pH. In general, there are two approaches for the collection of sediment pore waters: *in-situ* and *ex-situ methods* (EPA, 2001b). *In-situ* methods are preferable if toxicity testing is of primary concern and typically involve suction techniques (EPA, 2001b). However, these approaches typically yield low volumes of pore water. *Ex-situ* methods are preferable when toxicity testing is not the primary objective and when greater volumes of pore waters are desired. Typical methods for *ex-situ* pore water collection include centrifugation, sediment squeezers, and pressurized/vacuum devices (EPA, 2001b). Containers used for pore water collection should be filled completely to minimize alteration of contaminant bioavailability resulting from changes in DO content. Procedures for stabilization are dependent on the analyses to be performed. When non-volatile compounds are the target analytes, acidification often is recommended, while organic carbon and methane may be stabilized with saturated mercury chloride (Mudroch and MacKnight, 1994).

Additional considerations upon retrieval of diffusion pore water samplers include:

- Handling of samplers should be conducted within a nitrogen- or argon-purged inert atmosphere chamber, such as a glovebox or glove bag. Any caps or membranes should not be removed until they are within the inert atmosphere chamber.
- Pore water from the samplers should be decanted within the nitrogen/argon-purged glovebox into a bottle of the appropriate volume to eliminate any headspace before shipment to the lab.
- For the analysis of sulfides, pore water can be decanted into media bottles containing zinc acetate and sodium hydroxide preservative that prevents the oxidation of sulfides. Transfer of pore water must be conducted within the inert atmosphere chamber. Samples must be handled to prevent aeration to avoid volatilization or oxidation of sulfide, both of which artificially lower the actual sulfide concentration that ultimately will be measured.
- For many metals (*e.g.*, Resource Conservation and Recovery Act metals), acidification usually is required. Acidification is conducted typically with nitric or sulfuric acid depending on the exact metals being analyzed. For example, sulfuric acid is recommended to acidify samples for arsenic analysis because nitric acid will oxidize As(III) to As(V) (Electric Power Research Institute, 1986). Preparation of samples for the analysis of Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, and Zn is described in EPA (1986a).
- All sample containers should be sealed in zip-lock plastic bags and placed in a cooler on ice for shipment to the analytical laboratory.

4.5.2 *In-Situ* Analysis of Interstitial Water: Microelectrodes and Thin Films. Microelectrodes have become an important tool for looking at sub-millimeter level depth distributions of redox sensitive components involved in early diagenesis in surficial sediments. To date, electrochemical methods with millimeter-scale resolution have been developed for oxygen (O_2), sulfide (HS^-/H_2S), manganese (Mn^{2+}), iron (Fe^{2+}), iodide (I^-), pH, nitrate + nitrite (NO_X), nitrous oxide (N_2O), carbon dioxide (pCO_2), redox potential, hydrogen (H_2), conductivity, and temperature. In addition, microelectrode techniques have been developed for the measurement of several trace elements (copper, lead, cadmium, and zinc) in sediments (Brendel and Luther, 1995; Nolan and Gaillard, 2002; Sundby *et al.*, 2005; Luther *et al.*, 2008). Limitations of microelectrode application to geochemical characterization of sediments include depth of the microelectrode penetration and the small number of commercially-available microelectrodes specifically used for environmental monitoring.

Thin film probes are created by layering a diffusive gel of known thickness between the medium to be investigated (ambient water or interstitial pore fluid) and any medium capable of reacting with the analytes of interest (Davison and Zhang, 1994). The gel is held in a rigid plastic frame with a window to allow exposure to the matrix being studied (Davison *et al.*, 2000). A filter membrane usually is placed over the exposure window to prevent mechanical damage and biological fouling of the gels. The technique of diffusive equilibration in thin films (DET) establishes equilibrium between solutes in pore waters and in a hydrogel that contains 95% water (Davison, 1991). For trace elements, the reacting medium is often a chelating ion exchange resin, such as Chelex®, that is contained in a thin layer of gel (Warnken *et al.*, 2004). By controlling the pore size of the diffusive gel, it is possible to exclude particulate phases, large macromolecules, and colloids and, hence, achieve a physical measurement of the metal speciation in solution (Warnken *et al.*, 2004). Thin film probes also have been developed to measure sulfide in sediments (Teasdale *et al.*, 1999; DeVries and Wang, 2003), phosphorous in soils (Mason *et al.*, 2008), arsenic (Campbell *et al.*, 2008), and mercury (Cattani *et al.*, 2008). Davison (1991) developed a DET technique for measuring iron and manganese in interstitial pore waters of sediments at millimeter-scale resolution. The method subsequently was expanded to include other trace metals (Morford *et al.*, 2003). A related technique, diffusive gradients in thin films (DGT), expands on the DET technique to quantify both horizontal and vertical gradients of trace metals and metalloids in fresh water and marine sediments (Zhang *et al.*, 1995, 2002; Davison *et al.*, 1997; Tankere-Muller *et al.*, 2007; Campbell *et al.*, 2008).

4.5.3 Measuring Sediment-Water Exchange: Benthic Flux Chambers. Benthic flux chambers are *in-situ* sampling devices designed to obtain a measure of the exchange of constituents in interstitial pore water with overlying water. Flux chambers also are used to measure metabolic processes driven by microorganisms in sediments. Flux chambers are typically small surface area (< 0.5 m^2) enclosures that are placed over the sediments and capture a portion of the ambient bottom water that is in direct contact with the sediments. The concentration of the constituent of interest is monitored over time in the captured water, and an exchange flux is determined from the change in concentration of the constituent in the chamber over the deployment period. Deployment periods vary from a few hours in near-shore environments to several days in deep sea environments. Chambers used in shallow areas tend to be simple devices that are deployed and sampled by Scuba divers. Flux chambers used in deep water (*e.g.*, the open ocean) are much more sophisticated and deployed from a landing platform that controls placement and sampling intervals. Benthic flux chambers have been used in marine and fresh water systems to determine the exchange of trace metals, nutrients, and organic carbon, as well as quantify benthic respiration (DO) (Burdige and Homstead, 1994; Rowe *et al.*, 1994; Gill *et al.*, 1999; Berelson *et al.*, 2002, 2003; Warnken *et al.*, 2000, 2001, 2003, 2008).

4.5.4 Analysis of Key Geochemical Constituents in Sediments

4.5.4.1 pH. Sediment pH is one of the single most important factors controlling speciation and equilibrium for many chemicals including sulfide, ammonia, cyanide, and metals, all of which ionize at different pH values defined by their acid dissociation constant (pKa). Metal (Cr, Cd, Cu, Ni, Pb, and Zn) speciation and bioavailability are known to be affected by pH (Schubauer-Berigan and Ankley, 1991). Generally, pH is measured using a pH meter consisting of a potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are submersed. General purpose pH electrodes are available in a wide variety of configurations for in-line and submersion applications. Detailed methods for measuring pH in water and sediment are described in EPA (1983, 1986a).

4.5.4.2 Ammonia in Pore Water. Nitrogen, a nutrient associated with over-enrichment of aquatic environments, exists in several forms including ammonia. Ammonia is highly soluble in water where it is found in an un-ionized form (NH_3) and an ionized form (NH_4^+). The extent of ionization is dependent on pH, temperature, and salinity (in sea water). Ammonia in sediments and pore water is generally a product of microbial degradation of nitrogenous organic material such as amino acids (Ankely *et al.*, 1990).

4.5.4.3 Total Organic Carbon Content. The TOC content in sediment is a measure of the total amount of oxidizable organic material. TOC is the sum of DOC, POC, and colloids. TOC is an important parameter in sediments because it is a major determinant of non-ionic organic chemical bioavailability (DiToro *et al.*, 1991). Metal bioavailability is affected by the amount of TOC present in sediments. TOC usually is expressed as a percentage of the bulk sediment and used to normalize the dry-weight sediment concentration of a chemical to the organic carbon content of the sediment. EPA Equilibrium Partitioning Guidelines estimate bioavailability as a function of contaminant concentration sorbed to sediment organic carbon and contaminant concentration in pore water under equilibrium conditions (EPA, 1994a). Several methods have been used for measuring organic carbon content in sediments, including wet oxidation titration, modified titration, and combustion after removal of carbonate by the addition of HCl and subsequent drying. EPA methods (1986a, 1987b), including SW-846 and 430/9-86-004, often are used to measure TOC.

4.5.4.4 Particle Size Distribution (Percent Sand, Silt, and Clay). Particle size is used to assess the physical characteristics of sediments. Because particle size influences both chemical and biological properties, it can be used to normalize chemical concentrations and account for some of the variability found in biological assemblages or laboratory toxicity testing (EPA, 2000). Particle size can be characterized in varying detail. The broadest divisions that generally are considered useful for classifying particle size are the percentages of gravel, sand, silt, and clay. However, each of these size fractions can be subdivided further so that additional characteristics of the size distribution (*e.g.*, elemental distribution, surface area analysis, etc.) can be determined (Puget Sound Estuary Program [PSEP], 1986). Both PSEP (1986) and EPA (1995) provide recommended methods for measuring sediment PSDs.

4.5.4.5 Percent Water or Moisture Content. Water content is a measurement of sediment moisture and usually is expressed as a percentage of the whole sediment mass. It is known to influence toxicity and is used to aid in the interpretation of sediment quality investigations. Sediment moisture content is calculated as the difference between the wet and dry masses of the sediment following oven drying at 50°C to 105°C to a constant mass. Percent water is used to convert sediment concentrations of substances from wet weight to dry weight. Methods for determining moisture content are described by Plumb (1981). Additional methods are provided in EPA (1987b).

4.5.4.6 Salinity of the Pore Water (Marine Sediments). Salinity is a measure of the mass of dissolved salt in a given mass of solution. The most reliable method to determine true or absolute salinity is complete chemical analysis. However, this is time consuming and costly. Therefore, indirect methods are more suitable. Because the colligative properties of water (*e.g.*, salinity, density, and conductivity) co-vary, one property can be measured to estimate the value of another property. Indirect methods include conductivity, density, sound speed, or refractive index (American Public Health Association [APHA], 1995). Because sea water contains relatively constant ion ratios, chloride (the most abundant anion) can be measured and related to the total salt concentration; salinity is then calculated from the empirical relationship between it and the indirect measurement. Conductivity measurements have the greatest precision but respond only to ionic solutes (APHA, 1995). Density measurements respond to all solutes. APHA (1995) recommends the electrical conductivity method because it is sensitive and easily performed. APHA (1995) also recommends the density method using a vibrating flow densitometer. EPA (1986a) methods also may be consulted. A salinity refractometer can be used for quick readings of salinity in solutions such as sea water. These refractometers are easy to read, non-corrosive, and lightweight. They have dual scales and an adjustable focus. Temperature and non-temperature compensating refractometers are available.

4.5.4.7 Total Sulfides. Total sulfides represent the combined amounts of acid-soluble H_2S, HS^-, and S^{2-} in a sample. Sulfides are often measured because they are common in some sediments, particularly those that are anoxic, and they can be toxic to aquatic organisms. PSEP (1986) describes a method to measure total sulfides in sediments. Oxygen is removed from the sample using nitrogen gas, methyl orange and hydrochloric acid are added, and the mixture is heated. Amine solution and iron chloride are added to develop a colorimetric reaction product, and sample absorbance is measured spectrophotometrically.

