

# TECHNICAL GUIDE

## Monitored Natural Recovery at Contaminated Sediment Sites

ESTCP Project ER-0622

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# Acronyms and Abbreviations

<sup>7</sup> Be	beryllium-7
<sup>137</sup> Cs	cesium-137
<sup>210</sup> Pb	lead-210
AOC	area of concern
ARAR	applicable or relevant and appropriate requirements
AVS	acid volatile sulfide
BRAC	Base Realignment and Closure
BSAF	biota-sediment accumulation factor
BUI	beneficial use impairment
BURE	Beale's Unstratified Ratio Estimator
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm/s	centimeters per second
cm/yr	centimeters per year
COC	chemical of concern
Cr(VI)	hexavalent chromium
Cr(III)	trivalent chromium
CSM	conceptual site model
DBT	dibutyltin
DELT	deformities, eroded fins, lesions, and tumors
DENIX	Defense Environmental Network and Information Exchange
DERP	Defense Environmental Restoration Program
DoD	Department of Defense
DOE	Department of Energy
DQO	data quality objective
EMNR	enhanced monitored natural recovery
EqP	equilibrium partitioning
ESB	Equilibrium Partitioning Sediment Benchmark
ESTCP	Environmental Security Technology Certification Program
FDA	U.S. Food and Drug Administration
FS	feasibility study
HPS	Hunters Point Shipyard
IBI	Index of Biological Integrity
MBT	monobutyltin
MCUL	Minimum Cleanup Level
MDP	management decision period
MLW	Mean Low Water
mg/kg	milligrams per kilogram
MNR	monitored natural recovery
NCP	National Contingency Plan
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
NRD	natural resource damage
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
POP	persistent organic pollutant
PRP	potentially responsible party
RAO	remedial action objective

RCRA	Resource Conservation and Recovery Act
RI/FS	Remedial Investigation and Feasibility Study
ROD	Record of Decision
Se	selenium
SEM	simultaneously extracted metal
SERDP	Strategic Environmental Research and Development Program
SWAC	spatially weighted average concentration
TBT	tributyltin
TTBT	tetrabutyltin
UCL	upper confidence limit
µg/g	micrograms per gram
µg/kg	micrograms per kilogram
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

# Preface

## *Document purpose and organization*

This document provides a technical guide for project managers and management teams evaluating and implementing monitored natural recovery (MNR) at contaminated sediment sites. It is primarily intended to support environmental restoration at United States Department of Defense (DoD) sites; however, many aspects of the document also may be useful for other government organizations, potentially responsible parties, communities, and stakeholders involved in management of sediment cleanup. Specific objectives include:

- Establishing principles and evaluation criteria for the comprehensive and cost-effective evaluation of MNR as a remedial option.
- Providing a framework to properly design, implement, and monitor MNR and to predict the long-term performance of natural recovery processes in managing or reducing ecological and human health risks.

In meeting these objectives, this technical guide promotes consistency among practitioners in developing lines of evidence to evaluate the site-specific suitability of MNR and in applying MNR to sediment sites. It provides a framework to consider alternative remedies or, as appropriate, to enhance MNR via thin-layer capping or other actions that might be required to achieve appropriate risk reduction within an acceptable time frame.

## Why This Document is Needed

Environmental restoration of active and formerly used military installations poses a major challenge for the DoD due to the sheer number and diversity of facilities and past activities that have released contaminants into the environment. While soil and groundwater issues tend to dominate installation restoration programs at DoD facilities, contaminated sediment issues can be significant for installations located near or containing ecologically sensitive aquatic environments.

Contaminated sediment remedial efforts typically are more complex and costly than remedial efforts for most soil and groundwater sites (NAVFAC 2004, NRC 2003a) due to several factors:

- Sediments are subject to long-term accumulation of persistent contaminants, with the potential for remobilization and biomagnification.
- In aquatic systems, bioaccumulative chemicals can reach high concentrations in animal tissue, with implications for both ecological and human health.
- Sediments can act as a “sink” for contaminants from multiple sources, some of which may be ongoing and some of which may be unrelated to DoD operations.
- Sediment cleanup can be complicated by the challenges of managing contaminated material under water and by complex dewatering and disposal requirements.

These and other complexities and challenges have prompted government and industry to invest in the development of alternative technologies to improve sediment assessment and remediation and to provide a broader range of cost-effective risk-management alternatives. The consideration of a full range of technology options promotes expedited environmental cleanup and restoration, increased cleanup effectiveness, and reduced remedy costs.

⇒Refer to Chapter 6 for information about regulatory context and DoD resources.

Development of this document is part of the DoD’s strategic plan to improve the cost-effectiveness of sediment remediation by advancing the science and engineering of in-place sediment management approaches (SERDP and ESTCP 2004). The U.S. Environmental Protection Agency (USEPA) also recognizes the need to improve the range and scientific foundation for contaminated sediment remedy selection by improving risk characterization, site characterization, and understanding of different remedial options, in order to effectively reduce risks to humans and the environment and to optimize the cost-effectiveness of remedial actions (USEPA 2005a). The USEPA (2005a) recognizes MNR as one of three major remedial approaches or alternatives available for managing risks from contaminated sediment and encourages combining approaches to achieve protection of human health and the environment, particularly at large complex sites. At some sites, a combined approach can optimize remedy effectiveness by integrating MNR with capping or dredging, or with innovative technologies that promise to accelerate natural recovery processes.

As with all remedy decisions, MNR will be most successful when the regulatory community and stakeholders are involved early in the remedy selection process and fully support the remedy decision. Although MNR is not an “innovative technology” per se, it is a relatively new remediation technology and relies on a rigorous understanding of relatively complex processes. DoD and USEPA have established several programs to promote the use of new or innovative technologies (Table P-1), many of which can be accessed via the Internet.

TABLE P-1. New and innovative technology programs.

Initiative	URL
<b>Department of Energy (DOE) Environmental Technology Directorate</b>	<a href="http://agg.pnl.gov/encap/monitored.asp">http://agg.pnl.gov/encap/monitored.asp</a>
<b>Environmental Security Technology Certification Program (ESTCP)</b>	<a href="http://www.estcp.org">http://www.estcp.org</a>
<b>Federal Remediation Technologies Roundtable</b>	<a href="http://www.frtr.gov">http://www.frtr.gov</a>
<b>Interstate Technology and Regulatory Council</b>	<a href="http://www.itrcweb.org/">http://www.itrcweb.org/</a>
<b>Naval Facilities Engineering Service Center</b>	<a href="http://portal.navfac.navy.mil/portal/page?_pageid=181,5346904&amp;_dad=portal&amp;_schema=PORTAL#slide_show_end">http://portal.navfac.navy.mil/portal/page?_pageid=181,5346904&amp;_dad=portal&amp;_schema=PORTAL#slide_show_end</a>
<b>Remediation Technology Development Forum</b>	<a href="http://www.rtdf.org/public/sediment">http://www.rtdf.org/public/sediment</a>
<b>Strategic Environmental Research and Development Program (SERDP)</b>	<a href="http://www.serdp.org">http://www.serdp.org</a>
<b>U.S. Army Corps of Engineers (USACE) Dredging Operations Environmental Research</b>	<a href="http://el.erdc.usace.army.mil/dots/doer">http://el.erdc.usace.army.mil/dots/doer</a>
<b>USEPA Technology Innovation Program</b>	<a href="http://www.clu-in.org">http://www.clu-in.org</a>

## Document Overview

This technical guide focuses on the role of natural recovery processes in the remediation of contaminated sediments. Case studies and generic examples are included to demonstrate concepts at work in real-world situations. No one-size-fits-all approach exists for MNR, capping, or dredging at contaminated sediment sites. Thus, conditions at actual contaminated sediment sites vary, and actions to be taken are necessarily site-specific and contaminant-specific.

This document is organized into eight sections and three appendices (Table P-2) to provide a step-by-step conceptual primer for applying MNR at sediment sites.

TABLE P-2. Document organization.

Chapter	Description
<b>1: MNR Overview</b>	Key definitions, processes, objectives, and considerations for MNR
<b>2: MNR Within the Sediment Risk Management Framework</b>	Overview of risk management of contaminated sediment
<b>3: Integrating MNR into Conceptual Site Models</b>	Development of a process-based conceptual site model (CSM) as a tool to identify and characterize natural processes that contribute to MNR
<b>4: MNR Lines of Evidence</b>	Information needed to establish specific natural recovery mechanisms
<b>5: Numerical Models</b>	How the CSM is translated into quantitative models to explore and predict the performance of natural recovery processes in reducing risk
<b>6: MNR and the Remedy Selection Process</b>	Comparing MNR to other remedies in the feasibility study process
<b>7: Natural Recovery Monitoring and Remedy Success</b>	A goal-focused framework for MNR implementation
<b>8: References</b>	Source material and further reading
<b>Appendix A: MNR Case Studies</b>	Profiles of representative sites where MNR has been evaluated and implemented
<b>Appendix B: Contaminant-Specific Factors</b>	Contaminant-specific considerations for natural recovery processes
<b>Appendix C: Summary of Relevant Models</b>	Summary of relevant models commonly used or applicable to MNR

# 1 Monitored Natural Recovery Overview

*Definitions, underlying processes, conceptual models, lines of evidence, and considerations for implementation and verifying effectiveness*

Natural processes that are fundamental to the recovery of contaminated sediments include chemical transformation, reduction in contaminant mobility/bioavailability, physical isolation, and dispersion. The monitored natural recovery (MNR) remedy relies on these processes to reduce ecological and human health risks to acceptable levels, while monitoring recovery over time to verify remedy success. MNR remedies are not free of monetary costs. Site characterization and long-term monitoring activities associated with MNR typically involve significant effort and can be even more expensive than for capping and dredging. On the other hand, there are generally no construction costs associated with MNR.

A conceptual site model (CSM) depicts how specific natural recovery processes operate to reduce risk at a contaminated sediment site and forms the basis for evaluating natural recovery processes during the remedy selection and implementation phases.

MNR lines of evidence are developed from rigorous analyses (e.g. literature reviews, laboratory and field studies, modeling, hydrodynamic investigations, and other activities) that define the role of natural processes in reducing risk. Key factors for determining whether MNR is an appropriate remedy include the ability to achieve and sustain an acceptable level of risk reduction through natural processes within an acceptable period of time. Predicting natural recovery rates may require site-specific numerical models, which quantify processes described in the CSM and associated lines of evidence. Numerical models can generate estimates of time to recovery using baseline data to determine likely effectiveness of MNR implementation.

Natural recovery processes operate regardless of the selected remedy. Effective sediment remedies may incorporate MNR in combination with approaches such as capping or dredging. Factors particularly favorable to MNR include evidence that natural recovery will effectively reduce risks within an acceptable time period, the ability to manage human health risks through institutional controls during the recovery period, and (where physical isolation is important) a low potential for exposure of buried contaminants.

CHAPTER CONTENTS	
☆	Sediment Remedy Approaches
☆	What Is MNR?
☆	MNR Is Not...
☆	Natural Recovery Processes
☆	Natural Recovery and Conceptual Site Models
☆	MNR Lines of Evidence
☆	Modeling Natural Recovery Trajectories
☆	Evaluating MNR as a Remedy Alternative
☆	Monitoring Natural Recovery to Evaluate Remedy Effectiveness and Success

In this chapter, we provide an overview of MNR, including basic definitions and important conceptual and practical components for evaluating, implementing, and verifying MNR as a remedy for contaminated sediment.

## 1.1 Sediment Remedy Approaches

Typical sediment remediation approaches include removal (dredging), capping of contaminated areas, and MNR. Dredging or capping can be expensive and can impact surface water hydrology and aquatic habitat. MNR involves leaving sediments in place and relying upon effective source control and ongoing natural processes to reduce environmental risks posed by contaminated sediments. Like other remedies, MNR typically includes:

- Site investigation
- Development of a CSM that describes chemical fate and transport, and ecological and human health risks
- Contaminant source control
- Long-term monitoring

The suitability of MNR—both as a primary remedy and in combination with other remedies—for sediment sites has been established by several studies and affirmed by U.S. Environmental Protection Agency (USEPA) and other regulatory authorities (USEPA 2005a). Under appropriate site conditions, MNR is associated with low implementation risk and a high level of remedy effectiveness and permanence. Although MNR has several advantages, there are concerns regarding exposure to contaminants remaining at the site and uncertainty regarding the time required for recovery. A comprehensive MNR site assessment will carefully and transparently examine processes that contribute to risk reduction, the time frame within which these processes will operate, and the uncertainties associated with the remedy in order to determine whether MNR can be implemented appropriately and effectively.

In this document, we use the term “constructed remedies” to refer to remedies other than MNR that involve some level of onsite construction. Constructed remedies generally refer to dredging and capping but also may include thin-layer placement of clean sediment to enhanced MNR (EMNR), reactive amendments, or other innovative remedies.

## 1.2 What Is MNR?

The National Research Council (NRC) defines MNR as a practice that “relies on un-enhanced natural processes to protect human and environmental receptors from unacceptable exposures to contaminants” (NRC 2000). The successful implementation of MNR depends on the following conditions:

- Natural recovery processes are transforming, immobilizing, isolating, or removing chemical contaminants in sediments to levels that achieve acceptable risk reduction within an acceptable time period.
- Source control has been achieved or sources are sufficiently minimized such that these natural recovery processes can be effective. This condition is common to all sediment remedies but particularly to MNR because slow rates of recovery could be outpaced by ongoing releases.

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*MNR relies on physical, chemical, and biological processes to isolate, destroy, or otherwise reduce the bioavailability or toxicity of contaminants in sediment.*

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During the remedial investigation and feasibility study (RI/FS), information is gathered and studies are conducted to establish lines of evidence to support selection of a remedy. For example, lines of evidence can be established to determine the effectiveness of source control, identify and quantify contaminant fate and transformation processes, and establish relationships between these processes and potential human and ecological risk reduction. During MNR implementation (i.e., long-term monitoring), lines of evidence should be established to verify acceptable rates and relative permanence of risk reduction measured and/or predicted during the RI/FS.

As a sediment remedy, MNR relies on physical, chemical, and biological processes to isolate, destroy, or otherwise reduce exposure to or toxicity of contaminants in sediment (USEPA 2005a, NRC 1997) to achieve site-specific remedial action objectives (RAOs). These processes may include biodegradation, biotransformation, bioturbation, diffusion, dilution, adsorption, volatilization, chemical reaction or destruction, resuspension, and burial by clean sediment. Monitoring is needed to assess whether risk reduction and ecological recovery by natural processes are occurring as expected. Monitoring programs should evaluate the critical lines of evidence identified during the RI/FS to both verify with adequate certainty the ongoing effectiveness of natural processes and quantify the trajectory toward adequate risk reduction. Potential advantages, disadvantages, and technical considerations of an MNR remedial approach are discussed in USEPA guidance for contaminated sediment remediation (USEPA 2005a).