Potentiometric methods for measuring sulfides in aqueous samples are described by APHA Method 4500 (APHA, 1995). Sulfide ions are measured using a sulfide ion-selective electrode in conjunction with a double-junction, sleeve-type reference electrode. Potentials are read using a pH meter or a specific ion meter having a direct concentration scale for the sulfide ion. Samples are treated with sulfide anti-oxidant buffer, which fixes the solution pH at a highly alkaline level and retards air oxidation of sulfide ion in solution. This ensures that measured sulfide represents the total sulfides as S^{2-} ion, rather than as HS^- or H_2S found at lower pH values. APHA Method 4500 (APHA, 1995) provides both qualitative and quantitative methods to determine aqueous sulfide concentrations. Qualitative methods include the antimony test, the silver-silver sulfide electrode test, the lead acetate paper test, and the silver foil test. Quantitative methods include the photometric method, the automated photometric methylene blue colorimetric methods, and the iodometric titration method for standardizing stock solutions.

4.5.4.8 Cation Exchange Capacity of Sediments. Cation exchange capacity (CEC) is a parameter that provides information relevant to metal bioavailability studies (Black, 1965). Cations, such as positively charged elements (*e.g.*, calcium, magnesium, hydrogen, and potassium), are attracted to negatively charged surfaces of clay and organic matter. A continuous exchange of cations occurs between sediment and water. CEC is a measure of the sediment's ability to retain cationic elements. It is also a measure of clay activity and mineralogy, which is used to calculate mineralization rates and leaching rates and to predict interactions with contaminants. The degree of CEC is dependent on the type and amount of suitable surfaces such as organic matter and clay. High cation exchange capacities are associated with high clay content, and high organic matter and changes in CEC are typically associated with changes in the organic carbon content and pH of the sediment. Organic matter generally supplies a greater number of exchange sites than clay particles. CEC can be measured by treating samples with ammonium acetate such that all exchangeable sites are occupied by the NH_4^+ ion, digesting the samples with sodium hydroxide during distillation, and then titrating to determine the ammonium ion concentration. The amounts of exchangeable cations are expressed in milliequivalents of ammonium ion exchanged per 100 g of dried sample. More detailed methods are provided in Bascomb (1964), Black (1965), Klute (1986), and EPA (1986b).

4.5.4.9 Redox Potential (Eh) of Sediments. Redox (Eh) is a measure of the oxidation-reduction potential of sediments. Measurements of Eh are particularly important for metal speciation and determining the extent of sediment oxidation. Eh values below approximately -100 millivolts may indicate biologically important sulfide concentrations if the sediment contains significant amounts of sulfur. As discussed, some trace metals form insoluble complexes with sulfides, rendering them unavailable for uptake by biota. Since free ionic metals generally are thought to possess the greatest toxicity potential, measuring the conditions that control binding dynamics, such as pH and Eh, is critical.

Potentiometric measurements of Eh using a millivolt reader can be obtained with a platinum electrode and a standard hydrogen electrode (Plumb, 1981). APHA (1995) does not recommend using the standard hydrogen electrode, as it is fragile and impractical. Instead, their method recommends the use of a silver-silver-chloride or calomel reference electrode. APHA (1995) also recommends a graphite rather than a platinum electrode for sediments. Once the Eh equilibrium is reached, the difference between the platinum or graphite electrode and the reference electrode is measured. This potential then is normalized to report the Eh of the system relative to the standard hydrogen electrode. For a more detailed explanation on how to calculate the Eh, see APHA (1995).

A number of problems are associated with the accurate measurement and interpretation of Eh in sediments, particularly in marine sediments. Therefore, considerable attention should be paid to the use of proper equipment and techniques. Some of the problems identified by Whitfield (1969) and Murdoch and MacKnight (1994) include measurement inaccuracy resulting from disturbance of the sediment sample during insertion of the electrode, instability and poor reproducibility of the measurements, and differential responses of platinum electrodes under different environmental conditions. It is recommended that published studies on the problems associated with measuring and interpreting sediment Eh be consulted before any attempt is made to measure this parameter in sediment samples (Berner, 1963; Morris and Stumm, 1967; Whitfield, 1969).

4.5.4.10 Dissolved Oxygen. Measures of DO refer to the amount of oxygen contained in water and define the living conditions for oxygen-requiring (aerobic) aquatic organisms. DO concentrations reflect an equilibrium between oxygen-producing processes (*e.g.*, photosynthesis) and oxygen-consuming processes (*e.g.*, aerobic respiration, nitrification, and chemical oxidation), and the rates at which DO is added to and removed from the system by atmospheric exchange (aeration and degassing) and hydrodynamic processes (*e.g.*, accrual/addition from rivers and tides versus export to ocean).

The two standard methods for measuring DO concentrations are membrane electrodes and the Winkler (iodometric) titration method. Membrane electrodes are the most practical for *in-situ* determinations and continuous monitoring protocols. The biochemical oxygen demand is another standard procedure used to determine the oxygen requirements of raw wastewater and treated effluents. It measures the oxygen utilized during a specified period of organic matter degradation. The solubility of oxygen is affected non-linearly by salinity and water temperature. Therefore, DO measurements often are expressed as percentage saturation values as this parameter is independent of temperature and salinity.

Most instrumentation for DO measurement can convert DO to % DO when the salinity, temperature, and altitude are known. Spot measurements of DO or % DO are not very useful. The full diurnal range of DO concentrations is required for proper data interpretation and can be used as an indicator of primary production (*i.e.*, the accumulation of organic carbon and concomitant formation of oxygen via photosynthesis). Diurnal DO changes can be tracked over time using moored, continuously-recording DO sensors. At a minimum, measurements should be taken at mid-day and dawn to approximate the diurnal range.

4.5.4.11 Dissolved Organic Carbon in Pore Water. DOC often consists of humic substances and is the fraction of the organic carbon pool that is dissolved in water and passes through a 0.45-μm glass fiber filter. DOC is an indicator of the chemically reactive organic fraction and accurately measures the dissolved organic load. Sediment pore waters can be rich in humic acids, which can bind metals. Gilek *et al.* (1996) measured DOC using a TOC apparatus and infrared detection of CO_2. Borga *et al.* (1996) measured DOC using flow-injection analysis interfaced with inductively-coupled plasma atomic emission spectrometry (ICP-AES). Three methods for measuring DOC, including the combustion-infrared method, the persulfate-ultraviolet oxidation method, and the wet-oxidation method, have been adapted from APHA Method 5310 (APHA, 1995) for TOC. Adjustments for inorganic carbon interference may be required.

4.5.4.12 Alkalinity and Hardness of Pore Water (Fresh Water Sediments). Studies have shown that toxic effects of metals are influenced by alkalinity as it alters speciation and bioavailability. For a formal definition of alkalinity and hardness, the reader is referred to Stumm and Morgan (1996), as well as to Section 4.2 of this document. APHA (1995) recommends a color-change titration method to measure alkalinity. The sample is titrated with standard acid to a designated pH, and the endpoint is determined electrometrically (*i.e.*, pH meter) or by the color change of an internal indicator. The inflection points along the curve are used to determine the alkalinity of the sample. The color-change titration method is most commonly used. Hach (Method 8202) has developed a portable water chemistry kit based on the APHA (1995) color-change titration method and an additional method using sulfuric acid with a digital titrator (Hach, Method 8203).

Hardness is the concentration of metallic cations, with the exception of alkali metals, present in water samples. Generally, hardness is a measure of the concentration of calcium and magnesium ions in water. Hardness usually is expressed as a calcium carbonate equivalent in mg/L. The APHA describes two methods to measure hardness: 1) the calculation method, and 2) the ethylenediaminetetraacetate (EDTA) titrimetric method (APHA, 1995). The calculation method is based upon the results of separate determinations of calcium and magnesium ions, and hardness is expressed as milligram equivalents of $CaCO_3$ L^{-1}. In the titrimetric method, calcium and magnesium ions in water are sequestered by the addition of EDTA. The endpoint of the reaction is measured by means of Chrome Black T3, which is red in the presence of calcium and magnesium ions and blue when both are sequestered. APHA recommends the calculation method because it is more accurate. The method uses direct determinations of calcium and magnesium to calculate hardness. Hach has developed portable water chemistry kits (Methods 8222, 8204, 8030, 8226, 8213, 8338, and 8329) for a variety of hardness determinations using a spectrophotometer or titration methods with a decision tree for selecting the appropriate procedure. Three of the Hach methods were adapted from APHA Method 2340 (APHA, 1995): 1) the burette and 0.020-N titrant method (8222), 2) the ManVer 2 burette and 0.020-N titrant method (8226), and 3) the burette titration method (8338). The APHA EDTA titration method most often is used.

4.5.4.13 Conductivity of Pore Water (Fresh Water Sediments). Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability is dependent on the presence of ions in the solution, the concentration of the ions, their mobility and valence, and temperature. Solutions of inorganic compounds are usually good conductors, while those of organic compounds are usually poor conductors. Calcium, potassium, sodium, and magnesium chlorides and sulfides enhance conductivity. Meters can be used to measure the degree to which electrical current can travel through water. The unit of measure is 1 mS/m = 1 millisiemens/meter or 1 µS/cm = 1 microsiemens/centimeter. The reading is related to the amount of ions in the water, with a higher conductivity indicating higher amounts of ions. While traditional chemical tests for hardness measure calcium and magnesium, they do not consider other ions (*e.g.*, sodium); thus, conductivity is a better indicator of a solution's ionic strength than is hardness.

4.6 Analytical Approaches to Metal Speciation in Sediments: Sequential Extraction, SEM/AVS, and Spectroscopic Techniques

4.6.1 Analysis of Metals from Sediments: Sequential Extraction. Low levels of trace metals occur naturally in the environment, but elevated levels in sediment are generally associated with anthropogenic contaminant loads. Metals may partition among several phases in sediments (Gambrell *et al.*, 1976). From an environmental perspective, the most important forms of metals in sediments are those that are bioavailable to benthic organisms, either directly or following diagenic transformations. Great care must be taken in collecting and handling soil and sediment samples to prevent changes in pH, redox potential, and water content that may change the chemical forms and associations of the metals in the soils and sediments (Kersten and Förstner, 1986, 1991).

Sequential extraction or leaching schemes have been used extensively to partially characterize the phase associations of metals in sediments and to identify the fraction or fractions of total metal that are, or could become, bioavailable (Tessier and Campbell, 1987). None of these selective extraction techniques is completely specific for a particular metal fraction in sediment, and none adequately defines the bioavailable fraction (Luoma and Bryan, 1979, 1981; Salomons and Förstner, 1984). However, the ultimate design behind a sequential extraction of a sediment is to characterize the partitioning of a metal phase between a more mobile (*i.e.*, exchangeable, or more bioavailable) fraction and a less mobile (residual, or less bioavailable) fraction (Filgueiras *et al.*, 2002). These selective extraction techniques are reasonably selective when applied to oxidized, sulfide-poor sediments; however, they are not sufficiently selective for use with anoxic, sulfide-rich sediments (Rapin *et al.*, 1986). In sulfur-rich anoxic sediments, it was noted that copper, iron, and zinc were particularly sensitive to the maintenance of oxygen-free conditions during sample acquisition and pre-treatment (Rapin *et al.*, 1986); thus, anaerobic conditions are of the utmost importance in maintaining sample integrity for sequential extraction approaches to understanding metals speciation/bioavailability in sediments. Selective extraction approaches are bolstered when coupled with quantitative spectroscopic measures, such as X-ray diffraction (XRD) (Ryan *et al.*, 2002; Haus *et al.*, 2008) Furthermore, it should be noted that sequential extraction methods do not yield a quantitative and conclusive description of *in-situ* metal speciation or metal partitioning into the various solid phases due to: 1) the redistribution of metals during the sequential extraction procedure, 2) non-selectivity of the reagents for the various relevant pools, 3) incomplete extraction of the target metals from the various solid phases, and 4) the precipitation of new minerals during the extraction procedure (Burton *et al.*, 2006; Bacon and Davidson, 2008; Haus *et al.*, 2008).

Three to six fractions usually are defined in sequential extraction schemes (Salomons and Förstner, 1984). These include: 1) exchangeable cations, 2) carbonates, 3) easily reducible phases, 4) moderately reducible phases, 5) organic plus sulfide fraction, and 6) residual fraction.

In some extraction schemes, two or more fractions are combined and extracted with a single extractant. The exchangeable metal cations (Fraction 1) are extracted with a solvent that contains cations that are more strongly complexed to the binding sites on sediment particles than are the metal cations. Metal ions bound to the carbonate fraction of sediments can be extracted with a weak acid. Metals in this fraction include those adsorbed to inorganic carbonate particles and those incorporated into the calcium carbonate crystal lattice during biodeposition of skeletal carbonates (mainly calcium carbonate) or precipitation of carbonates. Carbonate precipitates are known to form in fresh water environments, especially where calcium carbonate minerals are found; however, these are generally special cases and carbonate minerals are more frequently encountered in salt water or brackish environments.

The residual or detrital fraction contains metals that are: 1) tightly bound to or incorporated into the crystalline lattice of clays, other silicates, or heavy minerals, 2) precipitated or co-precipitated as stable heavy metal sulfides (*e.g.*, cinnabar and pyrite), or 3) adsorbed to crystalline iron oxides or highly refractory organic matter (*e.g.*, humic acids). These residual metals usually are extracted with mixtures of concentrated strong acids (*e.g.*, aqua regia) at a high temperature. Hydrofluoric acid may be added to the aqua regia to dissolve metals associated with silicate minerals. Generally, at least 50% of most metals and occasionally as much as 98% of some metals are associated with the residual fraction of sediments. Residual metals are not bioavailable to plants and animals.

4.6.2 The Simultaneously Extracted Metals/Acid Volatile Sulfide Concept. Building on the sequential extraction methods described above, it was observed that metals bound to the organic fraction of soil or sediment can be extracted with a hot acidic solution of hydrogen peroxide and nitric acid or weak (1-M) hydrochloric acid (Tessier and Campbell, 1987). These two extractants also extract the more labile metal sulfides (Allen *et al.*, 1993; Ankley, 1996). The observation that the potentially bioavailable metals (Fractions 1 through 4) are extracted along with AVS with weak 1-M HCl led to the development of the SEM/AVS approach of quantifying the bioavailable fraction of metals in sediments. According to Huerta-Diaz *et al.* (1998), AVS equals the sum of amorphous FeS, mackinawite (FeS), and greigite (Fe_3S_4) and can be defined as those sulfides that are readily extracted by a cold extraction of the sediment in 1-M HCl. The analytical method, purge and trap, involves conversion of solid sulfides to gaseous H_2S, which then is purged from the system and trapped in an aqueous solution. The trapped sulfide may be detected with a sulfide probe or by following a wet chemistry method (DiToro *et al.*, 1990). SEM can be defined as the sum of metals extracted under the same conditions as AVS. The equivalent release of sulfide (AVS) and metal, however, does not necessarily mean that the metal is bound by sulfide alone. SEM, therefore, is essentially an operationally-defined pool of metals theorized to be associated with sulfides and any other metal-bearing phase that is extracted in cold 1-M HCl (Allen *et al.*, 1993). For example, metal sorbed onto iron oxides and POC also will be extracted. As with operationally-defined pools of metals in sedimentary environments, which are defined by an experimental laboratory manipulation, a mechanistic understanding of chemical reactivity is necessarily limited. Cautionary considerations for the implementation of the SEM/AVS approach to understanding site- and metal-specific bioavailability are elaborated below (Section 4.6.3).

In intertidal sediments, where sulfide occurs in significant concentrations, the reductive dissolution of Fe(III) oxyhydroxide phases is followed by the formation of $FeS_{(aq)}$, $FeS_{(s)}$, and $FeS_{2(s)}$ (Theberge and Luther, 1997). The formation of pyrite in anoxic conditions is rapid and occurs by reaction between H_2S or (S^o) and aqueous (or solid) FeS (Luther, 1991; Rickard, 1997; Rickard and Luther, 1997). Di Toro *et al.* (1990, 1992) have proposed an SEM/AVS model based on the recognition that AVS is a reactive pool of solid-phase sulfide that is available to bind with metals to form insoluble metal sulfide complexes that are not bioavailable. Since FeS has a higher solubility product (K_{sp}) than do other trace metal sulfides (MeS), metals will displace the iron to form the more insoluble MeS under equilibrium conditions, as illustrated by the reaction below. This reaction reflects the stoichiometric relationships between iron sulfides and other metal sulfide phases with lower solubilities, but is not intended to invoke a mechanistic interpretation for the *in-situ* formation of metal sulfide precipitates, or define the time frame required for this exchange to complete

$$Me^{2+} + FeS_{(s)} = MeS_{(s)} + Fe^{2+} \qquad \text{(Eq. 4.1)}$$

It is important to note that each cationic metal has a different binding affinity for sulfide (EPA, 1994a; Stumm and Morgan, 1996). Currently, there is considerable debate regarding the relative affinities of each of the metals. Relative affinities of metals for sulfide increase as the log K_{sp} decreases, which is an equilibrium consideration and does not take into account kinetic considerations for the formation of different sulfide minerals. Mercury and copper have the lowest log K_{sp} values (Table 4-1), indicating that the affinity of these metals for AVS is higher than that of the other metal cations. The mercury concentration in sediments, however, is nearly always much lower than the concentrations of all other metals, so it doesn't compete with other metals for complexation with AVS. It usually is assumed that, at equilibrium, copper preferentially reacts with AVS, displacing all other metals. If the available AVS is not completely saturated by copper, then the remaining metals react in the following order: lead, cadmium, zinc, and nickel. In this model, the fraction of copper in the sediment that is considered as bioavailable and potentially toxic is defined as follows:

$$Cu_b = ([Cu_{SEM}] - [AVS]) \times (MW_{Cu}) \qquad \text{(Eq. 4.2)}$$

where

Cu_b = fraction of copper that is bioavailable
$[Cu_{SEM}]$ = molar concentration of copper as defined by simultaneous extraction
$[AVS]$ = molar concentration of AVS
MW_{Cu} = molecular weight of copper (mg/mole).

The concentration (mg/kg sediment) of bioavailable copper in sediments is:

$$Cu_{bioavailable} = [Cu_{sediment}] \times Cu_b \qquad \text{(Eq. 4.3)}$$

where $[Cu_{sediment}]$ is the concentration of total copper in sediment.

The SEM/AVS difference provides insight into the extent of either the additional metal binding capacity with reduced sulfur or the magnitude by which AVS binding has been exceeded. When organism response is considered, this metric can indicate the potential magnitude of importance of other metal binding phases and which metals may be of concern (Hansen *et al.*, 1996). For example, the SEM/AVS model predicts that when the measured AVS concentrations exceed the concentration of SEM (SEM/AVS molar ratio < 1), the pore water levels of free metal ions should be very low, resulting in the prediction of minimal toxicity (Chapman *et al.*, 1998). Alternatively, when SEM exceeds AVS, higher pore water concentrations of bioavailable forms of the metal(s) are predicted, possibly leading to metal toxicity. Recently Di Toro *et al.* (2005) extended the SEM/AVS-based approach by coupling it to a biotic ligand model with more explicit consideration of POC as a metal-binding phase. This approach has been successful in predicting toxicity, or lack thereof, in metal-contaminated sediments (Di Toro *et al.*, 2005). The bioavailable fraction of the other metals in sediment may be determined in the same manner following the order described above. For each successive metal, the molar concentration of AVS applied should be decreased according to the molar concentration of the preceding metal; when the concentration of AVS is zero, all remaining metals are assumed to be bioavailable.

4.6.3 Limitations and Cautions in the Use of SEM/AVS. The major limitations in the use of the SEM/AVS model stem from the fact that the measurement of AVS is operationally defined and does not provide a mechanistic understanding of metals speciation, transformation, or bioavailability. Several fundamental misconceptions regarding the recovery of iron sulfide minerals are addressed by a collection of review articles devoted to this topic (Luther, 2005; Meysman and Middelburg, 2005; Rickard and Morse, 2005). In these review articles, the authors examine the reactivity of different iron sulfide minerals and the molecular nature of sulfur recovered by the AVS extraction. Where there has been a call to abandon the use of AVS due to the inherent limitations of an operationally-defined reservoir of sedimentary sulfur (Rickard and Morse, 2005), others have tempered these criticisms with the utility of the AVS method in understanding sulfur and trace metal biogeochemistry in sediments (Luther, 2005; Meysman and Middelburg, 2005). Their synopses, in addition to the studies mentioned below, describe the pertinent issues regarding the use of the SEM/AVS method for estimating metal speciation, reactivity, and bioavailability in sediments.

The principal limitation of the SEM/AVS protocol for understanding metal speciation and bioavailability in sediments is due to the sensitivity of sediments to geochemical conditions, such as pH and redox. For example, artificial changes in metal speciation may occur during operational manipulations of the sediment samples. These changes may occur from the moment of sampling to laboratory manipulations during extraction and can bias interpretation of AVS/SEM analyses. During sample collection, care must be taken to ensure sample integrity to avoid changes in metal speciation of the *in-situ* sulfide phases, particularly oxidation upon exposure to atmospheric conditions. Secondly, metals speciation can be unintentionally altered due to the formation of insoluble precipitates and/or the formation of other adsorbed species onto those newly precipitated phases during the acid extraction stages, which can shift metal speciation from that found in the original sediments (Wilkin and Ford, 2002; Scheckel *et al.*, 2003; D'Amore *et al.*, 2005). The re-adsorption of copper, lead, and cadmium and re-precipitation of lead (in phosphorous-containing soils) during sequential extractions has been documented (Rendell *et al.*, 1980; Scheckel *et al.*, 2003). The precipitation of arsenic sulfides (orpiment or realgar) during acid extraction of arsenic-containing sediments has also been observed (Wilkin and Ford, 2002). Furthermore, a considerable quantity of metals may be contained within a sulfide mineral or precipitate that is not extractable by HCl; however, this reservoir may be susceptible to oxidation and subsequently bioavailable (Morse, 1994; Cooper and Morse, 1998). For example, Morse observed that the degree of HCl soluble trace metals in marine sediments increased three-fold after exposure to oxic sea water (Morse, 1994). Therefore, the use of a weak acid extraction can underestimate trace metal bioavailability due to under-extraction of metals associated with oxidizable phases and also due to the precipitation of new solid phases as a consequence of the acid extraction used for the SEM/AVS analysis.