### 1.3 MNR Is Not ...

**M**onitored natural recovery is not a “no-action” approach. Effective selection and implementation of MNR relies on a fundamental understanding of the underlying natural processes that are occurring at the site. Thus, MNR remedies involve extensive risk assessment, site characterization, predictive modeling, and targeted monitoring to verify source control, identify natural processes, set expectations for recovery, and confirm that natural processes continue to reduce risk over time as predicted. If natural recovery does not achieve adequate risk reduction or does not proceed as predicted, site managers may take further action to accelerate recovery through enhanced MNR by implementing an alternate remedy or by combining MNR with other sediment remedies such as capping, removal, or institutional controls.

MNR is not cost-free. Whereas MNR relies on natural processes, the monetary costs of characterization, long-term monitoring, and associated maintenance activities can be substantial. Site investigations to characterize and evaluate MNR and long-term monitoring activities can be more expensive than investigations associated with capping or dredging remedies. On the other hand, because there are no construction-related costs, capital costs associated with MNR are very low. As with other remedies, contingent costs may need to be considered to address the possibility that long-term monitoring will demonstrate inadequate risk reduction.

MNR is not necessarily appropriate for sites that present no risk or negligible risk. Sites that pose negligible risk typically do not require action. For any remedy to be appropriate, risk attenuation or risk management must be required.

### 1.4 Natural Recovery Processes

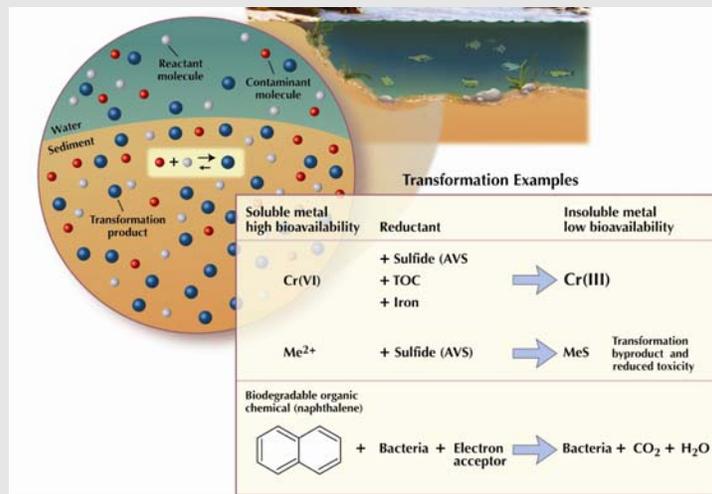
**T**he processes that contribute to reduced contaminant exposure and natural recovery of contaminated sediment can be divided into four primary categories (USEPA, 2005a; Reible and Thibodeaux, 1999), namely:

1. Chemical transformation (Table 1-1)
2. Reduction in contaminant mobility and bioavailability (Table 1-2)
3. Physical isolation (Table 1-3)
4. Dispersion (Table 1-4)

⇒Refer to Chapter 4 for more information about natural recovery processes.

TABLE 1-1. Overview of natural recovery processes: Chemical transformation.

Description	Effectiveness
<p>Change in chemical structure or valence state. Mechanisms include:</p> <ul style="list-style-type: none"> <li>• Abiotic chemical reaction or biological degradation</li> <li>• Mineralization</li> <li>• Redox transformation</li> </ul>	<p>Achieves risk reduction to the extent that transformation processes eliminate, detoxify, or reduce the bioavailability of the contaminant.</p> <p>Due to the potential for complete elimination of the contaminant, EPA views this mechanism favorably as the basis of an MNR remedy (NCP 2008, USEPA 2005b).</p>



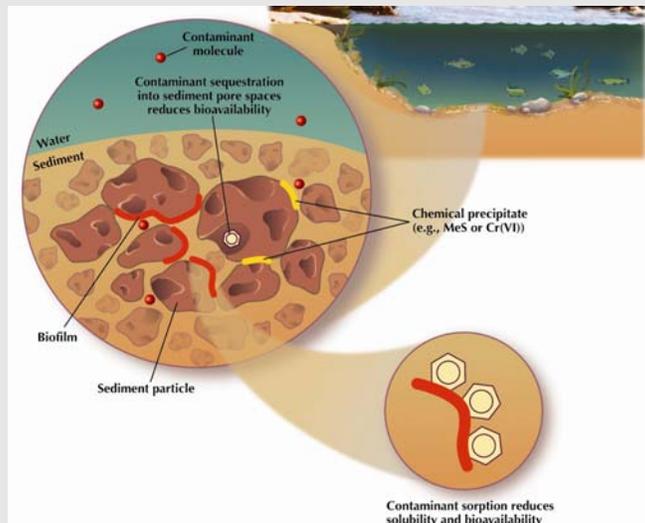
**Examples**

- Degradation of explosive compounds in Halifax Harbor sediment, Canada (Yang et al. 2008).
- Transformation and mineralization of polycyclic aromatic hydrocarbons (PAHs) in surface sediments at Wyckoff/Eagle Harbor Superfund Site, Puget Sound, WA (Brenner et al. 2002).
- Degradation and mineralization of PAHs in tidal marsh sediments, Charleston, SC (Boyd et al. 2000).
- Degradation of organotins following a spill into Red Bank Creek, SC (Landmeyer et al. 2004).

Note: Me refers to a generic divalent metal.

TABLE 1-2. Overview of natural recovery processes: Reduced contaminant mobility and bioavailability.

Description	Effectiveness
Sequestration via sorption (association or bonding with solids) or precipitation to a less bioavailable solid form	<p>Effective in achieving risk reduction to the extent that reduced mobility and bioavailability minimize the potential for human or biological exposure and uptake.</p> <p>Because contamination is left in place, these processes may require a more comprehensive effort to verify permanence in support of MNR.</p>



**Examples**

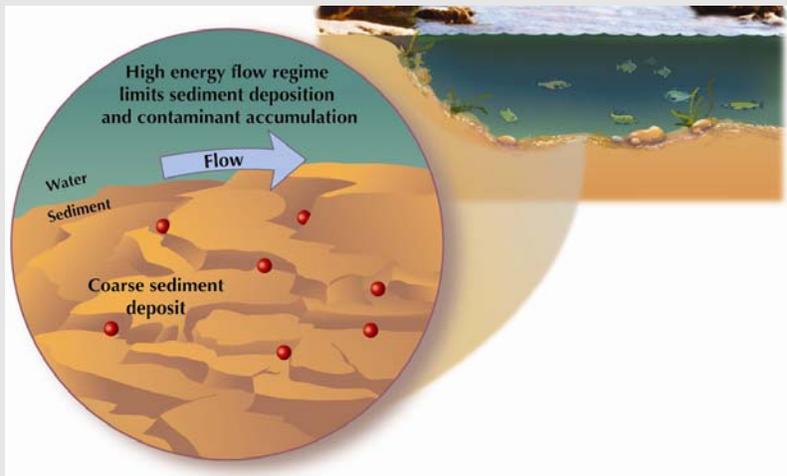
- Formation of insoluble cadmium and nickel sulfide complexes in Foundry Cove, NY (USEPA 2005c).
- Hexavalent chromium (Cr(VI)) reduction, subsequent precipitation as trivalent chromium (Cr(III)), and corresponding chromium detoxification in the lower Hackensack River, Jersey City, NJ (Martello et al. 2007).
- Low bioavailability of PAHs sorbed to coal in Milwaukee Harbor, WI (Ghosh et al. 2003).
- Enhanced sorption of chlorinated hydrocarbons to the soot component of sediment organic carbon in Lake Ketelmeer, The Netherlands, and Frierfjord, Norway (Bucheli and Gustafsson 2001).

TABLE 1-3. Overview of natural recovery processes: Physical isolation.

Description	Effectiveness
<p>Physical containment via deposition of clean sediment that segregates contaminated sediment from benthic and pelagic organisms. Mechanisms include:</p> <ul style="list-style-type: none"> <li>• Burial via natural sedimentation</li> <li>• Surface sediment dilution via mixing with clean sediment</li> <li>• Consolidation and cohesion of sediment bed.</li> <li>• Natural sediment winnowing and bed armoring.</li> </ul>	<p>Achieves risk reduction by reducing direct exposure to contaminants in the surface sediment where receptors come into contact with contaminants. Reduces the potential for sediment scour, contaminated sediment suspension, and corresponding potential for exposure in the water column or for off-site transport.</p> <p>Because contamination is left in place, these processes may require a more comprehensive effort to verify permanence in support of MNR.</p>
<p><b>Examples</b></p> <ul style="list-style-type: none"> <li>• Isolation of polychlorinated biphenyl (PCB)-contaminated surface sediments at Bremerton Naval Complex (USEPA 2000a).</li> <li>• Burial of Kepone-contaminated sediment in the James River, VA (Luellen et al. 2006).</li> <li>• Burial, isolation, and reduced surface sediment PCB concentrations at the Sangamo Weston/Twelve-Mile Creek/Lake Hartwell Superfund Site, SC (Brenner et al. 2004).</li> <li>• Burial of PCB-contaminated post-dredging residuals in Manistique Harbor, MI (NRC 2007a).</li> <li>• Burial of mercury-contaminated sediment in Eight-Day Swamp in the Hackensack Meadowlands, NJ (Weis et al. 2005).</li> </ul>	

TABLE 1-4. Overview of natural recovery processes: Dispersion.

Description	Effectiveness
<p>Disturbances that physically transport sediment or otherwise disperse contaminants into the overlying water column, where they are transported away from the contaminated area:</p> <ul style="list-style-type: none"> <li>• Resuspension</li> <li>• Pore water advection and contaminant diffusion</li> <li>• Bioturbation/biomixing</li> </ul>	<p>Effective in achieving risk reduction to the extent that dispersion processes reduce exposure and bioavailability at the site without resulting in unacceptable offsite risk.</p> <p>Because of the potential for dispersion to incur exposure over a wider area, these processes may require a more comprehensive effort to analyze downstream or offsite risks.</p>



**Examples**

- Transport of PCB-contaminated sediment in Operable Unit (OU) 2 of the Fox River, Wisconsin from erosional areas to downstream depositional areas (WDNR and USEPA 2003).
- Dispersion of selenium-contaminated sediment in Belews and Hyco Lakes, North Carolina, from nearshore areas to deep areas with limited ecological exposure (Finley and Garrett 2007).
- Dispersion of Kepone from source areas and high-energy areas of the James River, Virginia, followed by deposition and burial in lower-energy areas (Luellen et al. 2006).

## 1.5 Natural Recovery and Conceptual Site Models

⇒ Refer to Chapter 3 for more information about conceptual site models.

Within the RI/FS process at contaminated sediment sites, the conceptual site model (CSM) traces the relationships amongst suspected contaminant sources, release and transport mechanisms, contaminated media, exposure routes, and receptors (US Navy 2003). Thus, one of the first steps in evaluating sediment remedies is the development of a site-specific CSM. Further, one of the first steps in evaluating and implementing MNR as a remedy is the integration of the fundamental natural recovery processes into the CSM.

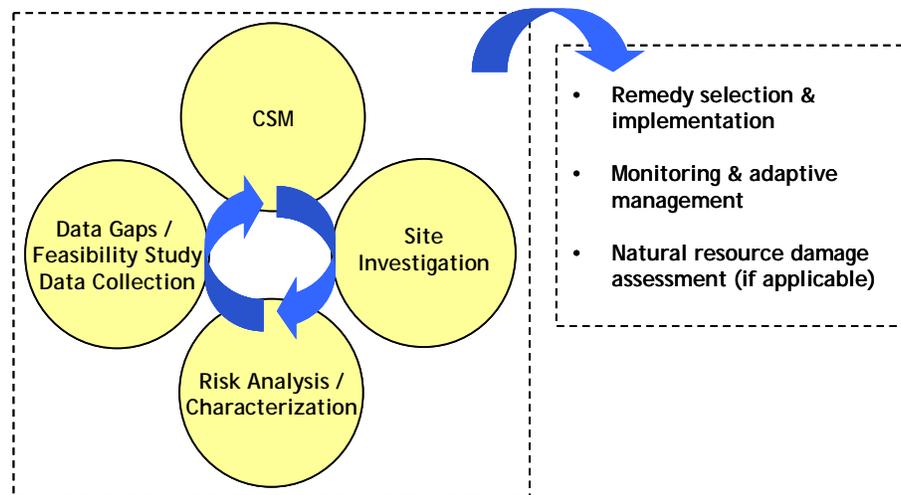


FIGURE 1-1. Conceptual site model as the basis for developing a remedial strategy.

A CSM suitable for evaluating MNR frames the four natural recovery processes within a site-specific context and identifies hypotheses regarding the presence and contribution of each natural recovery process toward risk reduction. The CSM is a graphical and narrative formulation of contaminant sources, fate and transport processes, exposure pathways, and receptors. Risk assessments targeting chemicals of concern (COCs) and ecological and human health risks help focus MNR investigations on natural processes that directly reduce risks. Additionally, the environmental processes illustrated in the CSM form the basis for evaluating the natural recovery processes during implementation (i.e., long-term monitoring) of MNR. Figure 1-1 demonstrates the relationship of the CSM to the RI/FS, remedy selection, and remedy implementation.

⇒Refer to Appendix B for contaminant-specific fact sheets on natural recovery mechanisms.

Because natural recovery processes are both chemical- and site-specific, they do not contribute to risk reduction to the same degree at all sites. Each site presents a unique set of physical and chemical circumstances under which one or more of the natural recovery processes are operating (Chadwick et al., 2006). Natural recovery processes that rely on physical transport of materials, such as physical isolation and dispersion, are particularly affected by hydrodynamic conditions and sediment transport processes. Natural recovery processes that rely on chemical mechanisms, such as chemical transformation and reduced contaminant mobility and bioavailability, are greatly affected by contaminant geochemistry, microbiology, and site-specific physicochemical conditions. Contaminant-specific considerations for MNR are generally applicable across sites and should be captured in the CSM.

The CSM typically is prepared during the RI and evolves as a part of the FS remedy evaluation process. The CSM is a living document that is continually refined and updated based on empirical investigations, modeling, literature, and other lines of evidence collected during the RI/FS.

## 1.6 MNR Lines of Evidence

⇒Refer to Chapter 4 for more information about lines of evidence.