In some cases, toxicity was observed when, according to the SEM/AVS model, no metals should have been bioavailable (*i.e.*, SEM << AVS) (Lee *et al.*, 2000; O'Day *et al.*, 2000). For example, in laboratory incubation experiments, metal accumulation in two clam species was observed when the concentration of SEM was only a fraction of AVS. The total level of metals that were bioaccumulated displayed a linear relationship with total metals irrespective of AVS or pore water metal concentrations

(Lee *et al*., 2000). In an example of a field-scale test of the SEM/AVS model, metal bioavailability and toxicity were evaluated in sediment from Naval Air Station Alameda (O'Day *et al*., 2000). In this case, it was ultimately determined that the observed toxicity was not caused by metals, but was due to the presence of either other contaminants that were not measured or to naturally-occurring geochemical conditions that were detrimental to the organism used for the toxicity test. Toxicity tests in surficial sediments resulted in no or low toxicity; however, deeper sediment (30 to 60 cm) displayed high toxicity. The observed toxicity of the deeper sediments was attributed to the lack of DO and high levels of ammonia, and was not linked directly to the high levels of metal contaminants (*e.g.*, cadmium, lead, chromium, zinc, copper, and nickel) (O'Day *et al*., 2000). Additional factors may contribute to observed toxic responses, which emphasize the importance of thorough geochemical sediment characterization, and the limitations of relying solely upon the SEM/AVS model for evaluating sediment toxicity.

The presence of reactive geosorbent materials, in addition to sulfides, that are able to sequester metals from the aqueous phase presents an additional limitation to the SEM/AVS model. For example, when extractable metals exceed the molar equivalent of AVS, sediment phases other than AVS such as organic sorbents and/or clay minerals, will become important in metal binding (Oakley *et al.*, 1981; Luoma and Davis, 1983; Tessier and Campbell, 1987; Rivera-Duarte and Flegal, 1997; Trivedi and Axe, 2001). Metal binding by POC and iron hydroxide phases is dependent on pH with the highest amounts being adsorbed in the range of pH 5 to pH 7 (Lion *et al.*, 1982; Millward and Moore, 1982; Stumm and Morgan, 1996). Sediment-water partition coefficient (K_d) values typically decrease substantially as pH decreases, or as negatively charged surface sites become protonated and electrostatic considerations become less favorable for metal cation adsorption (Stumm and Morgan, 1996; Tessier *et al.*, 1996; Trivedi and Axe, 2001). Thus, when [SEM – AVS] > 0 (*i.e.*, excess of labile metal cations), an exposure risk is to be presumed; however, toxicity might not be observed due to metal uptake by organic matter, oxide, and/or clay mineral phases.

Further limitations of this approach stem from interpretations of data from acid extractions of sulfide minerals. As noted, the most common approach taken is to measure the concentrations of H_2S and SEM following leaching of the sediment with dilute acid, typically 1-M HCl, although other acids and acid strengths also have been used. Rickard and Morse (2005) argue that: 1) because AVS is operationally defined, it should never be used as directly equal to sedimentary FeS, 2) different protocols (*i.e.*, acid strength, temperature, leaching time, and use of antioxidants) leach different amounts of AVS materials, in some instances varying by five-fold with the same sediment, 3) the SEM concentration also varies with time and location, 4) it is not a reasonable expectation that aqueous S(-II) components and sulfide minerals undergo the same reactions with sedimentary trace metals, 5) it cannot be assumed that, for any given AVS yielding S(-II) concentration, they have similar influences on the toxicity of metals, 6) because of complex biogeochemical dynamics, sediments can have very different AVS depth distribution patterns, which precludes that there is a universally correct sampling interval for the AVS/SEM method, and 7) AVS may undergo major concentration changes on time scales of hours to a few days to seasonally in response to hypoxia/anoxia in overlying waters resulting in the AVS-to-SEM ratio constantly changing. They conclude that all of these complications ultimately result in confusion in drawing conclusions about potential metal toxicity or exposure risks in sediments.

4.6.4 Promising Spectroscopic and Analytical Techniques. Modern instrumental methods being applied to the analysis of trace metal speciation include: 1) electrochemistry (*e.g.*, differential pulse polarography), 2) spectrophotometry (*e.g.*, silver diethyldithiocarbamate), 3) atomic absorption/emission spectroscopy coupled to chromatography, 4) X-ray synchrotron techniques, 5) inductively coupled plasma mass spectrometry (ICP-MS; also coupled to a chromatographic technique), and 6) neutron activation (PSEP, 1997; D'Amore *et al.*, 2005). X-ray methods, at the time of the publication of this document, offer the most promise in understanding *in-situ* metal speciation, with potential for bridging gaps in understanding metal speciation and bioavailability. Examples of X-ray methods to determine metal speciation in environmental soils and sediments include: 1) synchrotron X-ray fluorescence (Isaure *et al.*, 2002; Manceau *et al.*, 2004), 2) X-ray emission (Isaure *et al.*, 2002), X-ray absorption (XAS) (Scheckel *et al.*, 2003), 3) X-ray absorption near edge structure (XANES) (Manceau *et al.*, 1992; Bang and Hesterberg, 2004), and 4) extended X-ray absorption fine structure (EXAFS) (Ford *et al.*, 1999; Scheckel *et al.*, 2000; Randall *et al.*, 2001; Isaure *et al.*, 2002; Manceau *et al.*, 2004; Scheckel and Ryan, 2004). These studies offer promising insight into both the technical limitations of sequential extraction methods and an improved understanding of the *in-situ* metal coordination environment of inorganic contaminants in sedimentary environments.

The development of many of the aforementioned methods and techniques are aimed specifically at identification of *in-situ* metal speciation. Metal speciation drives the interaction between metals and the overall environmental milieu. For example, metals uptake by local biota is dependent on the metal species present and, by extension, ecological risks are determined by metal speciation and not by total metal concentration. The suite of analytical techniques for understanding metal speciation can be separated into those applied to solid phase-associated metals and those that can be applied to aqueous phase speciation. Analysis of solid phases typically exploits three principal properties of solids:

1) the ability of surface-associated metals to absorb or reflect (diffract) X-rays (these techniques include XRD and X-ray absorption methods including XAS, EXAFS, and XANES);
2) the ability of solids to interact with magnetic fields (techniques useful for magnetic solids include nuclear magnetic resonance, electron paramagnetic resonance and Mössbauer methods); and
3) the characteristic vibrational frequencies that are unique to different solid surficial metals and metal-associated functional groups. Techniques used for vibrational frequency analysis include infrared spectroscopy and Raman spectroscopy.

Analysis of dissolved phase species typically are accomplished by colorimetric/ spectrophotometric methods that suffer from a general lack of specificity, a lack of sensitivity, and the potential for artificial changes in speciation during sample treatment. Electrochemical methods (*e.g.*, differential pulse polarography and stripping voltammetry) are sensitive to the unique redox potentials of metals with multiple valence states. Therefore, the presence of multiple metals in complex environmental samples can be analyzed simultaneously. However, application of electrochemical methods to *in-situ* metal speciation is restricted by the depth to which electrodes can penetrate sediments and to the limited range of commercially available electrodes that are sufficiently robust for use in environmental settings. ICP-MS or ICP-AES allows for the determination of many metals at sub-ppb levels with little pretreatment (Crecelius and Bloom, 1987; Berry *et al.*, 1999). Another commonly used instrumental method to analyze sediments for metals is atomic absorption spectrometry (PSEP, 1997).

4.7 Model Approaches to Predicting Equilibrium Metal Speciation

It is well established that many geochemical factors influence the speciation of metals in water and sediments. Nearly all the mathematical models that are used to predict metal speciation and bioavailability in sediments are based on thermodynamic equilibrium conditions. Although it is understood that most sedimentary systems are not truly at equilibrium, thermodynamic models allow us to make educated predictions of how a particular system will change, for example, with shifts in pH, Eh, or total ligand concentration (Porter *et al.*, 2004). Several of the paradigms that explain the relationships between these geochemical factors and metal bioavailability and toxicity are described below.

4.7.1 Free Ion Activity Model. As discussed, the formation of organic and inorganic metal complexes and metal sorption to particulate material reduces metal bioavailability and toxicity in the water compartment (Pagenkopf *et al*., 1974; Sunda and Guillard, 1976; Sunda and Hansen, 1979; Pagenkopf, 1983; Di Toro *et al*., 2001). As a result, the relationship of metal toxicity to total or dissolved concentrations can be highly variable depending on ambient water chemistry (Di Toro *et al*., 2001). Initially, the free ion activity was considered the best index of metal toxicity, resulting in the formulation of the Free Ion Activity Model (FIAM). The FIAM is a model that describes how variations in the levels of metals can be explained on the basis of metal speciation and metal interactions with the organisms (Morel, 1983; Paquin *et al*., 2002). Being based on thermodynamic estimates of metal speciation, the FIAM contains the implicit assumption that toxic effects are proportional to the flux of the metal in question and predict a first-order linear relationship between biological accumulation and free metal ion aqueous concentration. This assumption has been demonstrated to underestimate metal uptake by microorganisms, especially in situations where organisms may possess active uptake transport mechanisms (Hassler and Wilkinson, 2003).

4.7.2 Windermere Humic Acid Model. A number of chemical speciation or equivalent models provide good characterization of the metal species in a solution containing inorganic ligands and well-characterized organic ligands. As binding of metals to organic matter is often one of the most dominating processes in natural water, it is essential that such speciation models include an accurate description of organic matter reactions with trace metals. The Windermere Humic Aqueous Model (WHAM, Model V) was developed to simulate chemical equilibrium of waters, sediments, and soils dominated by NOM (Tipping, 1994). WHAM was the outcome of a series of models developed to describe NOM chemistry and interactions with metals. The capabilities of WHAM (Model V), along with extensive calibration to published datasets, make this a comprehensive model for simulation of metal chemistry where interactions with NOM are important.

4.7.3 Reactive Transport Modeling. Reactive transport models (RTMs) are highly beneficial for simulating interplay between metal speciation and complex chemical reactions and describing how these processes influence metal transport processes both spatially and temporally in the environment on a variety of scales. RTM has been used to describe early diagenesis processes in sediments (Wang and Van Cappellen, 1996; Boudreau, 1999). RTMs applied to sediments consider the reaction couplings among the principal reduction-oxidation elements (carbon, oxygen, nitrogen, sulfur, iron, and manganese). They can consider dissolved, interfacial, and solid-state chemical species, and incorporate major biogeochemical reaction pathways (*e.g.*, organic matter destruction and sulfate reduction) and transport processes, both biotic (bioirrigation and bioturbation) and abiotic (diffusion). Examples of the use of RTMs in the sedimentary environment include prediction of metal cycling in fresh water sediment (Canavan *et al.*, 2007), modeling pH distributions in aquatic sediments (Jourabchi *et al*., 2005), describing organic matter mineralization in fresh water lakes (Canavan *et al.*, 2006), and predicting sediment oxygen demand from carbon and nitrogen cycling (Hantush, 2007). One modeling tool currently available for conducting RTM is the Biogeochemical Reaction Network Simulator described in Aguilera *et al*. (2005) and Jourabchi *et al*. (2005). Additional information is available online from the RTM group at: http://www.geo.uu.nl/~rtm/index.php?page=intro.

4.8 Summary

A decision to implement MNR at a site requires a thorough understanding of the biogeochemical behavior of the elements of interest and the specific environmental conditions at the given site that will influence chemical and phase partitioning and biological interactions. The behavior and fate of trace elements and metalloids in the environment are complex and depend on many interrelated chemical, biological, and environmental processes. In sediments and surface water, factors that may influence metal toxicity and mobility include the presence, abundance, and forms of reduced sulfur, redox conditions, pH, acid-buffering capacity, abundance of organic matter and iron and manganese oxide minerals, and the chemical and phase speciation of the specific metal or metalloid. A number of modeling tools are available that can help to integrate these processes and make predictions about behavior and fate in relation to the MNR decision-making process.