The appropriateness and effectiveness of MNR for reducing risk to human health and the environment is evaluated quantitatively using multiple lines of evidence. These lines of evidence establish the effectiveness of natural processes in reducing human and ecological risk to acceptable levels within the context of achievable source control and future site use and controls. Lines of evidence for natural recovery should be identified in the CSM and documented within the data quality objectives for the underlying risk assessments, numerical models, site investigations, and feasibility studies (USEPA, 2000a). Table 1-5 provides an overview of investigation and monitoring objectives as they relate to the different natural recovery processes and project phases.

Because multiple physical, chemical, and biological mechanisms may contribute to the four major natural recovery processes (Table 1-6), at more complex sites a clear understanding of these mechanisms and corresponding rates typically are developed from carefully planned and executed field and laboratory investigation, literature review, site characterization, and modeling. All of these investigations may not be needed at every site.

Table 1-5. Overview of investigation and monitoring objectives aligned with natural recovery processes.

		Natural Recovery Process			
		Chemical Transformation	Reduction in Contaminant Bioavailability and Mobility	Physical Isolation	Dispersion
<b>R/I/S and Baseline</b>	Verify measurements will allow a robust statistical baseline to which future data will be compared	Determine if COCs subject to transformation	Determine if COCs subject to immobilization	Determine if sedimentation is occurring and if newly-deposited sediments will remain in place	Determine if dispersion is occurring and likely to continue
		Determine if transformation pathways are active under site conditions	Determine if immobilization mechanisms are active under site conditions	Determine effect of site and watershed conditions on sedimentation rates	Determine effect of site conditions on dispersion rates Determine potential risks for downstream contamination
		Determine if transformation rates can meet risk-based goals in desired timeframe	Determine if immobilization rates can meet risk-based goals in desired timeframe	Determine if physical isolation can meet risk-based goals in desired timeframe	Determine if dispersion can meet risk-based goals in desired timeframe
		Determine if ongoing sources add contaminants at a rate that exceeds the observed or predicted rate of risk reduction afforded by natural recovery			
		Periodically confirm transformation is occurring			
<b>Long-term Monitoring</b>	Determine progress toward remedial goals and cleanup levels	Periodically confirm transformation is occurring	Periodically confirm immobilization is occurring	Periodically confirm sedimentation is occurring and sediments remain stable	Periodically confirm dispersion is occurring
		Monitor site conditions likely to affect transformation	Monitor site conditions likely to affect immobilization	Monitor site conditions likely to affect sedimentation and stability	Monitor site conditions likely to affect dispersion Monitor potential risks for downstream contamination
		Determine if transformation rates can meet risk-based goals in desired timeframe	Determine if immobilization rates can meet risk-based goals in desired timeframe	Determine if physical isolation can meet risk-based goals in desired timeframe	Determine if dispersion can meet risk-based goals in desired timeframe
		Verify that sources remain adequately controlled			
		Identify statistical trends			
	Remedial goals and cleanup levels achieved	Verify that COC transformations are stable, and that transformation reversals do not adversely increase risk	Verify that COCs remain immobilized in the event of site disturbances or changing site conditions	Verify that COCs remain isolated in the event of site disturbances or changing site conditions	Verify that offsite risk transfer remains acceptable in the event of site disturbances or changing site conditions
		↓	↓	↓	↓
		Exit if transformation is demonstrated to be stable/irreversible	Exit if immobilization is demonstrated to be permanent/highly irreversible	Exit if isolation is demonstrated to be adequately stable	Exit if dispersion is demonstrated to be unlikely to recontaminate the site or offsite areas

TABLE 1-6. Lines of evidence for natural recovery processes.

Natural Recovery Process	Lines of Evidence
<p><b>Chemical Transformation</b></p>	<ul style="list-style-type: none"> <li>• Historical trends in chemical concentrations and loadings</li> <li>• Chemical indicators of previous or potential chemical weathering and biodegradation</li> <li>• Characterization of factors that may regulate chemical transformation, including:                             <ul style="list-style-type: none"> <li>○ Chemical solubility, hydrophobicity, or volatility</li> <li>○ Oxidation/reduction potential</li> <li>○ Electron donors/acceptors</li> <li>○ Microbial community</li> <li>○ Other general aqueous geochemical and physiochemical conditions</li> </ul> </li> <li>• Modeling of long-term trajectories balancing source control vs. dominant chemical transformation processes</li> </ul>
<p><b>Reduction in Contaminant Mobility and Bioavailability</b></p>	<ul style="list-style-type: none"> <li>• Historical trends in chemical mobility, bioavailability and uptake</li> <li>• Chemical partitioning into sediment pore water</li> <li>• Chemical solubility, hydrophobicity, or volatility</li> <li>• Age of contamination and degree of sequestration</li> <li>• Geochemical precipitation (metals)</li> <li>• Sediment and aqueous geochemical and physiochemical conditions</li> <li>• Modeling</li> </ul>
<p><b>Physical Isolation</b></p>	<ul style="list-style-type: none"> <li>• Sediment core profiles demonstrating burial of historical contaminant deposits and reductions in surface sediment concentrations over time</li> <li>• Hydrodynamics (water depth and velocity) under a range of flow conditions</li> <li>• Geophysical conditions such as bathymetry or subbottom profiling</li> <li>• Radiogeochemistry (e.g., lead-210 or cesium-137) to measure historical deposition and deposition rates</li> <li>• Sediment critical shear strength to predict sediment scour potential under a range of flows</li> <li>• Benthic biological activity and the role of benthic organisms in surface sediment mixing and transport (bioturbation) or as a vector for food-web uptake</li> <li>• Modeling</li> </ul>

TABLE 1-6. Lines of evidence for natural recovery processes (continued).

Natural Recovery Process	Lines of Evidence
<b>Dispersion</b>	<ul style="list-style-type: none"> <li>• Desorption or dissolution processes and kinetics</li> <li>• Upstream and downstream water column analyses</li> <li>• Hydrodynamic conditions</li> <li>• Sediment critical shear strength to predict sediment scour potential under a range of flows</li> <li>• Empirical evidence of sediment transport, such as the absence of sediment deposits followed by historically formed deposits downstream of the source</li> <li>• Modeling</li> </ul>

## 1.7 Modeling Natural Recovery Trajectories

⇒Refer to Chapter 5 for information about numerical models.

Predicting natural recovery performance typically benefits from input of the site investigation results and the relationships embodied in the CSM into numerical models. Model predictions determine the expected level of effectiveness, rate of recovery, and certainty bounds associated with natural processes under the range of current and expected future site conditions. Numerical models also can determine the recovery trajectories (i.e., reductions in exposure over time) that form the basis for gauging remedy success in relation to verification data collected during long-term monitoring. Predictions may incorporate knowledge of future site use and institutional controls.

Generally, successful modeling hinges on the ability to parameterize the underlying natural processes using the process-specific lines of evidence, such as those described above. Project managers should be aware that substantial empirical data may be required to appropriately calibrate numerical models, especially for surface sediment data, which typically display significant heterogeneity (USEPA, 2005a). A critical assessment of uncertainty in modeling projections is important in providing risk managers with the information required to make effective remedy selection and implementation decisions.

The lines of evidence developed through modeling inform remedy selection, gauge remedy performance during MNR implementation, and predict permanence and stability of natural recovery processes after RAOs are achieved. Modeling also can serve to inform long-term monitoring data quality objectives.

## 1.8 Evaluating MNR as a Remedy Alternative

Natural recovery processes occur at all contaminated sediment sites, and all sites should consider the manner and extent to which natural processes contribute to recovery, regardless of the final selected remedy (Magar and Wenning, 2006; USEPA, 2005a; NRC, 2001). The extent to which these processes can be relied upon to achieve acceptable risk reduction will be determined by the results of the RI/FS. Site conditions that are particularly conducive to MNR include the following (USEPA, 2005a):

- Natural recovery processes are expected to continue at rates that contain, destroy, or reduce the bioavailability or toxicity of contaminants within an acceptable time frame.
- Human exposure can be reasonably limited by institutional controls during the recovery period.
- Contaminant exposures in biota and the biologically active zone of sediment are moving toward risk-based goals.
- For sites where buried and otherwise inaccessible contaminants are left in place, the sediment bed is reasonably stable and likely to remain so (i.e., sediment mobilization is unlikely to produce unacceptable risks).

As part of determining whether MNR is an appropriate remedy (or remedy component), it is necessary to understand and quantify contaminant fate and transport processes that may support or hinder recovery, and to consider future pathways of human and ecological exposure to sediment contaminants. Decisions should consider potential changes in conditions with time, whether seasonal or over multiple years.

Source control is critical to the success of any sediment remedy, including MNR. However, MNR is particularly sensitive to source control. Lack of understanding and management of sources can compromise the ability to monitor and quantify MNR processes and can limit the effectiveness of the remedy itself if natural recovery rates are outpaced by ongoing releases. Potential lines of evidence to demonstrate source control or source minimization include investigations to determine historical and ongoing sources of releases and to establish historical or ongoing termination of those releases. Other lines of evidence include empirical evidence of site recovery, such as historical reduction of

surface sediment contaminant concentrations. Any sediment remedy will ultimately be ineffective in reducing risk if contaminant releases to the site persist at a rate that outpaces the rate of risk reduction by natural recovery processes.

Conclusions regarding the effectiveness of an MNR remedy are based in part on the lines of evidence outlined above and the relative potential for MNR and alternative remedies to meet risk-based remedial goals specific to the site and COCs. In addition to the lines of evidence to evaluate remedy effectiveness and permanence, other considerations, such as overall protection of human health and the environment (e.g., including habitat destruction and risk for workers and the community) and cost must be considered, particularly when comparing MNR to more intrusive and potentially disruptive remedies such as dredging or capping. Taken together, these considerations support a comparative evaluation of overall risk reduction. Remedy selection and engineering must balance various competing objectives that are relevant to site remedy decision and evaluate the ability of each remedial alternative to satisfy those objectives, including combined approaches that integrate MNR, capping, dredging, and innovative approaches.

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*There is no presumptive remedy for any contaminated sediment site, regardless of the contaminant or level of risk (USEPA 2005a).*

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Natural recovery processes should be factored into every remedial action, even in cases when MNR is not expected to be the sole or primary remedy for a contaminated site (Magar and Wenning, 2006; USEPA, 2005a; NRC, 2001). Environmental scientists and managers should recognize that natural processes are always ongoing and that natural recovery processes can be combined with other engineering approaches to increase the overall success of the remedial action.

Contaminated sediment sites often extend over multiple water bodies or sections of water bodies with differing characteristics or uses, or differing levels or types of contaminants. Projects that combine a variety of remedial alternatives and approaches are frequently the most promising at such complex sites. Many sites combine dredging, capping, and MNR. For instance, if a lengthy natural recovery period is predicted, dredging or capping may be selected to address areas of elevated risk, whereas MNR may be selected for areas of less risk that show evidence of recovery. MNR processes also are likely to continue after dredging and capping, and may contribute to long-term, post-remediation ecosystem recovery.

When considering the use of MNR as a follow-up measure to dredging or capping remedies (e.g., MNR to address residual contaminant risks after dredging), project managers should consider the change in conditions caused by remedy implementation and potential impacts on natural

processes. These conditions should be summarized in the CSM, so that the CSM can continue to provide value to both assessment and management activities.

Examples of combination remedies incorporating MNR include:

- MNR to control risk from areas of widespread, low-level sediment contamination following dredging or capping of more highly contaminated areas where analysis reveals that MNR cannot achieve acceptable risk reduction within targeted time frames.
- MNR in highly depositional areas, combined with in-situ capping and armoring of contaminated sediment in more erodible areas.
- MNR combined with thin-layer placement of clean sediment (i.e., EMNR) at sites where the natural rate of sedimentation is insufficient to bury contaminants in a reasonable time frame but where thin-layer placement can accelerate reductions in surface sediment concentrations (USEPA, 2005a).
- MNR to reduce risks after dredging or excavation when dredging alone is not expected to achieve risk-based goals or where dredging residuals are present.

## 1.9 Monitoring Natural Recovery to Evaluate Remedy Effectiveness and Success

⇒Refer to Chapter 7 for more information about MNR implementation and remedy success.

**R**emedy success is determined by the ability of the remedy to achieve remedial goals within an acceptable time, and relies on monitoring the key lines of evidence identified during the RI/FS. MNR does not involve construction-related activities. Instead, MNR implementation is achieved through monitoring and analysis of data in relation to predetermined lines of evidence. Monitoring is intended to support analyses conducted during the RI/FS and the processes represented in the CSM. Monitoring should be sufficiently robust to evaluate the long-term performance of natural recovery processes and to reduce uncertainties associated with those processes without re-characterizing the site during every event. By evaluating lines of evidence established under the RI/FS that establish contaminant transformation, reductions in bioavailability or mobility, physical isolation and stability, or dispersion, monitoring can reduce uncertainty and strengthen lines of evidence supporting the CSM.

Monitoring the effectiveness of natural recovery of contaminated sediments should include physical and chemical processes (exposure assessment), stability, and biological processes (effects assessment), as appropriate, so that the CSM can be adaptively refined to reduce uncertainty. Monitoring also can verify the continued success of source control measures.

Specific monitoring components should be determined by the RAOs and natural processes that contribute to site recovery. Each monitoring component should have a specific, defined purpose. Monitoring for cleanup levels and remedial goals may focus on source control and contaminant concentrations in sediment and fish tissue; pore water or surface water may be included to further monitor bioavailable concentrations. Ecological recovery monitoring may include such measures as sediment toxicity, benthic community status, or population status of key fish or wildlife species. Sediment bed stability monitoring should evaluate conditions that demonstrate the integrity of the remedy under normal and high-energy events through time. Stability can be monitored using such methods as bathymetry, coring and contaminant profiling, sediment profile imagery, and visual assessment following storm events; at issue is whether and to what extent sediment deposition or erosion change contaminant exposure and risk on and off site.

Declaration of the success of MNR at contaminated sediment sites can occur if risk-based goals have been achieved and:

- Additional monitoring is not required, or
- The monitoring data support transitioning to a long-term, low-level maintenance program (e.g., only monitoring in the event of a change of site conditions).

Ultimately, a successful MNR remedy can lead to site closure (e.g., no further action) and spending no more money on the site. However, where uncertainty exceeds an acceptable level of tolerance, some amount of additional monitoring may be required even after all cleanup levels and RAOs are achieved. Thus, traditional “no further obligation” site closure may not be attained at MNR sites, nor for that matter at dredging or capping sites, until monitoring adequately addresses uncertainties in addition to documenting RAO attainment.

## 2 MNR within the Sediment Risk Management Framework

*Risk assessment and management frameworks for comparing sediment management options*

Reduction of risks to acceptable levels is the primary objective of contaminated sediment management. The most appropriate remedy or combination of remedies to achieve this goal depends on site-specific conditions; there is no presumptive remedy.

Sediment-related risks include potential harm to aquatic life, wildlife, and human health. Risk assessment supports risk management by quantifying the likelihood and potential magnitude of such effects. Risk management integrates the results of risk assessment with other technical, political, legal, social, and economic objectives to develop and implement risk reduction and prevention strategies.

Understanding natural recovery processes is closely linked to understanding risks. Elucidating mechanisms of reduced bioavailability and chemical transformation can help to understand relationships between chemical concentrations and biological effects under baseline conditions. Determining how natural processes may continue to affect human and ecological exposures to sediment contaminants is important to predicting future risks. Thus, investigations of the potential effectiveness of MNR as a remedy are also useful in assessing risks, and vice versa.

Comparative net risk evaluation is an important component of remedy selection. Quantitative comparisons of net risk reduction require information on baseline risks, projected remedy effectiveness, the action of natural processes, and implementation-related risks.

**E**valuation and subsequent implementation of MNR must be considered from the standpoint of accepted risk management principles. Within this framework, MNR is one option for managing risk, which can be considered both in comparison to, and in concert with, other management strategies.

## 2.1 Contaminated Sediment Risk Management Objectives

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CHAPTER	
CONTENTS	
☆	Contaminated Sediment Risk Management Objectives
☆	How Risk Assessment Informs Risk Management
☆	Resources and Tools for Evaluating Sediment Risks
☆	Comparative Risk Evaluation

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**R**isk reduction is the primary objective of environmental management of contaminated sediments, consistent with U.S. Navy (2002), National Contingency Plan (NCP, 2008), and USEPA (2005a; 2002a) policy and guidance. In aquatic environments affected by sediment-associated contaminants, risk management strategies are designed to interrupt exposure pathways by which contaminants pose an ecological or human health risk over time (Magar and Wenning, 2006). Three major sediment remediation approaches pursue this objective, including sediment removal (dredging), capping (which may be combined with the addition of amendments to remediate or sequester contaminants), and MNR.

Site-wide health and/or ecological risk assessment combined with watershed-scale perspectives that balance potential risks and benefits against implementation risks to human health and the environment establish a sound basis for selecting environmentally appropriate and protective remedies for contaminated sediment sites. Developing an understanding of the risks posed by contaminated sediments and the potential benefits to be gained by alternative remedial strategies present both challenges and uncertainties. The USEPA Superfund feasibility study process (USEPA, 1988) and comparative net risk evaluation approaches (USEPA, 2005a) offer sound foundations for remedy assessment and selection. A comprehensive approach for considering and comparing the risks and benefits of alternative remedial strategies can be used to identify remedies that minimize overall risks and maximize overall benefits.

Historical sediment management practices often presumed that the removal of contaminant mass by dredging would accelerate recovery and prevent future risks due to unforeseen extreme events that could mobilize contaminated sediments. These assumptions were often supported by a lack of tools and quantitative case studies to support the selection of other remedies. At the same time, risk managers often relied on conservative baseline risk assessments to support the selection of very low cleanup targets, which typically have been difficult to achieve.

As alternative strategies have emerged and potential issues with dredging's ability to achieve acceptable risk reduction have been identified (Bridges et al., 2008; NRC, 2007a), risk managers increasingly recognize that a range of remedial alternatives can and should be considered and compared as part of the decision-making process

(Bridges et al., 2006; USEPA, 2005a). A sound remedy selection process balances several factors, including forecasted environmental benefits, impacts, costs, and implementability (Wenning et al., 2006; USEPA, 2005a). Figure 2-1 lists USEPA's remedy selection criteria (NCP, 2008), highlighting risk-based elements.

⇒ Refer to Chapter 6 for more information about remedy selection criteria.

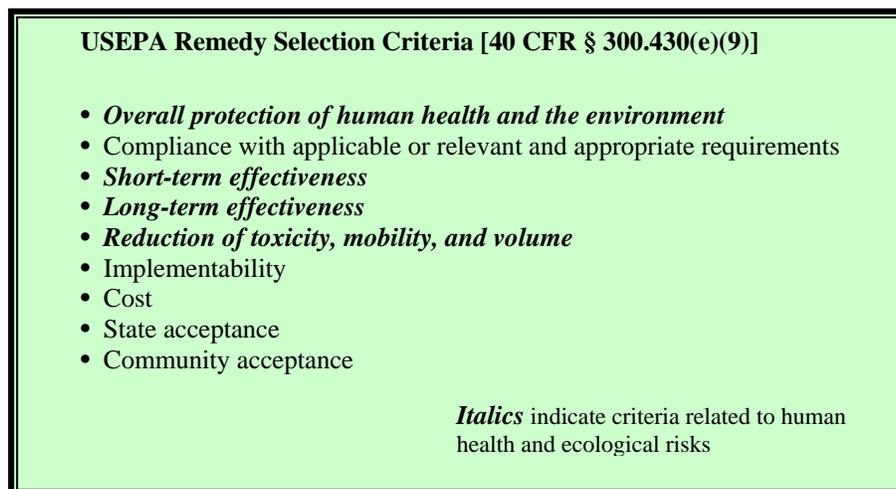


Figure 2-1. USEPA remedy selection criteria.

USEPA's policy is that there is no presumptive remedy for any contaminated sediment site, regardless of the contaminant or level of risk (USEPA, 2005a; 1998a). Thus, it is incorrect to presume that removal of contaminated sediments from a water body will be more effective or permanent than capping or MNR, or vice versa. Acceptable levels of effectiveness and permanence should be based upon site-specific criteria and an evaluation that considers all relevant NCP remedy selection criteria (USEPA, 2005a). The feasibility study (FS) process provides a framework to evaluate the suitability of alternatives, including MNR, for a given site, wherein a range of remedies is considered using risk assessment methods and protocols followed by the application of risk management principles (USEPA, 2005a).

While each remedial strategy must be considered on a site-specific basis, it is important to recognize certain attributes of MNR in relation to constructed remedies such as capping and dredging. For example, the time frames required to reach acceptable risk reduction for MNR, capping, and dredging can be expected to vary, depending on site conditions, rates of key natural recovery processes, and conditions contributing to residual risks. In some cases analysis will support the conclusion that capping or dredging will reduce risks more quickly than MNR. In other cases, MNR would yield a similar risk reduction

POTENTIAL EFFECTS OF CONTAMINATED SEDIMENTS	
☆	Human health impacts from eating fish/shellfish
☆	Human health impacts from direct contact
☆	Ecological impacts on wildlife and aquatic species
☆	Loss of recreational and subsistence fishing opportunities
☆	Loss of recreational swimming and boating opportunities
☆	Loss of traditional cultural practices by Indian tribes and others
☆	Loss of fisheries
☆	Economic effects on development, property values, or property transferability
☆	Economic effects on tourism
☆	Increased costs of drinking water treatment, other effects on drinking water or other water uses
☆	Loss or increased cost of commercial navigation

⇒ Refer to Appendix A for examples of risk assessment and risk management.

trajectory, especially when realistic time frames for selecting, designing, and implementing dredging and capping projects are considered. Where MNR has been ongoing for many years or decades since the original chemical release to the environment, the results of natural processes are readily apparent. MNR will generally pose minimal implementation risks relative to dredging and capping; MNR minimizes the potential for habitat disturbance, contaminant releases, and risks to workers and the community that may occur during the construction phase of capping or dredging. MNR may have significant advantages with respect to implementability and cost (although monitoring costs can be significant) but may present challenges for regulatory and community acceptance that require additional investment in stakeholder engagement and risk communication.

Risk-based management decisions involve an iterative decision process that compares the short- and long-term risks and risk reduction of all potential cleanup alternatives, consistent with statutory and regulatory requirements (USEPA, 2005a, 2002a; U.S. Navy, 2002). Any decision regarding the specific choice of a remedy or combination of remedies for a contaminated sediment site should be based on a careful consideration of the ability of the available approaches to meet the project's varied objectives (e.g., RAOs and the NCP selection criteria) in view of site-specific conditions. Trade-offs are inherent to all decision making. A comparative analysis of alternative remedies or remedy combinations that includes consideration of net risk reduction will improve project outcomes. This analysis will include considering the risk reduction associated with reduced human and ecological exposure to in-place sediment-associated contaminants, as well as risks introduced by remedy implementation (e.g., contaminant releases, transportation accidents, air emissions).

## 2.2 How Risk Assessment Informs Risk Management

**R**isk assessment supports contaminated sediment management by quantifying the likelihood that short-term or long-term adverse effects may occur, and the potential magnitude of those effects. In the context of contaminated sediments, risk may take several forms, including potential harm to aquatic life, wildlife, and human health. For the MNR remedy, success is based on an understanding of the relationship of these risks to natural processes, and the effectiveness of those processes in reducing risk to acceptable levels.

Assessing risk requires quantification of exposure levels, pathways, and the response of representative endpoints under the influence of site-specific processes such as sources, mixing, transport, erosion, burial, degradation, and sequestration (Apitz et al., 2005; NRC, 2001). Sediment risk management uses the information gathered from site-specific investigations, risk assessment, and lessons learned from waterways facing similar challenges (USEPA, 2005a) to make decisions that achieve risk reduction, the long-term goal of contaminated sediment management.

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*Risk management decision making should consider the net risk reductions achieved by different sediment management options.*

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Kiker et al. (2005) describe the transition from risk assessment to risk management as the second phase of risk-based decision making, integrating criteria that are informed by the results of risk assessment with information related to other technical, political, legal, social, and economic objectives in order to develop and implement multi-objective risk reduction and prevention strategies. Consistent with USEPA (2005a, 1998a) and U.S. Navy (2002) guidance, risk management decision making should consider the net risk reductions achieved by different sediment management options by comparing the expected effectiveness and relative risk-reduction potential of remedial alternatives in an FS.

## 2.3 Resources and Tools for Evaluating Sediment Risks

Numerous federal guidance documents offer defined approaches for the quantitative evaluation of sediment risks (Table 2-1). These documents typically call for the application of multiple assessment and measurement endpoints and consideration of multiple lines of evidence to support risk assessment through weight-of-evidence analysis.

TABLE 2-1. Selected risk assessment guidance and resources.

Guidance	URL
<i>USEPA Resources</i>	
<i>Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments</i> (1997a)	<a href="http://www.epa.gov/oswer/riskassessment/ecorisk/ecorisk.htm">http://www.epa.gov/oswer/riskassessment/ecorisk/ecorisk.htm</a>
<i>Ecological Risk Assessment and Risk Management Principles for Superfund Sites</i> (1999a)	<a href="http://www.epa.gov/oswer/riskassessment/pdf/final10-7.pdf">http://www.epa.gov/oswer/riskassessment/pdf/final10-7.pdf</a>
<i>Guidelines for Ecological Risk Assessment</i> (1998b)	<a href="http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12460">http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12460</a>

TABLE 2-1. Selected risk assessment guidance and resources (continued).

Guidance	URL
<i>A Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems</i> (2002b)	<a href="http://www.cerc.usgs.gov/pubs/sedtox/guidance_manual.htm">http://www.cerc.usgs.gov/pubs/sedtox/guidance_manual.htm</a>
<i>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms</i> (various compounds: 2003a,b,c, 2005b, 2008a)	<a href="http://www.epa.gov/nheerl/publications/">http://www.epa.gov/nheerl/publications/</a>
<i>Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual (Part A)</i> (1989) and related guidance	<a href="http://www.epa.gov/oswer/riskassessment/risk_superfund.htm">http://www.epa.gov/oswer/riskassessment/risk_superfund.htm</a>
<i>Risk Characterization Handbook</i> (2000b)	<a href="http://www.epa.gov/OSA/spc/pdfs/rhandbk.pdf">http://www.epa.gov/OSA/spc/pdfs/rhandbk.pdf</a>
<i>Exposure Factors Handbook: Intake of Fish and Shellfish</i> (1997b)	<a href="http://www.epa.gov/ncea/efh/">http://www.epa.gov/ncea/efh/</a>
<b>U.S. Navy Resources</b>	
<i>Navy/Marine Corps Installation Restoration Policy on Sediment Investigations and Response Actions</i> (2002)	<a href="http://web.ead.anl.gov/ecorisk/policy/pdf/Navy_IR_Sediment_Policy.pdf">http://web.ead.anl.gov/ecorisk/policy/pdf/Navy_IR_Sediment_Policy.pdf</a>
<i>Navy Guidance for Conducting Ecological Risk Assessments</i> (2004)	<a href="http://web.ead.anl.gov/ecorisk/">http://web.ead.anl.gov/ecorisk/</a>
<i>Navy Guidance for Conducting Human Health Risk Assessments</i> (2008)	<a href="http://www-nehc.med.navy.mil/hhra/">http://www-nehc.med.navy.mil/hhra/</a>
<i>Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities</i> (2003)	<a href="http://web.ead.anl.gov/ecorisk/related/documents/rev_fin_Implement_Guide_for_Sediment_1.pdf">http://web.ead.anl.gov/ecorisk/related/documents/rev_fin_Implement_Guide_for_Sediment_1.pdf</a>
<b>USACE Resources</b>	
<i>Ecological and Human Health Risk Assessment Guidance for Aquatic Environments</i> (1999)	<a href="http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=ADA374564&amp;Location=U2&amp;doc=GetTRDoc.pdf">http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=ADA374564&amp;Location=U2&amp;doc=GetTRDoc.pdf</a>
<i>Trophic Trace: A Tool for Assessing Risks from Trophic Transfer of Sediment-Associated Contaminants</i> (2005)	<a href="http://el.erdc.usace.army.mil/trophictrace/">http://el.erdc.usace.army.mil/trophictrace/</a>

A broad range of physical, chemical, and biological studies can provide inputs to the risk assessment process. The purpose of these studies is to quantify site-specific risks, trace their causes, identify potential impacts, determine the extent to which risk attenuation is required, and collect

⇒ Refer to Chapter 4 for more information about investigative tools used to understand MNR processes.

sufficient information to support remedy comparisons and selection to manage risks. Figure 2-2 identifies in-situ, laboratory, and literature-based assessment tools that can quantify the risks associated with contaminated sediments and the geochemical conditions that govern those risks (Magar et al., 2008b; Martello et al., 2007; Sorensen et al., 2007). The use of these tools and the associated level of effort should be commensurate with the magnitude of risk and the magnitude of the real or perceived environmental challenge, the anticipated costs of managing the challenge, and the potential impacts of the remedy activity itself (Wenning et al., 2006; Sorensen et al., 2004; NRC, 2003b).