5.0 LONG-TERM MONITORING AND SITE FORECASTING WITH PREDICTIVE MODELS

5.1 Monitoring Rationale and Strategies

Potential risks posed by contaminated surface sediments, the rate of change in surface sediment chemical concentrations, and the rate of recovery of ecological resources are site-specific features that will influence the effectiveness of MNR and guide any corresponding long-term monitoring requirements. Long-term monitoring in support of MNR may focus on surface sediments (establishing concentration reductions with time or evaluating and characterizing sediment erosion events), recovery of biological/ecological receptors, or both. Monitoring plans should be based on a clear understanding of remedial action objectives (RAOs), which in turn require familiarity with site-specific risk assessments, cleanup levels for sediment, remedial goals for surface water and fish tissue where applicable, and target time frames for achieving the goals of confirming continuation of natural recovery. RAOs for MNR may include attainment of risk-based contaminant concentrations in surface sediment, reduction of chemical mobility to achieve risk-based chemical concentrations in pore water or sediment, and/or achievement of target contaminant concentrations in biota.

Most sites requiring remedial action, such as MNR, will have site-specific sediment, aquatic, or biotic target concentrations considered protective of human health and ecological receptors. These targets form the basis of long-term recovery goals expected to be achieved in a reasonable time period. The goals of long-term monitoring should be to: 1) evaluate the extent to which chemical concentration targets are achieved, and 2) determine whether measured chemical and biological recovery continues at acceptable rates. Monitoring may include surface sediment sampling over time, sediment coring, pore water sampling, water column monitoring, and biota tissue monitoring. In addition to establishing expectations of future surface sediment chemical concentrations, the MNR CSM should form the basis of the long-term monitoring program to determine sampling locations, sampling methods, sample counts, sampling frequency, and monitoring duration.

The following six-point process for developing and implementing a long-term monitoring plan is presented in EPA (2005). This section adds to EPA’s (2005) discussion by focusing on MNR monitoring goals.

Step 1. Identify Monitoring Plan Objectives

Step 2. Develop Monitoring Plan Hypotheses

Step 3. Formulate Monitoring Decision Rules

Step 4. Design the Monitoring Plan

Step 5. Conduct Monitoring Analyses, and Characterize Results

Step 6. Establish Management Decision Guidelines

Short- and long-term monitoring may be considered as the collection of field data (chemical, physical, and/or biological) to determine present conditions at a particular point in time and/or a trend in conditions over a period of time for specified environmental parameters or characteristics, relative to clearly defined management objectives. Likewise, for both short- and long-term monitoring, clearly identified temporal boundaries for the monitoring program should be established. The period of time designated for evaluation of short- and long-term performance may be related to a 5-year project review (*e.g.*, ROD 5-year review) or to a site-specific environmental condition. The data, methods, and time endpoints should be directly related to the RAOs and cleanup levels or remediation goals for the site. The success of the long-term monitoring plan can be evaluated according to the EPA (2005) measure of remedy effectiveness, delineated according to short- and long-term evaluation criteria:

1) Short-term remedy performance – Have the sediment cleanup levels been achieved?
2) Long-term remedy performance – Have the sediment cleanup levels been reached and maintained for at least 5 years and thereafter, as appropriate?
3) Short-term risk reduction – Do data demonstrate a reduction in fish tissue levels, a decrease in benthic toxicity, and/or an increase in species diversity or other community indices after 5 years?
4) Long-term risk reduction – Have the remediation goals in fish tissue been reached, or has ecological recovery been accomplished?

The long-term monitoring plan implemented for MNR should include quantitative metrics to measure long-term performance according to the above evaluation criteria. Short- and long-term metrics should be included as well as contingencies for situations where MNR may not perform according to site-specific RAOs.

5.2 Metrics for Long-Term Monitoring

Long-term monitoring is an essential component of MNR and should be included in any remedial plan. Long-term monitoring, as discussed above, is useful for short-term assessment and long-term remedy evaluation. Long-term monitoring can also be used to confirm predictions developed during the RI phase, such as predicted sediment deposition/erosion rates, corresponding changes in surface sediment contaminant concentrations with time, predicted sediment stability under normal- or high-energy events, predicted contaminant weathering processes, and predicted recovery of ecological receptors in response to physical changes in the environment. Thus, careful selection of the appropriate monitoring metrics consistent with the CSM is critical to the evaluation of model predictions and remedy effectiveness with field-scale analytical data. Given the broad range of environmental variables potentially available for monitoring, selection of monitoring metrics should be considered within a conceptual system designed to reduce the amount of data required for long-term site evaluation of MNR remedy effectiveness. The tiered analysis approach, introduced in Section 2, provides the necessary framework to develop a cost-effective long-term monitoring plan.

The objective of the tiered analysis approach is to reduce progressively the overall quantity of data required to execute site-wide monitoring for MNR evaluation and quantification. The tiered analysis approach, described in detail for application to metals contaminated groundwater (EPA, 2007c), consists of four tiers for evaluation of a site being considered for MNR:

1) Demonstration of contaminant containment
2) Determination of the mechanism and extent of contaminant containment
3) Determination of the capacity of the sediments for contaminant attenuation
4) Design and implementation of a site-specific, long-term monitoring program.

The purpose of Tiers 1 through 3 is to guide site Remedial Project Managers in selecting site characterization data to evaluate sites for implementation of MNR. Field sampling approaches and appropriate models for Tiers 1 and 2 as applied to sediment transport and stability are discussed in Section 2. Tier 4 specifically details elements of a long-term monitoring strategy to evaluate MNR performance for sites where MNR has already been selected as the site remedy. The two objectives of

Tier 4 analysis are to: 1) develop a monitoring program, and 2) identify alternative remedies that can be implemented at sites where MNR is failing as the principal remedy. The first objective in Tier 4 analysis is the focus of this section. Any contingency plans for alternative remedies should be developed on a site-specific basis.

An important aspect of developing a monitoring plan for recalcitrant or non-degradable contaminants is the identification of surrogate monitoring data that can serve as a trigger for impending MNR failure. For example, changes in water quality parameters such as pH or alkalinity might provide an indication that the system is chemically evolving to a state that is not favorable for continued immobilization. The same observation could be offered for a change in contaminant speciation that might change toxicity or bioavailability. This example relates to chemical parameters, but one could envision changes in system hydraulics due to land development/modifications or other factors becoming a concern. The bottom line is that MNR typically is selected based on knowledge of system function, so, in addition to contaminant analyses (typically expensive, so they are conducted infrequently), it is important also to monitor surrogate indicators that may be less expensive and easier to maintain on a more frequent basis.

Long-term monitoring may include monitoring of sediments, surface water and pore water, and/or biota. The following sections describe considerations for each of these media.

5.2.1 Sediment Monitoring. Where sediment erosion is a concern, a baseline sediment assessment strategy should be established, including monitoring of surface sediment concentrations and bathymetry. Sediment bathymetry can be monitored after high-energy events to evaluate bed elevation changes and compare with model-predicted behavior. Water column monitoring can also be used to support sediment stability assessments by monitoring water column suspended solid concentrations and/or turbidity and flows to back calculate the amount of suspension or deposition of sediments during normal- and high-energy events.

Bathymetric changes are considered a means of properly documenting the accretion of sediments at a site. Comparative bathymetry is an important and valuable technique in establishing historic sediment stability and accretion. However, practitioners must consider carefully the nuances of performing these types of comparisons. These comparisons are particularly subject to several error functions that arise from the various measurement techniques (both lateral and vertical) used in many bathymetric measurements.

Uncertainties in comparative bathymetry commonly arise from inaccuracy, imprecision, and/or lack of comparability in the following areas:

- Location control precision: Inaccuracy always exists in the horizontal plane when determining the position of each given sounding. For example, the degree of location control, and associated uncertainties, varies greatly when comparing survey location results with global positional system values.
- Depth measurement precision: Inaccuracies in measurements made in the vertical plane result from such factors as resolution, equipment characteristics, calibration, datum, survey stability, the effects of vessel velocity, and echo sounding sensitivity to sediment materials.

The reader is referred to the engineering and design manual for hydrographic surveying (USACE, 2004) for descriptions of the methods used over the past century to measure water depths and prepare bathymetric surveys and for method-specific expected levels of precision and accuracy. For a discussion of methodologies to compare bathymetry, the reader should consult Herzog and Bradshaw (2005).

Although comparisons made from sediment monitoring provide relatively straightforward measures of physical and geochemical changes during MNR, the information derived from sediment monitoring presents several challenges:

- Obtaining a sufficient number of samples representative of heterogeneous site conditions can be difficult.
- Detecting small changes in contaminant concentrations over time may be difficult.
- Monitoring for long periods (years or decades) may be required before evidence of biological recovery is statistically significant.
- Linking surface sediment and water column contaminant concentrations to contaminant concentrations in ecological receptors may be difficult.

Sediment sampling strategies as part of a broader effort to evaluate MNR effectiveness should include considerations of the depth interval of concern, discrete or composite sample analysis, measurement of physical characteristics that affect bioavailability, and comparability to historical site data and relevant data available from other sources (such as regional monitoring programs). Sampling frequency and density should be scaled appropriately for the site. Spatial and temporal scales should be consistent with existing hydrodynamic forces (*e.g.*, combined base flow and storm flow, tidal mixing, and tidal excursion), sedimentation rates, chemical concentration ranges, source locations, and the anticipated rate of change in surface sediment chemical concentrations. Some sites may require years or decades to achieve significant reductions in contaminant concentrations, particularly when surface sediment concentrations asymptotically approach cleanup targets, or when high variability in the data limits the ability to discern relatively small changes in contaminant concentrations. Thus, when developing a long-term sediment-monitoring program, it is important to recognize the degree to which spatial heterogeneity and temporal variability may influence results.

5.2.2 Surface Water and Pore Water Monitoring. Surface water sampling typically provides short-term information relative to water column contaminant concentrations, but often does not provide information regarding advective or diffusive flux from the sediment unless monitored over discrete spatial and temporal intervals. Pore water monitoring may be used as a more attractive predictive metric to assess direct exposures of benthic organisms to surface sediment contaminants, particularly where the total concentration of contaminants in surface sediments is an unreliable indicator of sediment toxicity. Surface water monitoring is less common than is sediment monitoring but may be valuable if it is possible to demonstrate reduced exposure or risk and recovery of ecological receptors. This is especially true where aging of the contaminant in the sediment results in reduced toxicity via sorptive sequestration or encapsulation, two processes that do not necessarily degrade, mineralize, or transform the contaminant. For metals, particularly, but also for some organic contaminants, sediment pore water monitoring may provide a more direct measure of ecological exposures than would whole sediment analysis. If MNR relies on geochemical stability and reduced metal bioavailability, a long-term monitoring plan for metals could include pore water monitoring in lieu of whole sediment sampling. This approach would likely be predicated on prior demonstration that pore water contaminant concentration provides a more reliable indicator of toxicity than sediment contaminant concentration for a given site.

5.2.3 Biological Endpoint and Ecological Monitoring. In many sediment site risk assessments, biological endpoints serve as the primary line-of-evidence for assessing human health and/or ecological protection. Depending on the specific site conditions, relevant data often include fish and invertebrate monitoring of key biological endpoints such as tissue chemistry/residues, acute and/or chronic sediment toxicity bioassays, and community analysis. For this assessment, it is important to consider whether adequate and comparable biological endpoint data are available to support an evaluation of temporal trends. The site-specific risk assessment will likely define the relevance or appropriateness of the endpoints.