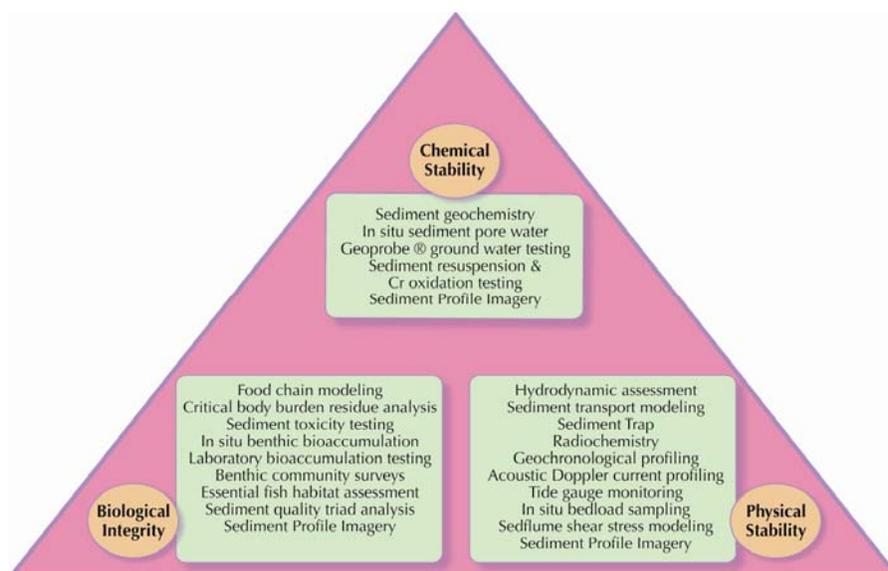
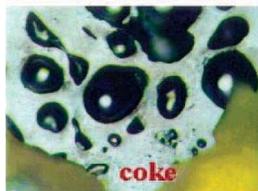
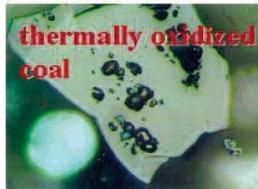
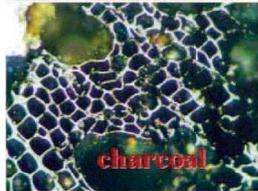


Figure 2-2. Example of tools assembled to assess baseline risks due to Cr(III) and Cr(VI) and to predict future trends for Study Area 7 (Hackensack River, Jersey City, NJ).

There is considerable overlap between the assessment of natural processes and assessment of baseline and future risks. For example, processes that reduce contaminant bioavailability strongly influence risk, as illustrated in Highlight 2-1. Physical sediment stability is relevant to the assessment of future risks at sites where buried sediment might pose a risk if exposed. To the extent that natural processes have already reduced bioavailable exposures to acceptable risk levels and are confirmed to be stable, risk assessment results may point to a no-further-action decision rather than an MNR remedy. However, even if risks have already declined to acceptable levels, monitoring may be needed to confirm physical and chemical stability over time if future risk predictions are uncertain. As described by USEPA (2005a), this would be termed a no-action decision with monitoring.

## BIOAVAILABILITY AND RISKS OF POLYCYCLIC AROMATIC HYDROCARBONS

The bioavailability of PAHs varies widely across sediments, with much of the variation explained by the varying nature and amounts of total organic carbon (Hawthorne et al., 2006, 2007). The USEPA (2003a, 2007a) developed a model to predict toxicity of PAH mixtures to benthic organisms based on PAH concentrations in pore water, as estimated assuming equilibrium partitioning (EqP) between organic carbon and pore water phases. However, the EqP component of the model tends to over predict pore water concentrations and bioavailability in many cases due to the presence of highly sorptive black carbon (e.g., McGroddy and Farrington, 1995). In such cases, direct measurement of contaminant concentrations in sediment pore water may be more appropriate than EqP modeling (USEPA, 2007a).



For example, sediments collected near an aluminum smelter in Kitimat Arm, British Columbia, were not toxic to amphipods or sea urchin larvae in laboratory tests, despite total PAH concentrations as high as 10,000 milligram per kilograms (mg/kg). Evidence of effects on resident invertebrate communities was minimal, and bioaccumulation in resident crabs was detectable but low (Paine et al. 1996). By comparison, the USEPA's EqP model predicts toxicity thresholds to be orders of magnitude lower than the concentrations found in Kitimat Arm (Swartz, 1999). Although the mechanism of reduced bioavailability was unknown at the time, the presence of PAHs as pitch or coal particles was hypothesized to have limited PAH bioavailability (Paine et al., 1996). The site-specific risk assessment documented low PAH bioavailability and consequently low risk. As a result, the extensive remediation initially anticipated based on bulk sediment PAH concentrations was not required (Chapman, 2008).

Research to clarify the mechanisms of reduced PAH bioavailability and to develop tools to measure bioavailable concentrations is ongoing (e.g., Hawthorne et al., 2007). Differences in partition coefficients among different sorbents (e.g., different types of organic carbon) prove critically important. For instance, Ghosh et al. (2003) found large differences in bioavailability among different sediment particles types (see photos).

The Sediment Contaminant Bioavailability Alliance, an ad hoc scientific consortium (<http://www.scbaweb.com>), is working with universities and commercial laboratories to develop analytical techniques to directly measure bioavailable PAH concentrations in sediment pore water. Techniques to measure pore water chemical concentrations directly have the potential to decrease uncertainty and improve accuracy in sediment risk assessments.

Petrographic identification of carbon particles in sediment from Hunters Point, CA. Reprinted with permission from Ghosh et al. 2003. Copyright 2003 American Chemical Society.

HIGHLIGHT 2-1. Evaluation of bioavailability in PAH risk assessments.

## 2.4 Comparative Risk Evaluation

**R**isk management decision making should be informed by a comparison of the net risk reduction provided by an appropriate range of sediment management alternatives, including source control, institutional controls, and remediation via MNR, capping, environmental dredging, and combination remedies (USEPA, 2005a, 1998a). Comparisons of baseline risks with risk reduction estimates and time trajectories for achieving risk-based goals require the use of relatively realistic assessments of baseline ecological and human health risks and projected future risks following implementation of each remedial alternative. Risk projection modeling relies on site-specific hydrodynamic data, sediment geophysical and contaminant properties, sediment and chemical fate and transport mechanisms, and ecological inputs. Risk projection modeling also requires quantification of processes that are integral to the implementation of a remedy (e.g., sediment or contaminant releases during remedy implementation and residual concentrations). The models or assessment tools selected depend on the type of risk evaluated, the manner in which exposure occurs, and the types of chemical transformation processes that may occur over time. For example, predicting the risk of exceeding species-specific critical body residues might involve the prediction of surface water concentrations and creating food chain models that incorporate changed conditions following a sediment remedy.

Remedy evaluation should consider not only risk reduction associated with reduced human and ecological exposure to chemicals in situ, but also the risks introduced by implementing a remedy alternative. It is important to recognize that sometimes intrusive remedies can cause ecological harm or increase risks to human health (e.g., accidents or increased human or ecological exposures) (Wenning et al., 2006). Interdisciplinary collaboration between engineers, economists, regulatory specialists, community stakeholders, and experts in risk-assessment-related disciplines is important to further development of objective, quantitative remedy alternatives analysis. Risk factors associated with implementation of some sediment management options may include (Wenning et al., 2006; USEPA, 2005a; NRC, 1997):

- Changes to contaminant exposure levels in sediment or surface water. For example, this could include decreased surface sediment concentrations due to the remedy, contaminant releases during remedy construction, and residual contamination following sediment removal.

- Habitat modification and destruction during implementation of an engineered remedy.
- Increased risk to workers or communities from construction and transportation activities, including factors such as traffic accidents and air emissions. .

Comparative net risk evaluation thus attempts to assist decision makers in their effort to consider and evaluate all project objectives in relation to the specific elements of remedy alternatives that will determine remedy effectiveness and success.

## 2.5 Summary

Sediment-related risks include potential harm to aquatic life, wildlife, and human health. Ecological recovery and reduction of risks to acceptable levels are the primary objectives of contaminated sediment management projects. It is the role of risk managers to identify the most appropriate remedy or combination of remedies that will satisfy these objectives, using information about site-specific risks and an understanding of natural and engineered processes developed during the RI/FS. Understanding physical, chemical, and biological processes that contribute to reduced contaminant exposures can elucidate natural recovery processes that contribute to risk reduction.

Risk reduction must evaluate baseline conditions, risk conditions during remediation, and post-remedy, long-term risks to determine how natural processes continue to affect human and ecological exposures to sediment contaminants and to predict future risks. A broad range of physical, chemical, and biological studies inform the risk assessment process. The purpose of these studies is to quantify site-specific risks, trace their causes, identify potential impacts, determine the extent to which risk attenuation is required, and provide sufficient information to support remedy comparisons and selection to manage risks.

## 3 Integrating MNR into Conceptual Site Models

*CSM purpose, risk considerations, capturing natural processes.*

The CSM describes the physical, chemical, and biological processes that determine the exposure pathways by which contaminants may reach human and ecological receptors. The CSM identifies key site-specific or chemical-specific factors affecting risk and potential remedy performance, and how these factors will change with time. It differentiates between important and insignificant exposure routes and natural recovery processes.

By presenting this information in an organized framework, the CSM clarifies the development of risk reduction strategies, promotes identification of key data gaps and uncertainties, and comprises a framework for quantitative evaluation of remedy performance, effectiveness, and permanence (including, in some cases, numerical modeling).

Conventional risk-based CSMs identify primary and secondary contaminant sources and release mechanisms, contaminated media, exposure routes, and human and ecological receptors. To establish a more rigorous basis for remedy selection, the CSM undergoes further refinement incorporating contaminant fate and transport processes and the physicochemical conditions that influence these processes.

Where important site characteristics and processes vary within a site, a spatially explicit CSM (or multiple CSMs) may be useful. Temporally explicit CSMs may be useful to represent changes in the rates or relative importance of natural recovery processes over time.

The CSM is more than a picture; it represents the state of understanding of contaminant source, fate, and transport and the exposure of receptors in narrative and graphical forms. Development of the CSM is an iterative process, whereby the CSM is refined as new information is incorporated to reduce important uncertainties.

**S**ound decisions about RAOs, contaminant cleanup goals, the design of effective remedies, implementation of monitoring programs, and evaluations of remedy success are informed by a firm understanding of cause-and-effect relationships among contaminant sources, transport mechanisms, exposure pathways, receptors, and potential adverse effects. These relationships are documented in the CSM

CHAPTER CONTENTS	
☆	Purpose of the CSM
☆	The Risk-Focused CSM
☆	The Fate-and-Transport-Focused CSM
☆	Spatially Explicit CSMs
☆	Temporally Explicit CSMs
☆	CSM Refinement
☆	CSM Checklist

(USEPA, 2005a), an organized framework for describing site-specific physical, chemical, and ecological conditions. In this chapter, we discuss considerations for integrating natural fate and transport processes into the CSM and using the CSM throughout the RI/FS process to develop understanding regarding these processes and how they influence natural recovery.

### 3.1 Purpose of the CSM

The CSM describes the physical, chemical, and biological processes that determine the transport of contaminants from sources to receptors (USEPA, 2005a) and serves as the basis for understanding processes and pathways that may pose risk. The CSM can be used to help identify critical data gaps and areas of uncertainty for further investigation, and to identify natural processes that contribute to MNR.

The development of a remedy-specific CSM is important for the sediment remedy selection process in general, but it is particularly critical for MNR remedies, as it comprises a framework that synthesizes all the available data to convey a thorough understanding of the site-specific natural processes and considerations that contribute to natural recovery. The CSM provides a basis for developing risk reduction strategies by differentiating between important and inconsequential routes of exposure. By summarizing key relevant fate and transport information, the CSM traces critical exposure pathways and the means by which various remedies, including MNR, interrupt or diminish those pathways (Chadwick et al., 2006). The CSM is also useful for identifying the site-specific natural recovery processes with the highest risk-reduction potential, enabling managers to prioritize the collection of data and organization of future investigations.

The CSM can support remedy characterization and evaluation through:

- Identification of key site characteristics or contaminant fate and transport mechanisms affecting receptors, exposure routes, risks, and potential remedy performance.
- Representation of how site characteristics and transport mechanisms will change with time, affecting future remedy performance.
- Explanation and improved understanding of how risk reduction strategies would work and their feasibility.

KEY RISK-FOCUSED CSM ELEMENTS	
☆	Primary contaminant sources
☆	Primary release mechanisms
☆	Secondary sources
☆	Secondary release mechanisms
☆	Contaminated media
☆	Exposure routes
☆	Receptors

KEY FATE-AND-TRANSPORT-FOCUSED CSM ELEMENTS	
☆	Sources
☆	Fate and transport mechanisms and pathways
☆	Environmental compartments
☆	Physicochemical conditions and influences
☆	Exposure routes
☆	Receptors

- Identification of critical data gaps and areas of critical uncertainty for additional investigation.
- Development of a basis for quantitative evaluation of remedy performance, effectiveness, and permanence (e.g., through mathematical modeling).
- Illustration of the interaction of natural recovery processes with site-specific physicochemical conditions associated with exposure pathways.

### 3.2 The Risk-Focused CSM

A risk-focused CSM is often represented as a process diagram describing exposure of receptors to contaminants and, by extension, risk. The risk-focused CSM identifies sources, exposure pathways, and receptors, and the links between them, tracing the routes by which contaminants released to the environment travel and ultimately result in an ecological or human exposure (Figure 3-1). This approach generally stops short of describing the dynamic processes that may influence recovery, but instead treats contaminant release, transport, and exposure pathways as static conditions at a relatively simplistic level. While a risk-focused CSM is required for risk assessments, its use as a management tool entails clarifying and expanding the process descriptions to include those associated with remedy alternatives; in the case of MNR this would include natural recovery processes.

### 3.3 The Fate-and-Transport-Focused CSM

When MNR is under consideration, the CSM typically undergoes further refinement to illustrate site-relevant natural recovery processes and identify possible site-specific physical, chemical, and biological processes that influence natural recovery over time. The fate/transport-focused CSM incorporates key elements of natural recovery that may not have been explicitly detailed in a preliminary, risk-based CSM and places the four natural recovery processes (i.e., transformation, reduced bioavailability, burial, and dispersion) in the context of site physicochemical conditions. An MNR evaluation focuses on the connection between sources of contaminants and site-specific contaminant fate and transport processes, and the resulting influence on human and ecological exposures.

The goal of the fate/transport-focused CSM is to describe the key processes affecting long-term recovery. Figure 3-2 graphically represents

3 : INTEGRATING MNR IN CONCEPTUAL SITE MODELS

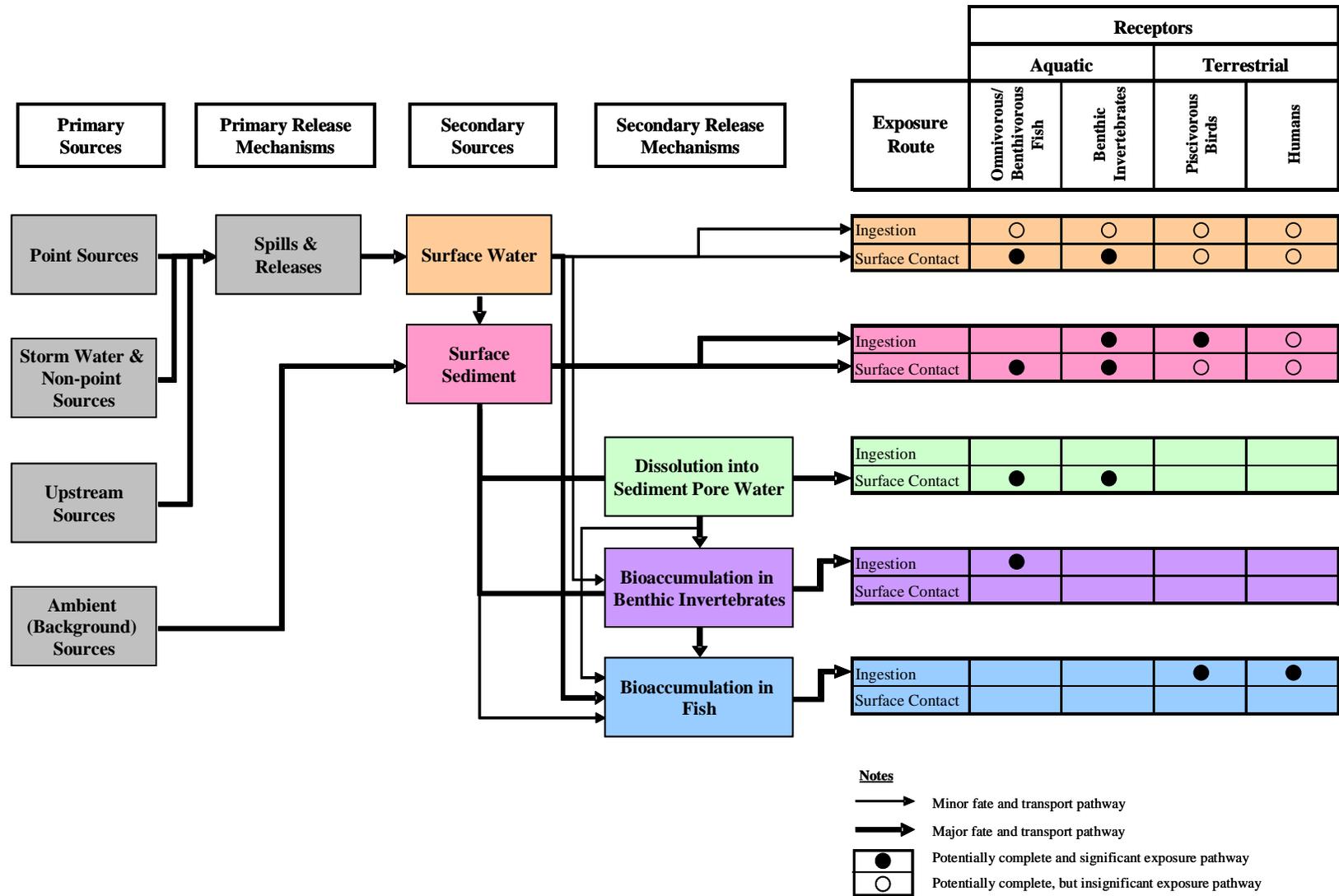


FIGURE 3-1. Example risk-focused CSM.

⇒ Refer to Chapters 1 and 4 for more information about natural recovery processes.

a generic fate/transport-focused CSM describing the broad range of physical, chemical, and biological mechanisms that contribute to the four potentially relevant natural recovery processes. This example CSM illustrates the interrelationships between the four natural recovery processes, and the effects of physicochemical conditions on the risk reduction potential offered by those processes. Figure 3-2 uses the following techniques to describe various rate-limiting processes:

GEOCHEMICAL CONSIDERATIONS	
☆	Dissolved oxygen levels and redox potential
☆	Salinity/ionic strength/pH
☆	Sulfides (often measured as acid-volatile sulfide)
☆	Total organic carbon
☆	Black carbon
☆	Contaminant biodegradation behavior
☆	Contaminant transformation kinetics
☆	Contaminant geochemical behavior
☆	Contaminant hydrophobicity

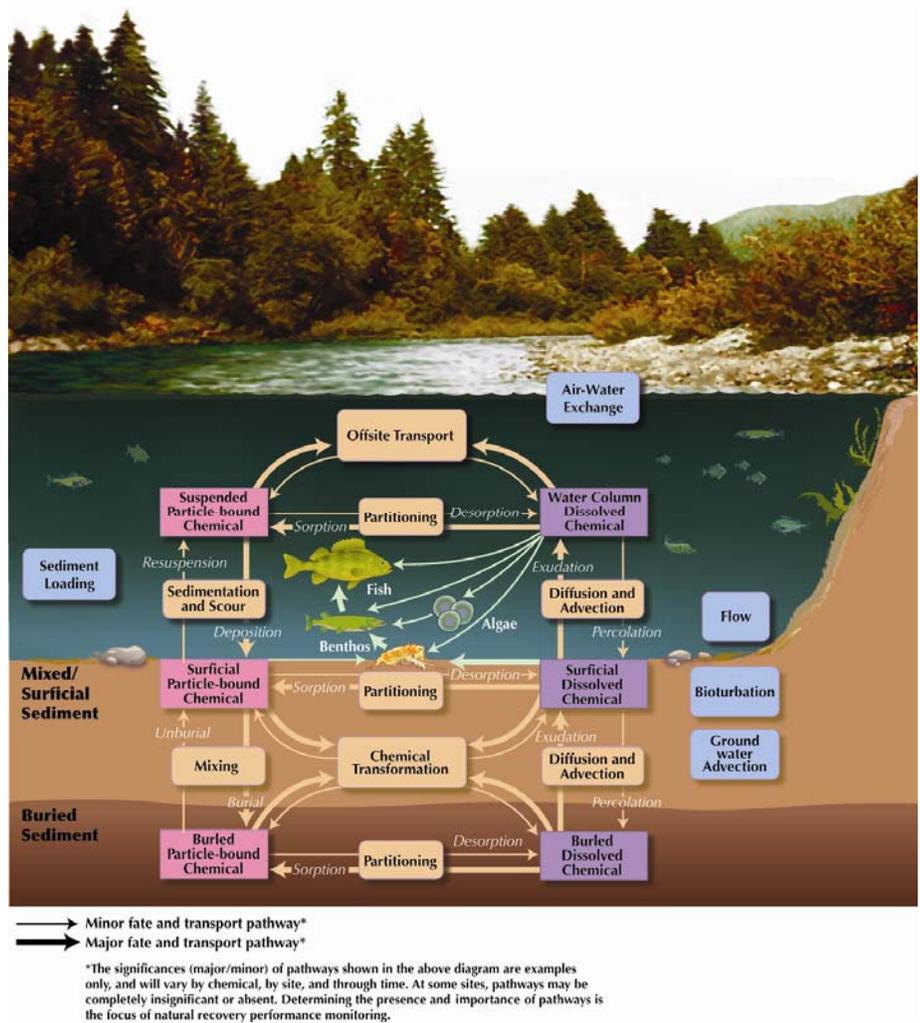


FIGURE 3-2. Fate/transport-focused CSM incorporating all four natural recovery processes.

- Major fate and transport mechanisms and key environmental compartments are represented as boxes connected by arrows. Larger arrows represent dominant chemical fate and transport mechanisms. For example, of the arrows connecting “Surficial Particle-bound Chemical” and “Chemical Transformation,” the

larger arrow indicates the dominant pathway of a potentially reversible transformation process. For irreversible processes, only one arrow would be shown.

- Boxes representing site-specific physicochemical influences to natural recovery processes are placed on the margin of the water and sediment environmental compartments. In addition to current physical site conditions, the CSM should consider whether future changes in the water body are planned that could affect fate and transport process, such as navigational dredging, dam removal, or removal of other physical structures.

PHYSICAL CONSIDERATIONS	
☆	Hydrodynamic conditions
☆	Current velocity
☆	Watershed sediment loading
☆	Groundwater advection
☆	Sediment scour
☆	Sediment deposition
☆	Sediment cohesiveness and sediment shear strength
☆	Bioturbation

Understanding contaminant sources is also critical to the CSM, as ongoing sources can contribute chemical mass to any of the environmental compartments and can potentially exceed the rate of risk-reduction afforded by natural recovery. Primary sources (e.g., industrial releases, run-off, outfalls, spills, or groundwater infiltration) and secondary sources (e.g., re-release and transport of upstream contaminated-sediment deposits) can act as ongoing sources to downstream locations via subsurface groundwater transport or contaminant deposition via chemical precipitation and settling or sorption.

Exposure pathways for receptors can be emphasized in a fate/transport-focused CSM and may serve as the basis for the risk-focused CSM. Determination of the most highly exposed receptors will depend on whether COCs at the site are bioavailable and significantly bioaccumulative; if so, human or wildlife consumers of fish may be subject to the greatest risks. The significance of human health risks typically depends on the importance of the site for fishing by local populations. Non-bioaccumulative chemicals are expected to exert effects most strongly at the base of the food web. For a specific chemical, identification of receptors and the contaminants and processes driving risk helps ensure that the selected remedy appropriately addresses those risks.

⇒Refer to Appendix B for more information about chemical-specific factors influencing natural recovery.

The fate/transport-focused CSM diagram may be optimized to focus on and draw attention to the primary natural processes that influence recovery. The relative importance of various natural processes will depend on chemical-specific factors affecting chemical transformations and reductions in bioavailability and mobility, as well as site-specific factors affecting sediment deposition and physical stability of deposited sediment. For example, chemical transformation processes will contribute much more significantly to natural recovery at sites

contaminated with petroleum hydrocarbons or explosives compared to sites contaminated with PCBs or dioxins. Highlight 3-1 presents a fate/transport-focused CSM for a PCB-contaminated lake. While CSM diagrams are useful for communicating key information, it is important to understand that the CSM is more than a picture. The CSM figure illustrates concepts that must be explained and justified through a CSM narrative and through quantification of process kinetics.

Process-based CSMs comprise a framework in which the chemistry, biology, and physics of the system can be represented. Representation of these processes necessarily imposes certain constraints on the system: the mass entering the system must balance with the mass stored and the mass leaving; advection/diffusion/reaction processes are limited by known physical constraints; and exposure and contaminant bioaccumulation must follow known physical/chemical partitioning relationships and kinetics. By quantifying these relationships, the CSM can be formalized into a numerical modeling framework. A numerical model can test the cause-and-effect relationships hypothesized in the CSM, characterize and predict contaminant behavior and site activity, plan empirical monitoring efforts, or evaluate remedial alternatives.

⇒ Refer to Chapter 5 for information about numerical models.

For a robust evaluation of MNR remedy performance that informs remedy selection, the CSM should establish a basis for quantitative evaluation. This can be facilitated by modeling that accounts for temporal changes in kinetics of natural recovery processes, such as changes in the rates of sedimentation, chemical transformation, sorption/desorption, changes in the flux of groundwater, or other physical dispersion mechanisms. To the extent possible, other time-dependent mechanisms, such as historical or anticipated changes in site hydrology or physicochemical conditions, also should be identified in the CSM and translated to predictive models that incorporate time as a variable.

### 3.4 Spatially Explicit CSMs

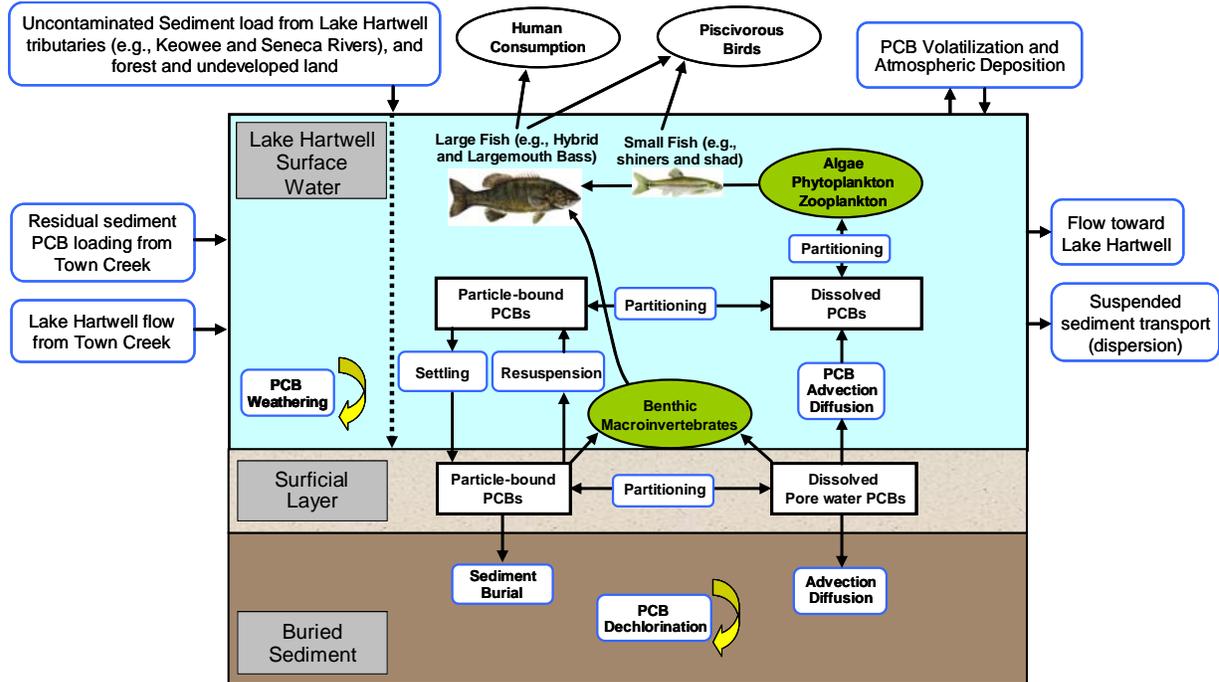
Conditions sometimes call for multiple CSMs with narratives that describe ongoing fate and transport processes and exposure pathways at different areas of the site. Where appropriate, spatially explicit CSMs may support different remedial approaches in different areas. Figure 3-3 represents a site at which all four natural recovery processes are operating; the dominant natural recovery mechanism differs from location to location within the site.