Establishment of historical trends should include sufficient sampling to provide adequate evaluations of temporal trends of the biological endpoint of interest to define spatial heterogeneity and temporal variability inherent at the site. Specifically, data should be available for a time period over which recovery could be expected, considering such factors as the life cycle and age of the biological community being addressed. The timing of sampling events and the number and location of samples collected also can have a significant impact on the confidence placed in the trend analysis.

Potential confounding factors to trend analysis with biological endpoints include:

- Differences in field collection methods for different sampling events (*e.g.*, changes in protocol for field filtration of samples, or use of different pore water samplers);
- Changes in laboratory analytical methods for a parameter during the monitoring period;
- Population dynamics;
- Fish migration patterns;
- Food chain dynamics;
- Seasonal variations in abundance or condition; and
- Spatial variation in organism:
    - Habitat quality
    - Density
    - Lipid content
    - Age
    - Sex
    - Size
    - Reproduction cycles.

Reducing or eliminating confounding factors may be achieved through selection of sampling or analysis methods that avoid introduction of artifacts in the collected data, as well as data evaluation approaches that incorporate explicit checks on procedure implementation and/or review of supplemental data that serve as indicators of inadequate data quality. Using appropriate data sets, trend analyses of relevant biological endpoints often can be used to corroborate risk reductions and biological recovery as may be indicated by chemical data. However, statistically valid methods for testing the significance of identified trends (parametric and nonparametric tests) should be employed only after testing and controlling for other potential confounding factors.

Though monitoring changes in contaminant concentrations in biota can be more challenging than monitoring changes in surface water and sediment, biota can provide direct measures of *in-situ* contaminant bioavailability, which reflects toxicity, exposure, and risk. Contaminant concentrations in tissues and bioaccumulation, however, are not in and of themselves biological effects, but may correlate with biological effects.

Biological monitoring may include:

- Direct measurement of contaminant concentrations in tissues of resident, typically native, species;
- Deployment of non-resident species within contained benthos samplers and measurement of contaminant concentrations in tissues over time;
- Determination of the potential for bioaccumulation using food-web models or biological surrogates;
- Measurements of fecundity, recruitment, and size- or age-class structure of populations; and
- Benthic community surveys.

Tissue concentrations alone do not necessarily correlate with deleterious biological effects. Despite the uncertainties involved in linking upper-trophic-level fish tissue concentrations to site-specific sediment concentrations, fish tissue measurement is often a valuable tool for assessing risk to humans and regional availability of environmental contaminants to fish. Edible fish sampling and analysis methods are established and documented elsewhere, as are considerations for species/size/age selection, specific tissues to be analyzed, sample compositing, and archiving (EPA, 2000). Tissue contaminant concentrations are not the only information provided by fish sampling. Other information gathered through fish sampling includes important metrics of the overall health of individual fish, such as gross morphological abnormalities, evidence of disease, and body condition, as well as information on the health of the overall population, such as fecundity, recruitment, and size- or age-class structure. These data can be useful in evaluating MNR effectiveness. For example, liver lesions in mummichogs were positively correlated with t-PAH concentrations in sediments from the Elizabeth River, VA (Vogelbein and Unger, 2003). Liver lesions have also been linked to sediment contaminants in Puget Sound flatfish and PAH metabolite concentrations in the bile of flatfish collected from Vancouver Harbor, British Columbia, Canada (Stein *et al*., 1990; Myers *et al*., 2000; Stehr *et al*., 2004). Toxicity and bioaccumulation tests also can be conducted over time to monitor changes in ecosystem toxicity.

Not all metrics are appropriate at every site; rather, monitoring metrics should be selected based on their ability to provide information relevant to the remedial goals for the individual site. The concentrations of contaminants in ecological receptors may be affected by a multitude of factors unrelated to sediment contaminants, such as diet from other sources (Fisk *et al*., 2001; Herbert *et al*., 2000) and individual age, sex, size, and reproductive stage. Thus, ecological monitoring is not necessarily as simple as monitoring contaminant concentrations in tissues over time. The following influences should be considered when sampling contaminant concentrations in biota:

- Annual or seasonal variability in uptake and food-web resources;
- Annual or seasonal variability in species abundance and distribution;
- Reproductive state and spawning condition;
- Sampling methods reproducibility with time and space;
- Collection of sufficient biota mass to detect chemical concentrations;
- Collection of sufficient individuals to establish site-specific spatial and temporal trends to overcome natural variabilities in contaminant concentrations and effects;

- Coordination of sampling among multiple trophic levels for estimating accumulation factors; and
- Use of reference sites to obtain comparable data and determination of whether reference sites should be relatively pristine, or comparably urbanized or industrialized but otherwise unaffected by the contaminant of concern.

The comparison of site environmental monitoring data to similar data collected at comparable reference areas is a widely-used approach for evaluating remedy effectiveness. A reference area is defined as a site, preferably located in the same water body or river system, with similar physical and geochemical sediment characteristics as the contaminated site and demonstrated not to be impacted by the contaminated site. It may not be possible to identify a reference area within the same water body or river system. In most cases, the difficulties in identifying a single reference site that contains all of the essential environmental and ecological features desired for evaluating the site can be overcome by using several reference sites that together contain all of the desired qualities (EPA, 1994b; Chapman *et al*., 1997; Hunt *et al.*, 2001; SPAWAR Systems Center, 2003; Apitz *et al.*, 2005b). These reference sites may or may not be proximal to the site.

Biological monitoring may also include benthic community monitoring. Not all metrics or data analysis approaches are appropriate at every site. The biological monitoring program should be designed to address site-specific questions and/or remedial goals (EPA, 2005e). The specific parameters or metrics for a site are selected to provide information about several independent community features. Table 5-1 lists several data analysis approaches (*e.g.*, classification and statistical) and their advantages and limitations for benthic community assessments. Individual parameters are analyzed and values are scored according to a predetermined scale to provide a snapshot of the ecosystem by consolidating multiple complex variables into a single number or set of numbers. This classic benthic community ecology approach requires the collection of discrete sediment samples using grab samplers or box corers of various sizes (Blomqvist, 1991; Somerfield and Clarke, 1997), consideration of the size of the samplers and quantity/quality of the sample taken by grab samplers (Blomqvist, 1991), and the mesh size to sieve samples after collection (Bachelet, 1990; James *et al*., 1995; Schlacher and Wooldridge, 1996a, 1996b). Sampling methods (sampler type, size, and sieve size) must be consistent between monitoring events.

Once data have been collected, it is necessary to determine whether the data actually indicate that natural recovery is taking place. Potential approaches include:

- Reference area comparisons;
- Sediment Quality Triad analysis;
- Biotic index analysis; and
- Organism-Sediment Index analysis.

Data analysis tools that incorporate sediment chemistry and toxicity measurements, and their advantages and limitations, are summarized in Table 5-2.

Table 5-1. Benthic Ecology Assessment Metrics and Analysis Tools

Metric/Analysis Tool	Description, Approach	Potential Advantages	Potential Limitations
Abundance and biomass	General features of population or community; abundance may provide an indication of condition of community relative to stress. Biomass may be used with abundance to evaluate level of disturbance or recovery. Use consistent sampling methods (*e.g.*, grab type, size, sieve size); sort samples to remove ≥95% organisms in sample.	Somewhat straightforward measurement. Biomass can be used as a surrogate for a functional aspect of community (secondary production).	Less than dramatic changes in abundance are difficult to interpret; can be cyclic, dependent on stochastic events; no change in abundance does not mean no change in community; may require multiple samples to reduce variability; characterizes structural, not functional, element; costly and time consuming. Biomass is a destructive method of analysis that requires collection of a separate sample; often, programs use wet weight, which is a very poor measure of biomass.
Diversity/ species richness	General community feature; may indicate community resilience and provide an indication of community condition relative to stress. Use consistent sampling methods (*e.g.*, grab type, size, sieve size); sort samples to remove ≥95% organisms; identify to lowest practical unit.	Sample "richness" (number of species) is straightforward measurement; relatively easy to understand.	Requires consistent taxonomy over life of monitoring program; indices increase complexity (*e.g.*, common index, Shannon diversity, varies with the logarithm used in calculation); sample richness varies with abundance and does not vary linearly with area sampled; taxonomic identifications are costly and time consuming; species counts are inadequate measures of diversity.
Dominant taxa	Describes communities by most abundant taxa; used to characterize community (*e.g.*, Nucula-Nephtys). Count numbers of each species present; determine relative abundance.	Simplistic characterization of community structure.	Assumes that numerical dominance equals functional importance.

Table 5-1. Benthic Ecology Assessment Metrics and Analysis Tools (continued)

Metric/Analysis Tool	Description, Approach	Potential Advantages	Potential Limitations
Indicator taxa: • Pioneer/opportunistic species • Bioturbator species • Valued ecosystem component species • Functional groups	Select key species, populations, or communities to indicate environmental impacts or recovery because not all parameters of potential interest can be measured. Requires knowledge of life history characteristics of species; select species carefully; indicators that have desired characteristics are preferable; recognize that abundance is often not an indication of value.	May provide cost- and time-effective means to assess ecosystem impacts; appeals to managers because of focus on aspects of ecosystem thought to have most importance. Pioneer species may indicate time since disturbance and/or state of recolonization; functional groups have been linked to various successional stages that occur during recovery from impacts. Bioturbators indicate potential contribution of biota to surface sediment mixing.	Correlation between indicator and desired metric may vary over large area; selected taxon may limit ability to detect impact or recovery; indicator may be influenced by “natural” environmental factors. Consensus about “value” may not be easy to reach; value may vary with changing environmental, social, and political situations. Functional groups may be difficult to characterize; species may occupy different groups, especially feeding groups, in different situations.
Classification analyses	Group samples based on overall similarity in species composition and relative abundance; also used for non-biological data. Identify and count species; measure other parameters of interest; run standard software.	Somewhat more realistic view of the community structure as it incorporates relative abundance of species.	Results often depend on method chosen to determine similarity; decision rules for using similarity levels to determine important clusters of samples are not well defined and are often arbitrary.
Statistical tests	Compares population or community data (abundance, species numbers, indicator species, etc.) across time and/or space. Identify and count species; measure other parameters of interest; run standard software.	Establishes statistical relationships between measured populations over time or space.	Lack of statistical difference does not equal lack of population or community change; statistical significance may not equal biological significance.

Table 5-1. Benthic Ecology Assessment Metrics and Analysis Tools (continued)

Metric/Analysis Tool	Description, Approach	Potential Advantages	Potential Limitations
Multivariate analyses	Reduces highly complex environmental and community data to a simpler, more easily understood form. Select appropriate analytical approach; run standard software.	Integrates multi-disciplinary data; provides visual output; allows tracking of temporal changes; can distinguish between two compositionally dissimilar communities that have the same univariate (abundance, species numbers) structure.	Despite sophistication of approach, tool is still correlative and does not indicate cause-effect relationship; output often hard to describe; many approaches have little guidance for selecting method.