### LAKE HARTWELL CSM IDENTIFIES THE PCB SOURCE AND PROCESSES THAT CONTRIBUTE TO RECOVERY

The 1994 Record of Decision (ROD) selected an MNR remedy for PCB-contaminated surface sediments in approximately 730 acres of the Twelve-Mile Creek arm of Lake Hartwell. The Sangamo-Weston Plant, situated on Town Creek, was responsible for PCB discharges from plant effluent and improper waste disposal practices. Particulate-sorbed PCBs transported through Town Creek to Twelve-Mile Creek and were deposited into the Lake Hartwell sediment bed.

Monitoring studies demonstrate steadily decreasing surficial sediment PCB concentrations due to burial, mixing, dispersion (Brenner et al., 2004), and dechlorination (Magar, 2005a; b). The dominant recovery process is burial with cleaner sediment. Sediment age dating indicated that the majority of surficial sediments in the Twelve-Mile Creek arm of Lake Hartwell would reach the 1 mg/kg cleanup goal between 2007 and 2011 (USEPA, 2004a).

CSMs aid in identifying the most important components of an MNR remedy.



The CSM highlights the pathway PCB contamination follows from sediment to humans. The site remedy mitigated risk by enacting fish consumption advisories for Lake Hartwell and implementing a public education program to increase awareness of the advisory and teach fish preparation methods that reduce the quantity of contaminants consumed. Long-term monitoring of fish tissue determines continuation or modification of the consumption advisory.

Identification of sediment deposition as the primary natural recovery mechanism focused attention on the effects of three upstream dams on sediment loading. Removal of two of these dams is specified in the natural resource damage settlement for the site and is intended in part to increase natural sedimentation in Lake Hartwell.

HIGHLIGHT 3-1. CSM based on conditions in Lake Hartwell, SC.

Figure 3-3 serves well as the graphical piece of a “site-wide” CSM, while more detailed, process-based CSMs (as in Figure 3-2) could be developed for specific areas of the site.

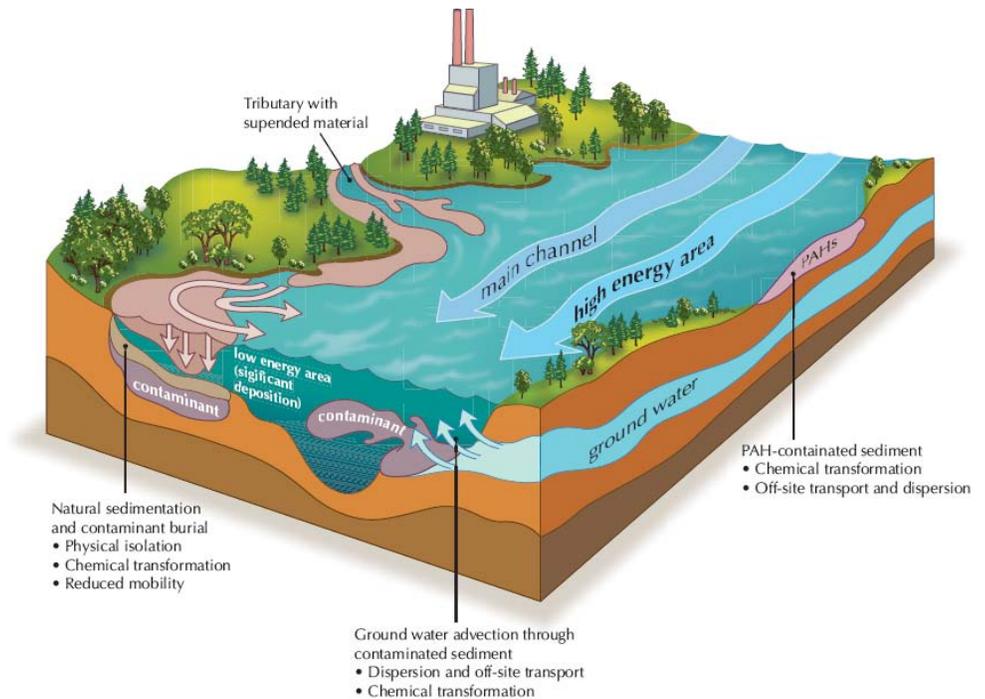


FIGURE 3-3. Site-wide CSM depicting all four natural recovery processes.

In Figure 3-3, the portion of the site downstream of the tributary (lower left) represents a low-energy environment characterized by low current velocities. These conditions encourage deposition of materials entrained by tributary waters, resulting in a high rate of sedimentation that could facilitate burial of contaminated sediment. Chemical transformation also may be an important MNR process for surficial or buried contaminants, in which case the CSM would include transformation processes.

The lower right of Figure 3-3 represents an area at which groundwater emerges. If the flow is sufficient and/or the chemicals are sufficiently water soluble, this site feature could disperse chemicals from contaminated sediments into the overlying water column. Assuming sufficient current in the area, dispersed chemicals could be transported off site. Emerging groundwater also could contribute to biological transformation processes by adding nutrients or oxygen to the sediment matrix, in which case the CSM would include transformation processes.

The area upstream of the groundwater emergence (upper right, Figure 3-3) represents a high-energy environment characterized by strong currents. These conditions may not encourage significant deposition; thus, dispersion would be the most dominant natural recovery process at this location. However, the extent to which sediment transport from this area contributes to the accumulation of contaminated sediments in low-energy, depositional areas elsewhere in the water body would need to be evaluated as part of the FS (bottom left, Figure 3-3).

The sediment transport analysis developed for the Lower Duwamish Waterway Superfund site in Seattle, WA (Windward and QEA, 2008), is an example of a spatially explicit CSM focusing on net deposition rates (Figure 3-4).

### 3.5 Temporally Explicit CSMs

Natural recovery processes may vary or change over time. This fact highlights the value of temporally explicit CSMs when evaluating MNR (as well as engineered remedies). MNR remedy success commonly involves multiple—perhaps all four—major natural recovery processes. Natural recovery is usually a dynamic process, dependent on the changing nature of contaminant sources and site conditions. Consequently, different processes will tend to dominate recovery at different times.

For example, chemical kinetics of reductions in mobility and bioavailability and chemical transformation are much faster for metals than persistent organic pollutants (POP). Thus, most risk reduction potential following metal releases is achieved by chemical transformation processes that precipitate metal species as metal hydroxides or sulfides, or bind them to clay or organic carbon. Additional risk reduction following these initial reactions is increasingly achieved by sediment burial, which physically isolates the metal, further reducing exposure and bioavailability.

Conversely, sites with POPs that exhibit slow environmental transformation rates often rely on burial for immediate risk reduction, though transformation can contribute to long-term detoxification over years or decades. For example, at PCB-contaminated sites such as Bremerton Naval Complex, WA, and Lake Hartwell, SC, the MNR remedy component relies primarily on fish consumption advisories and physical isolation for more immediate risk reduction. At Lake Hartwell, substantial physical isolation already has

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*Changing site conditions and chemical-specific changes may result in changes in the dominant natural recovery mechanism over time.*

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3: INTEGRATING MNR IN CONCEPTUAL SITE MODELS

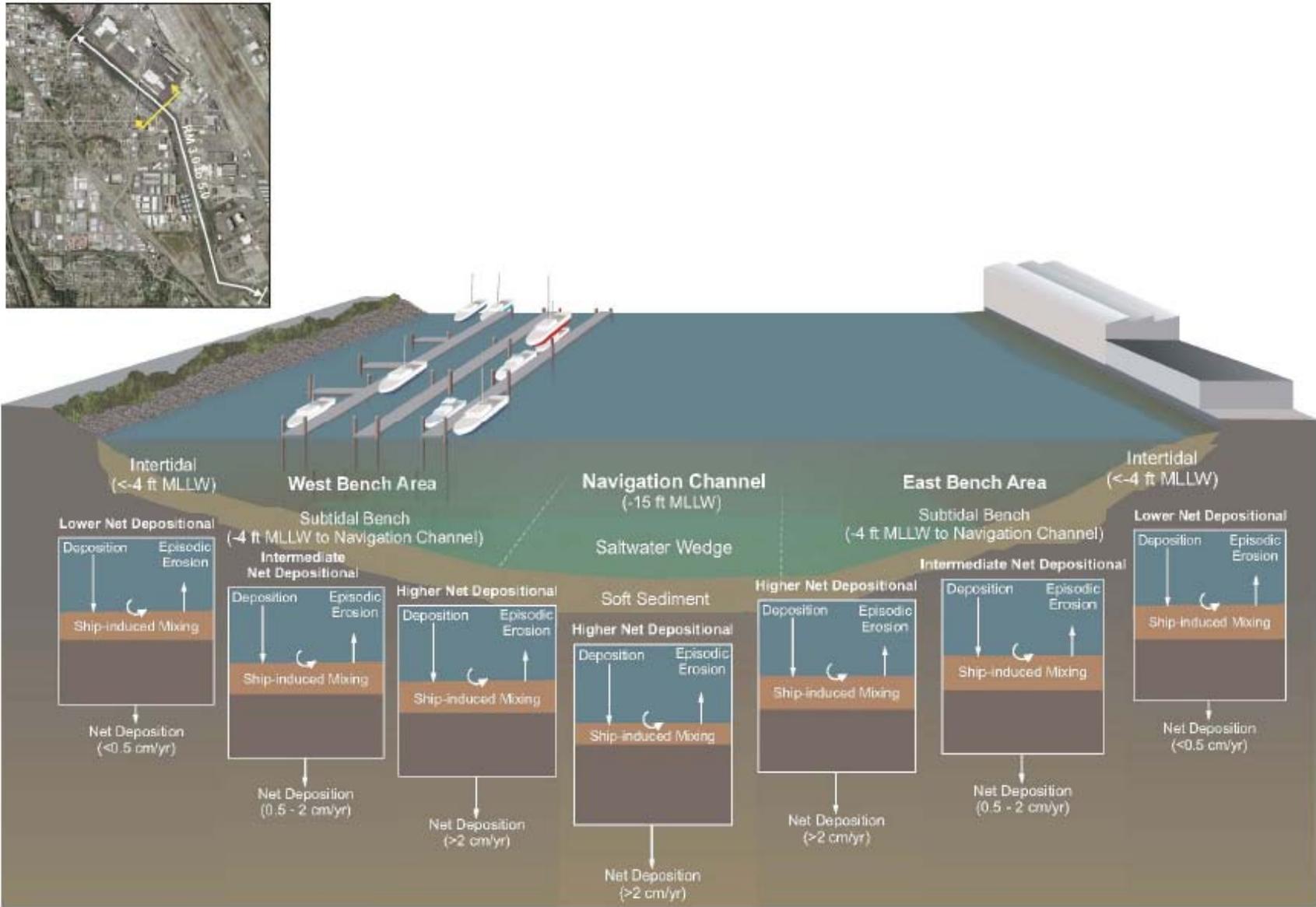


FIGURE 3-4. Lower Duwamish Waterway CSM.

occurred over the 30-year period since PCBs were regulated in the late 1970s (Brenner et al., 2004). Over time, burial through deposition of clean sediment reduces exposures and risk (i.e., by creating a sufficiently clean surface-sediment layer to reduce PCB concentrations in fish), and the relative importance of PCB dechlorination increases as PCBs in anaerobic subsurface sediment are transformed (dechlorinated) to less toxic congeners (Magar et al., 2005a,b).

Changing site conditions and chemical-specific changes also may result in changes in the dominant natural recovery mechanism over time. Changes in watershed runoff characteristics, improved river bank management practices, or changing water levels can alter sedimentation rates and corresponding rates of risk reduction brought about by physical isolation. Chemical transformation rates that depend on specific sediment geochemical properties (e.g., redox levels), chemical structure (e.g., low-versus high-molecular-weight PAHs or PCBs), or chemical concentration also can change with time.

Short-term physical disturbances are the most difficult temporal influences to predict and account for in CSMs. Short-term, event-driven processes such as 100-year storms can alter the performance of natural recovery and can result in either an increase in risk (if buried contaminants become exposed) or a decrease in risk (if the event is net depositional). For example, exposure at a site contaminated by POPs could increase following a physical disturbance that erodes recently deposited surface sediments, revealing higher contaminant concentrations in underlying contaminated sediments. Risk would continue to decrease following the event, assuming continued sediment deposition is occurring at the site. At many sites, risk of resuspension can be evaluated by reviewing chemical and radionuclide (i.e.,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ ) core profiles against the historical record of natural or anthropogenic high-energy hydrologic events (e.g., major storms, flood events, vessel traffic). Historical sediment bed stability through a major hydrological event can provide compelling evidence for long-term stability under comparable future events.

⇒Refer to Appendix B for more information about effects of redox changes on various metals.

In contrast, the 100-year flood event would have relatively little impact on a site contaminated by geochemically stable divalent metals or chromium because most of the metal mass in the freshly exposed sediments would have been transformed to insoluble mineral complexes that are unavailable for uptake. An exception to this rule would be metals that are susceptible to changes in geochemical conditions (i.e., changes in redox conditions) that cause a reversal of chemical transformation and sorption mechanisms during the period of exposure. For example,

relatively insoluble Cr(III) would not be expected to oxidize to Cr(VI) following exposure of anoxic sediments to oxygenated surface waters due to kinetic constraints (Magar et al., 2008a; Martello et al., 2007). Hence, a physical disturbance would have a negligible impact on risks associated with Cr in sediment because of the geochemical stability of Cr(III) under anaerobic and aerobic conditions. However, greater impacts could occur with a metal such as zinc, which is somewhat more susceptible to remobilization following oxidation (Cantwell et al., 2008).