Table 5-2. Biological Indices

Analysis Tool, Data Inputs	Description, Approach	Advantages	Limitations
Sediment Quality Triad: Measurements of stress sensors (contaminants); measurements of effects (toxicity); measurements of species richness/diversity (benthos)	Comparative, three-value interpretation of habitat quality by comparison to reference area. Reference area may be pristine or polluted; use multivariate analytical techniques (see Section 5.2.3).	Uses data from three types of studies to evaluate habitat; graphical output makes it easy to visualize differences.	Decision depends on selection and nature of reference or polluted area; costly and labor intensive.
Biotic Indices (Index of Biological/Benthic Integrity): Sediment grab samples, water samples, and fish trawls; sediment geochemistry; pore water properties; bulk chemistry; infauna	Single, integrative value interpretation of habitat quality. Analyze individual parameters; score values according to prepared scale; calculate average per discipline (water, infauna, etc.); calculate overall value.	Summarizes many parameters into single value; can incorporate data from several disciplines.	Scoring system is usually arbitrary; overall value can mask problem areas; based on "health" analogy that may not apply to ecosystems; based on structural features, not functional.
Organism-Sediment Index (OSI): Sediment profile imagery (SPI) camera images; successional stage, redox potential discontinuity, and gas voids	Single, integrative value interpretation of habitat quality. Determine values for individual metrics; score according to prepared scale. OSI range is +11 to −10; higher score indicates better habitat quality.	Summarizes parameters from three categories (relative percent difference, successional stage, and gas voids) into single value describing habitat quality.	Developed for northwest Atlantic estuarine, muddy habitats; needs calibration for use elsewhere; scoring system somewhat arbitrary.

5.3 Predicting Long-Term Recovery

The evaluation of long-term MNR effectiveness requires predictions of whether and how natural processes will reduce risk to human health and ecological receptors/resources over time. Models can integrate a broad range of physical, geochemical, and biological processes germane to sediment recovery. These may include, but are not limited to, sedimentation, sediment transport via hydrodynamic suspension, benthic mixing, chemical partitioning (sorption), and chemical transformation, the collective use of which improves the understanding of long-term chemical transport and behavior in aquatic environments. After empirically characterizing sediment deposition, recovery, and sediment erosion potential, sediment transport models can be applied to estimate long-term recovery of ecological receptors/resources. These models are discussed in Section 2. Data collected during site characterization are used to identify the specific contaminant and geochemical constituents of the sediment. These data are used in chemical speciation models to estimate organic contaminant sediment dynamics (*e.g.*, sorption, transformation, and degradation) as described in Section 3 or to estimate metal speciation as described in Section 4. This section (Section 5) describes how long-term ecological models could be linked to chemistry and sediment transport models to estimate the likelihood and trajectory of recovery of resident ecological receptors. By “model,” this document refers to a wide range of mathematical representations of aquatic, sediment, chemical, and biological processes, ranging from relatively simple spreadsheet models to highly complex, multi-dimensional fate and transport models. The appropriate complexity of models for a site will depend on the available data, project resources, site size, and scopes of decisions to be made. The goal of this section is to provide an overview of how models can be integrated to evaluate MNR processes (*e.g.*, long-term chemical behavior), the recovery of ecological resources, and the reduction in risk to ecological receptors and human health.

Models should be selected so that the site’s dominant processes are defined and represented with sufficient accuracy to provide a confident prediction of future trends. Section 5.3 presents some of the important considerations for selecting models to represent the dominant contaminant transport and transformation processes, including water column hydrodynamics, sediment bed processes, sediment transport, and contaminant transport. The remainder of this section summarizes the key considerations associated with modeling in support of MNR and identifies available modeling tools and their advantages and disadvantages. Section 5.4 discusses the application of one-dimensional modeling in support of MNR, and Section 5.5 covers numerical models for calculating sediment bed stability and transport.

5.3.1 Predicting Recovery of Ecological Receptors. Predicting the recovery of ecological receptors sensitive to sediments contamination (*e.g.*, bottom feeding fish and piscivorous mammals and birds) requires, among other things, an understanding of the key indicators (*i.e.*, biological endpoints) that should be assessed at different levels of organization (*e.g.*, organisms or populations) and the use of clearly defined data quality objectives. Indicators or endpoints may include:

- Chemical concentrations measured in organisms or populations representing important trophic links (food-web components) that can be used to model or predict effects on organisms; and
- Organism abundance, population, growth rate, and species diversity.

Tissue contaminant concentrations can be predicted by combining the sediment concentration expected from MNR with a site-specific BSAF (Burkhard, 2009). The resulting tissue concentration then can be used as an exposure point estimate in food-web modeling of expected risk to upper-trophic-level organisms. This approach assumes that site-specific accumulation factors have been developed in the field or laboratory using bioaccumulation tests with synoptic sediment chemistry or literature values. For large sites that might encompass a range of ecological settings in which monitored biological exposure occurs, it may be necessary to verify that the estimated BSAF value or range of values adequately represents site variability (Wong *et al.*, 2001; Burkhard *et al.*, 2005; Melwani *et al.*, 2009).

Food-web models, despite their complexity, provide a useful framework for identifying all contaminant sources to the receptor organism and a technique for estimating the magnitude of change in surface sediment concentrations to effect a reduction in an impacted species (EPA, 2009). If the ecological risk assessment performed as part of a baseline risk assessment in the remedial investigation/feasibility study is available, the same model may be used to evaluate pre- and post-implementation of the sediment MNR remedy.

Food-web models typically require site-specific validation to ensure that the model output adequately describes the actual food web at the site. Otherwise, a high level of uncertainty persists in exposure and risk estimates. Significant sources of uncertainty typically identified in ecological risk assessments and pertaining to the evaluation of sediment contaminant exposure and risk to ecological receptors include:

- Size, age, sex, reproductive state, and behavior (*i.e.*, competition for food) of receptor individuals;
- Percentage of time a receptor forages at the site (site use factor);
- Level of association of the receptor with sediment (trophic level of receptor);
- Percentage of time that prey forages or spends at the site;
- Level of association of prey organisms with the sediment (trophic level of prey);
- Percentage of the receptor diet represented by each prey organism; and
- Population dynamics of receptor and prey species.

In addition to focusing on remedy effectiveness at the individual organism level, models also may consider species populations and the larger ecological community at a site. This line of investigation would be accomplished either by modeling specific target populations of concern or surrogate indicator species.

5.4 One-Dimensional Transport Modeling to Predict Changes in Surface Chemical Concentrations

Site-wide model approaches are presented in this section to predict changes in chemical concentrations using one-dimensional (1-D) advection/diffusion models. These models require input on chemical species and how they partition, and with what affinity, to the sediment solids and pore water. Potential transport processes include diffusion, advection, and bioturbation (often modeled as a “special” kind of advection). For example, diffusive flux may predominant at sites where concentration and geochemical gradients are driven by mixing with overlying water. In contrast, sites with significant groundwater upwelling through the sediment bed may be governed by advective transport. Advective processes are also likely in coastal sites where tidal action influences groundwater movement. The relative influence of these processes will depend on site conditions, particularly the hydrologic setting. Advection/diffusion models are useful tools to discern those processes that most directly govern contaminant transport at a given site and, therefore, should be included among the monitoring design components (Jones and Lick, 2001; Lick, 2010; Wu and Gschwend, 1986).

To assess sediment concentration-reduction rates in the sediment bed, vertical 1-D models can be used if assumptions are made about the rates of deposition and erosion and overlying water column concentrations of contaminants. Figure 5-1 shows the results of a 1-D model used to estimate changes in surface sediment PCB concentrations at a hypothetical PCB-contaminated site (Battelle, 2004; Battelle, 2006). The figure presents three model runs: the first run (Figure 5-1a) includes diffusive processes but no deposition; the second run (Figure 5-1b) adds 0.5 cm/year deposition of clean sediments; and the third run (Figure 5-1c), which also includes 0.5 cm/year deposition, increases the net diffusion rate by increasing the bioturbation rate to simulate increased benthic biological activity and mixing. The model includes contaminant partitioning ($K_d = 1.2 \times 10^5$ L/kg), diffusion ($D_m = 10^{-7}$ cm^2/s), deposition rate (deposition = 0.5 cm/yr), and an effective diffusion rate due to bioturbation ($D_b = 10^{-7}$ cm^2/s for Figures 5-1a and 5-1b and $10^{-5} cm^2/s$ for Figure 5-1c). D_b in this model decreases with depth.

In this example, contaminant transport is dominated by deposition and surface mixing. In Figures 5-1b and 5-1c, deposition drives the peak contaminant concentrations downward, resulting in 52 cm burial at 0.5 cm/yr over a 100-year period (*i.e.*, the peak migrated from 23 cm to 75 cm below the sediment-water interface in Figure 5-1b and from 23 to 90 cm in Figure 5-1c). Mixing resulted in the gradual reduction of surface sediment concentrations and the asymptotic approach to zero at the sediment surface. The greater mixing coefficient used for Figure 5-1c resulted in increased mixing, which resulted in greater contaminant spreading and slower rates of change in surface sediment chemical concentrations. These processes are commonly observed at contaminated sites (Lick, 2010; Wu and Gschwend, 1986).

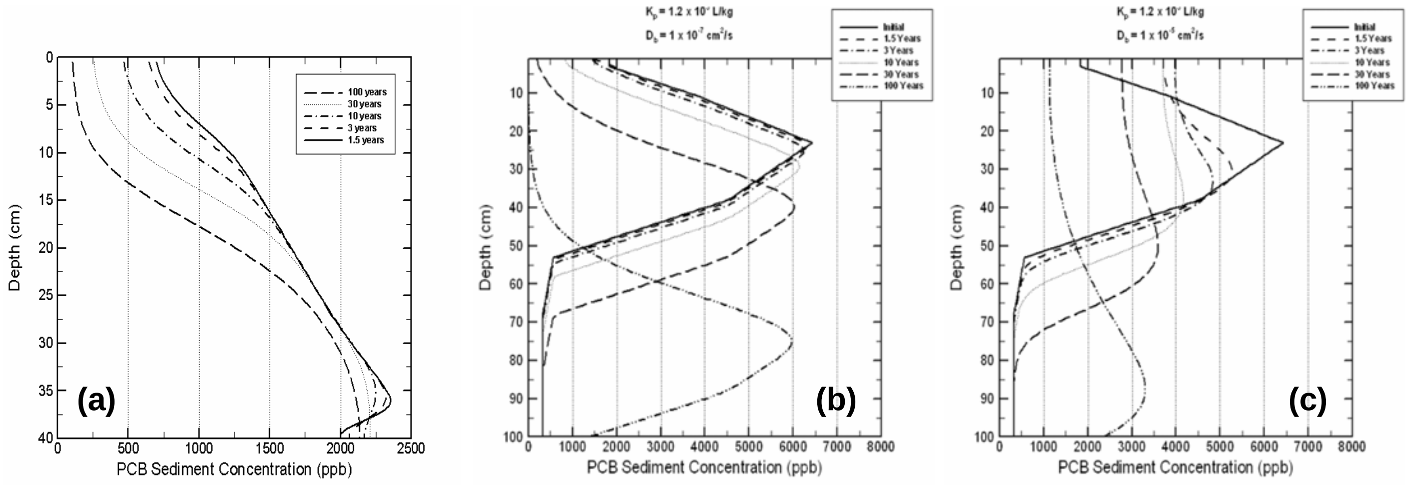


Figure 5-1. Example of Vertical 1-D Contaminant Transport Modeling of PCBs in Sediments using: (a) Diffusion Only, (b) Diffusion Plus Deposition with Mild Benthic Mixing, and (c) Diffusion Plus Deposition Plus Rapid Benthic Mixing (Developed by Dr. Craig Jones, Sea Engineering, Santa Cruz, California.)

The simplicity of the 1-D modeling approach is desirable for sites without the data or resources to support more complex monitoring. A 1-D model could be applied repeatedly to different areas of a site to evaluate chemical concentration profiles at different locations. This model approach does not incorporate individual depositional or erosional events, except to apply a net depositional or erosional term in the model.

5.5 Numerical Models

Sediment transport models commonly begin with a hydrodynamic model that is calibrated to site conditions. Sediment transport and chemical transport models build on the hydrodynamic model, and these models may be linked to a food chain model. Models mathematically characterize one or more of the following processes with different levels of detail depending on the model application and available data:

- Sediment transport processes, which can influence long-term contaminant transport;
- Contaminant partitioning between solid and aqueous phases (Ghosh *et al.*, 2000, 2003; Deane *et al.*, 1999; Lick *et al.*, 2004);
- Bioturbation, which can influence chemical transport in surface sediments and chemical flux at the sediment-water interface (EPA, 2005e); USACE (2001) presents a comprehensive review of the effects of bioturbation and provides suggested rates and effective depths for various regions throughout the United States; and
- Pore water chemical transport, which depends on pore water hydrodynamics, chemical solubility, and partitioning (Lick *et al.*, 2004).

The remainder of this section discusses hydrodynamic, sediment bed, and sediment transport modeling. Detailed comparisons of available modeling tools are provided in Tables 5-3, 5-4, and 5-5. Considerations associated with merging models are discussed in Section 5.5.4.

5.5.1 Hydrodynamic Modeling. Water column and sediment transport processes are often significant factors resulting in reduced exposure and risk at a given site. A hydrodynamic model, which typically focuses on the movement of water, can predict hydrodynamic shear forces at the sediment surface. The hydrodynamic model must be able to be interfaced with a sediment bed model (focus on movement of sediment), a contaminant transport model (focus on movement of contaminant), and possibly the food-web model (focus on biological uptake and associated toxicity of contaminant). If selected models do not easily share data, it may require significant effort to ensure accurate data transfer among models. Table 5-3 lists commonly available hydrodynamic models along with their respective advantages and limitations. A majority of these are finite difference models that use finite difference equations to approximate the solutions to ordinary differential equations. In contrast, finite element methods use linear algebraic equations to approximate the solutions to partial differential equations.

5.5.2 Sediment Bed Modeling. Sites that consider MNR may require some level of sediment bed modeling. The chemical concentrations and fluxes in the sediment bed and at the sediment-water interface are ultimately responsible for determining the long-term success of MNR. Modeling of long-term trends in sediments should accurately represent dominant physical, chemical, and biological processes. Table 5-4 shows various commonly-used sediment modeling frameworks along with advantages and disadvantages of each. A thorough and site-specific evaluation of each model should be conducted to judge the appropriateness of the model for predicting long-term recovery.

5.5.3 Sediment Transport Modeling. Accurate modeling of long-term sediment transport generally requires higher-level numerical modeling with site-specific measurements of the sediment bed critical shear strength and hydrodynamic shear forces. Table 5-5 summarizes several commonly-used sediment transport models. For each model, the table indicates if site-specific sediment bed and hydrodynamic data can be incorporated. Those that can incorporate site-specific measurements will typically have less uncertainty because they are constrained by measured data.

Table 5-3. Hydrodynamic Models

Hydrodynamic Model	Primary Application	Potential Advantages	Potential Limitations
SEDZL	2-D coastal and inland finite difference hydrodynamic model	Robust model that has been verified extensively at dozens of unique locations; more extensively verified than most hydrodynamic models.	Application requires high-level modeling and Fortran programming skills. Significant pre/post-data-processing requirements.
SMS – RMA2	2-D coastal and inland finite element hydrodynamic model	User-friendly interface and pre- and post-processing. Well-verified hydrodynamic model. USACE supported.	Difficult to interface finite element modeling with the most common contaminant transport models.
EFDC	3-D coastal and inland finite difference hydrodynamic model	EPA-supported, public-domain model with user-friendly interface. Based on the well-verified Princeton Ocean Model.	Custom model applications present difficulties for non-specialists. Still undergoing EPA revision.
ECOM	3-D coastal and inland finite difference hydrodynamic model	Well-verified 3-D hydrodynamic model based on Princeton Ocean Model.	HydroQual, Inc., proprietary model. No fee for use and readily available to the public.
MIKE 3 and MIKE 21	2-D and 3-D costal finite difference hydrodynamic models from DHI	Robust model with user-friendly interface. Widely used commercially. Well-verified 3-D hydrodynamics.	Expensive modeling package. Code is not open source, so custom applications are not easily developed.
DELFT-3D	3-D coastal and inland finite difference hydrodynamic model (Delft Laboratories)	Robust model with user-friendly interface. Well-verified 3-D hydrodynamics.	Expensive modeling package. Code is not open-source, so custom applications are not easily developed.
CH3D	3-D generalized curvilinear grid (“boundary-fitted grid”) for estuaries, lakes, and coastal waters with very fine grid-resolution	Combines long-term hydrodynamic circulation data with water quality parameters such as temperature, salinity, and nutrient concentrations. Has been used to model high-energy events, such as coastal storm surge and hurricane events.	Considerable knowledge of hydrodynamics is required to use the model effectively.

Table 5-4. Sediment Bed Models

Sediment Bed Model or Reference	Primary Application	Advantages	Disadvantages
Recovery (Ruiz *et al.*, 2000)	Long-term recovery of contaminated sediment beds	Standardized model for sediment and chemical transport covering a wide range of chemical species.	Does not provide a detailed mechanistic treatment of contaminant sorption processes. Assumes equilibrium partitioning.
Palermo *et al.*, 1998	Contaminant transport in sediment beds after remedial cap installation	Standardized model for cap design and contaminant transport in sediments and caps.	Geared specifically to contaminant penetration in remedial caps. Does not provide a detailed mechanistic treatment of contaminant sorption processes. Assumes equilibrium partitioning.
Di Toro, 2001	Various models of chemical species flux from sediments	Provides generalized equations for flux of most chemical species from sediments. Techniques are easily applied to different systems.	Parameterized techniques can oversimplify important mechanisms. Assumes equilibrium partitioning.
Lick *et al.*, 2004	Hydrophobic chemical transport model	Provides detailed mechanistic descriptions of hydrophobic chemical transport in natural systems. Includes non-equilibrium partitioning.	Limited to hydrophobic contaminants. Has not been widely applied. Proprietary model not available in the public domain.

Table 5-5. Sediment Transport Models

Sediment Transport Model	Primary Application	Advantages	Limitations
SED2D	Cohesive and noncohesive sediment transport model	Integrated with RMA2 hydrodynamics package in a user-friendly environment. USACE supported.	Only allows a single grain size per simulation. Generally not applicable for contaminant transport applications.
EFDC	Cohesive and noncohesive sediment transport model	Integrated with EFDC 3-D hydrodynamics. Includes multiple size classes, bedload transport, and bed armoring. EPA supported.	Based on dated cohesive sediment dynamics.
SEDZL	Cohesive and noncohesive sediment transport model	Integrated with SEDZL 2-D hydrodynamics model. Based on site-specific sediment data. Has been verified at a number of contaminated sediment sites.	Limited to 2-D hydrodynamics. Based on surficial sediment measurements only.
ECOM-SED	Cohesive and noncohesive sediment transport model	Utilizes SEDZL model coupled to 3-D hydrodynamics model.	Based on surficial sediment measurements only. Hydroqual, Inc. proprietary model. No fee for use, but not readily distributed.
SEDZL-J	Cohesive and noncohesive sediment transport model	Integrated with SEDZL 2-D hydrodynamic model. Based on site-specific sediment measurements of shear strength with depth into sediments.	Currently limited to 2-D hydrodynamics. Has not been applied widely.

5.5.4 Integrating Models. For MNR, virtually all modeling efforts are expected to examine processes at the sediment bed level, ideally using site-specific data. Complex hydrodynamic and sediment transport processes may benefit by merging hydrodynamic, sediment bed, sediment transport, and chemical speciation/partitioning models.

In the simplest scenario, a sediment transport model may quantify the net sediment deposition (*i.e.*, burial) processes that result in the slow but persistent burial of contaminated surface sediments. With increasing complexity, temporal variations in sediment transport can alter the distribution of contaminants in the sediment bed. Sediment transport processes may also be responsible for redistribution of contaminants on and off site. In these cases, hydrodynamic, sediment transport, and sediment bed models may be merged. The merging of the models also can affect the efficacy and uncertainty of models. Merging models can reduce errors and uncertainty that may be introduced through incompatible modeling assumptions or incompatible time and spatial scaling between individual models.

5.6 Summary

Establishing an effective monitoring plan requires an understanding of the rates of attenuation and driving processes, site-specific remedial goals, ecology, hydrodynamics, water chemistry, and sediment transport processes. It is particularly important that site managers and regulatory oversight staff be familiar with these parameters. A one-size-fits-all approach is not available or appropriate for monitoring biological and ecological responses (*i.e.*, recovery) to reduced chemical exposure via natural processes at sediment sites. Long-term monitoring plans need to be flexible so that the data collected can be adjusted as necessary to meaningfully measure recovery of ecological resources. An adaptive management approach, whereby site assumptions are tested and re-evaluated as new information is gathered, is critical for effective MNR and should be adopted where feasible (EPA, 2005e). Whether an adaptive management approach is cost effective is a site-specific decision (EPA, 2005e). Resources for adaptive management at sediment sites can be found in Environmental Cleanup at Navy Facilities (NRC, 2003). Scientists and resource management agencies in the United States and elsewhere increasingly understand that monitoring programs must have the flexibility for refinement during the course of measuring reduced exposure and recovery of ecological resources at a sediment MNR site.

A variety of tools and endpoints likely are needed and appropriate for each site. Sediment and water column chemical and physical characterization and monitoring frequently will dominate long-term monitoring programs. These measurements provide rapid, relatively inexpensive, and readily interpretable information on the state of the ecosystem. While such measurements can provide biologically relevant information regarding contaminant exposure and bioavailability, it is important to incorporate direct measures and estimates of recovery of ecological receptors. In some cases, species may recover faster or slower than indicated by sediment or water column recovery rates.

Aquatic biota may be monitored directly by collecting various species and measuring contaminant concentrations and responses in collected samples. Laboratory toxicity and/or bioaccumulation studies provide well-established and understood tools to measure chemical effects on biota. Sites may also be characterized by species abundance and diversity. Taxonomic indices may be used to compare sample sets. Such indices risk oversimplification, but nonetheless may provide a baseline for comparing sample sets over time and qualitatively assessing recovery at a site. When assessing recovery, long-term monitoring plans should recognize the large spatial and temporal scales governing MNR evaluation.

Models are generally important tools for evaluating the effectiveness of MNR in reducing risk because they facilitate the prediction of long-term recovery of ecological receptors. The appropriate modeling complexity will depend on available data, project resources, site size and complexity, and the scope of decisions being made. Numerical models are useful tools for evaluating the cumulative long-term effects of natural processes on chemical exposure, bioavailability, and risk reduction. The scale of the model should be appropriate to the scale of the site and available resources; full-scale models may not always be necessary. A simple, vertical, 1-D model may suffice and more effectively use resources available for some sites. At others where empirical lines-of-evidence adequately support the MNR decision framework, modeling may not be necessary. For larger and more complex and dynamic sites, numerical models may be needed to incorporate the combined effects of changes in chemical loadings, biological and chemical degradation processes, and natural transport and mixing processes that occur over a wide range of spatial and temporal scales. Food-web and population-based models are also important tools for evaluating and predicting the direction and pace of the recovery of ecological receptors due to changes in bioavailability of sediment contaminants.

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