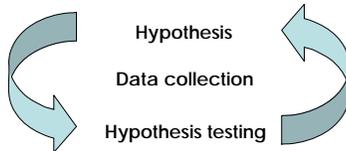
### 3.6 CSM Refinement

Once the initial CSM is drafted, uncertainties regarding the relative importance of environmental compartments, rates of fate and transport mechanisms, ongoing sources, and effects of site-specific physicochemical conditions or events on natural recovery rates can be more easily organized, prioritized, and communicated. Uncertainties are addressed via empirical investigations, modeling, and literature review, efforts that contribute to developing lines of evidence in support of study conclusions. Reliance on multiple lines of evidence, in contrast to a single line of evidence, helps reduce uncertainty and increase confidence in the conclusions reached during the FS process and the application of MNR (or other remedies). As part of an adaptive management approach to project execution, monitoring and iterative updating of the CSM during MNR implementation will provide a mechanism for reducing uncertainties and taking the actions necessary to achieve remedial objectives.

⇒ Refer to Chapter 7 for more information about adaptive management.

Development of the CSM should be the first step in the remedial investigation process and toward understanding MNR processes. The process of iteratively updating the CSM will serve as a guide for reducing uncertainties relevant to decision making, communicating current knowledge about the site, and documenting the role of MNR at the site. As data and model predictions build a coherent picture of the site, project managers, engineers, scientists, and stakeholders construct hypotheses which inform further data collection and CSM refinement. For remedies involving MNR, the CSM is refined to better characterize primary and secondary release mechanisms and physical, chemical, and biological processes that affect natural recovery processes and, ultimately, the ability of natural recovery to reduce risk.

The United Heckathorn Superfund site serves as an example of the importance of updating a CSM and investing in the development of an accurate fate/transport-focused CSM. It also serves as an example of the importance of thoroughly investigating potential sources and



implementing source control prior to remedy implementation. Following large-scale dredging of the Lauritzen Canal, previously unidentified contaminant sources led to recontamination of sediments and resident biota (Weston et al., 2002). Additional investigation was required to characterize these sources, which included a buried outfall and contaminated sediments beneath docks and pilings or on steep side slopes (NRC, 2007a). Similarly, in Lake Hartwell, SC, surface sediment PCB concentrations have declined as predicted by the MNR remedy, but fish tissue PCB concentrations for some species have not (USEPA, 2004a). Additional investigation of exposure pathways will be needed to update the CSM.

One tool that is applicable to updating CSM in regard to source delineation or other activities is the USEPA's (2007b) Triad approach to project management and data collection (not to be confused with the "sediment triad" method of assessing sediment toxicity). Under the Triad approach, systematic up-front planning and real-time measurement technologies, such as rapid sediment characterization tools (USEPA, 2006), allow decision making in the field to determine how, when, where, and why to conduct sampling and analysis. This approach supports spatially intensive site characterization while reducing the number of field mobilizations required, thus providing increased accuracy and cost control.

### 3.7 CSM Checklist

The following checklist identifies considerations for creating, modifying, and refining CSMs. While the first two questions and associated considerations should be applicable to any remedy, they are included in this checklist to highlight the focus on fate and transport processes necessary to effectively evaluate and implement MNR.

CHECKLIST 3-1. CSM considerations.

*In view of the decisions currently under consideration within the project:*

**1. Does the CSM adequately describe the physical, chemical, and biological processes that determine the transport of contaminants from sources to receptors? Consider the following components:**

- Chemical sources and release processes.
- Chemical nature and extent.
- Hydrologic conditions.
- Sediment transport conditions.
- Potential chemical exposure pathways to humans.
- Potential chemical exposure pathways to ecological receptors.

**2. Does the CSM provide sufficient understanding of the relationships among chemical fate, transport, exposure and risk at the site? Consider the following components:**

- Receptors and chemicals that may drive risk.
- Processes and pathways that may contribute to exposure and risk.
- The spatial distribution of chemicals in sediment areas of the site and water body that contribute to exposure and risk.
- Non-steady state processes (such as variation in flow velocity, if appropriate, or severe storm events) that may change exposure scenarios and increase either the number of receptors or routes of exposure.
- The need for adding more resolution in the risk assessment to include non-steady state relationships that affect the site. (An example might include confirming the nature of the site-specific relationship between flow velocity and sediment resuspension potential.)

**3. Does the CSM adequately describe the physical, chemical, and biological processes that contribute to natural recovery? Consider the following components:**

- Site-specific factors or processes that influence chemical transformation, bioavailability and mobility, physical isolation, or dispersion.
- Links between natural recovery processes predicted at the site and reduced exposure rates.
- Numerical variables (e.g., depositional rates, transformation or degradation rates, chemical partition coefficients) that help quantify MNR processes.
- Interrelationships among natural recovery processes and their effects on risk reduction.

**4. What temporal or spatial considerations may be included in the CSM to account for processes that influence natural recovery? Consider the following components:**

- Physical transport processes that contribute to vertical and lateral variability of chemical concentrations in site media, including sediment, soil, surface water and/or groundwater, and air as appropriate.
- Hydrodynamic variability, such as seasonal differences in river flow or diurnal differences in tidal range, and the extent to which variability influences contaminant transport and exposure.
- Sediment transport and variability in sediment loading, such as from changes to land use in the watershed or from the creation or removal of water control structures such as dams.
- Watershed changes such as runoff characteristics, river bank management practices, or changing water levels that can alter sedimentation rates and corresponding rates of risk reduction brought about by physical isolation (burial).

**5. Does the CSM adequately address uncertainties in processes, scales, and rates and consider future site conditions? Consider the following components:**

- Future hydrodynamic and sediment transport events (e.g., 10-year, 50-year, or 100-year weather events).
- Opportunities to enhance MNR effectiveness, such as through increased clean sediment inputs or altering site oxidation/reduction status.

- Management of long-term source control.
- Uncertainties regarding the importance of environmental media, fate and transport mechanisms, ongoing chemical inputs, and effects of site-specific events or physicochemical conditions on natural recovery rates.
- Changes in site conditions that could influence natural recovery processes (including the relative importance of different processes) and natural recovery rates over time.

## 4 MNR Lines of Evidence

*Tools for developing lines of evidence for natural processes, contaminant-specific considerations*

In order to evaluate the suitability of MNR as a remedy and to confirm its performance, lines of evidence are developed to understand baseline risk conditions, identify and quantify trends toward reduced chemical exposures and risks, and characterize the long-term protectiveness of risk reductions. As for any remedy, verification of source control also is critical.

A wide variety of investigative tools are available to develop the necessary lines of evidence, ranging from literature review to specialized analyses such as radio-isotope dating and sediment profile imagery. While the selection of lines of evidence for investigation is site-specific, employing a tiered approach, following the data quality objectives process, and integrating modelers and risk assessors into project planning can contribute to an efficient investigation.

Where chemical transformation is potentially important to natural recovery, lines of evidence should establish whether site conditions are conducive to transformation; the relative toxicity, bioavailability, and mobility of transformation products; transformation rates; and (for metals) the reversibility of the transformation.

Where reduction of mobility and bioavailability is potentially important, lines of evidence should establish whether site conditions are conducive to chemical sorption or precipitation, the degree of bioavailability reduction, effects on dissolution and advection processes, rates of ongoing reductions in bioavailability and mobility (if any), and the reversibility of sorption and precipitation reactions.

Where physical isolation is potentially important, lines of evidence should establish the chemical quality of newly deposited sediment, deposition rates, depths of benthic mixing (biological and hydrodynamic), erosion potential, and effects of sediment burial on chemical transformation and bioavailability processes.

Dispersion, as a natural recovery process, is defined by many of the same lines of evidence as physical isolation. Where dispersion is potentially important, additional lines of evidence should address where chemicals are transported and at what concentrations.

CHAPTER CONTENTS	
☆	Defining Lines of Evidence for MNR
☆	Developing MNR Lines of Evidence
☆	Planning to Investigate MNR Feasibility
☆	Source Control
☆	Lines of Evidence for MNR
☆	Process Interdependencies and Modeling Considerations
☆	MNR Lines of Evidence Checklist

The effectiveness of MNR depends on contaminant transformation, immobilization, isolation, and removal processes that reduce site risks over time. Evaluating MNR as a remedial alternative requires developing and refining the CSM based on specific, detailed information, and corresponding conclusions about site processes that are supported by site-specific lines of evidence. In this chapter, we define and describe the development of lines of evidence associated with the key natural recovery processes that generally support MNR as a remedial option.

Lines of evidence should be developed to support the following overarching objectives:

- Understanding baseline risk conditions. An accurate understanding of baseline risks will establish the anchor point for predictions about risk reduction trajectories for MNR and other remedies under consideration.
- Identifying and quantifying trends toward reduced chemical exposures and reduced risk.
- Characterizing and confirming the long-term protectiveness of risk reductions, through rigorous modeling predictions and long-term monitoring.

## 4.1 Defining Lines of Evidence for MNR

For MNR, lines of evidence are critical to determine the effectiveness of natural processes identified in the CSM, to verify that those natural processes lead to acceptable levels of risk reduction, and to compare MNR effectiveness to other remedy alternatives. In this context, literature, field, laboratory, and modeling investigations are used to develop lines of evidence that support the development and refinement of the CSM, and generate specific, detailed conclusions about site behavior.

Initial lines of evidence generally include information from scientific literature reviews, comparable case studies, and historical data (if available), especially in the early stages of the remedial investigation. As the RI/FS proceeds, lines of evidence based on literature and historical data are augmented with site-specific, empirical information and modeling as needed. Preliminary lines of evidence inform site-specific studies, as hypotheses and uncertainties are identified in the CSM.

Well-established scientific findings—such as the reduction of hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) in reduced environments (Martello et al., 2007; Berry et al., 2004) or rapid chemical transformation of trinitrotoluene in sediment (Conder et al., 2004; Elovitz and Weber, 1999)—may require only a thorough literature review to demonstrate widespread acceptance of an effective natural recovery process. Depending on the level of uncertainty of such initial conclusions, however, site-specific empirical studies and laboratory work could be required to demonstrate that the general principle holds in the particular case.

Site-specific investigations that evaluate the suitability of MNR generally include, but are not limited to:

- Determination of the nature and extent of contaminant distributions at the site.
- Identification of contaminant sources and verification of source control.
- Characterization of sediment and contaminant fate and transport processes.
- Risk assessment.

Fate and transport studies generally encompass the evaluation of the four primary natural recovery mechanisms (chemical transformation, reduction in mobility and bioavailability, physical isolation, and dispersion) and may require evaluation of hydrodynamic behavior, sediment bed stability, geochemistry, chemical forensics, biological studies, and modeling. Generally, these studies are conducted under the RI, or in targeted remedy- or process-specific studies as part of FS development.

## 4.2 Developing MNR Lines of Evidence

**L**ines of evidence are generally developed throughout the remedial process (Figure 4-1) to facilitate site characterization, risk assessment, remedy selection, remedy implementation, and evaluation of remedy effectiveness. Although the impetus for developing lines of evidence originates from the overall goal to refine the CSM, each stage of the RI/FS and MNR implementation process uses lines of evidence differently.

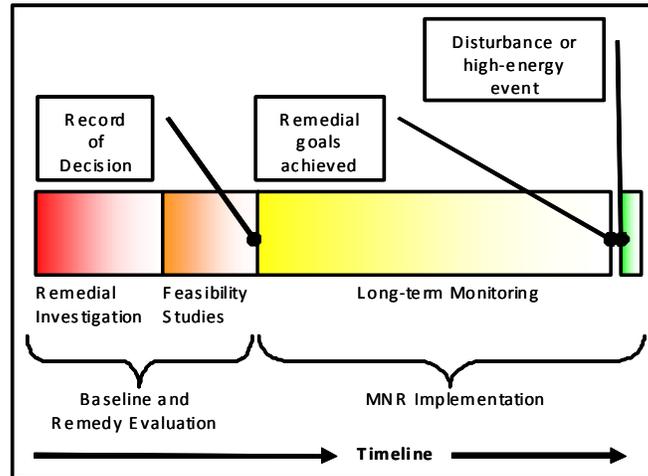


FIGURE 4-1. MNR timeline for a contaminated sediment site.

During the RI/FS. During the RI and FS stages, lines of evidence focus on site characterization, risk assessment, and remedy selection, including evaluating MNR as a candidate remedy. Conclusions drawn from multiple lines of evidence are typically captured in an FS and form the basis of the remedy design and implementation. The level of effort invested in developing lines of evidence is greatest during the baseline and remedy evaluation stage in the RI/FS (Figure 4-1). Key questions related to MNR include:

- Which natural recovery processes are occurring at the site?
- How are these processes affecting risk at the site?
- At what time scale are these processes expected to manage risk?
- How do the rate and magnitude of risk reduction compare to rates and magnitudes achieved by constructed remedies such as capping or dredging?
- How effectively can the risk be managed by natural recovery processes?
- What reasonably anticipated future events, such as navigational dredging, removal of dams or other structures, or major storms, have the potential to affect natural recovery processes?

- Is the risk reduction achieved via natural recovery processes expected to continue to be protective under anticipated future site conditions?
- Can the effects of high-energy events on natural recovery processes and risk be predicted at a desired level of certainty?

Lines of evidence developed during the RI/FS can serve as an organizing principle of site characterization activities: the goal is to collect sufficient site-specific evidence of natural processes to reduce uncertainty about the risk reduction potential of MNR. The amount of evidence required is driven by site-specific conditions as reflected by a CSM capable of supporting MNR. If MNR is selected as a remedy, lines of evidence collected during the RI/FS stages may comprise baseline data for long-term monitoring.

⇒Refer to Chapter 7 for more information about MNR implementation.

During MNR Implementation. Lines of evidence for monitoring remedy effectiveness address the following questions:

- Is natural recovery proceeding as expected?
- Does natural recovery meet risk-based goals over time and at rates predicted during the RI/FS?
- Are natural recovery performance data sufficiently robust to predict continued protectiveness at a desired level of certainty?

After achieving risk-based remedial goals, some additional monitoring may be required to confirm remedy stability and permanence during high-energy events. Monitoring should continue as needed to reduce uncertainties associated with high-energy events or to provide sufficient data for predictive modeling of such an event. Key questions include:

- Are high-energy events observed to retard or reverse natural recovery mechanisms?
- If yes, is the retardation or reversal of natural recovery mechanisms of sufficient magnitude and duration to pose unacceptable risk?
- Are natural recovery performance data sufficiently robust to predict continued protectiveness in the event of future high-energy events, with a desired level of certainty?

### 4.3 Planning to Investigate MNR Feasibility

The selection of specific lines of evidence to investigate MNR feasibility is determined by application of the scientific method to address the key site-specific questions arising from the CSM. Site conditions, characteristics of the chemicals of interest, and the type and complexity of the site being evaluated all enter into this decision process. Larger, more complex sites generally warrant the development of multiple lines of evidence to address each of several key questions associated with MNR processes, process kinetics, and risk. For smaller, less complex sites, a reasonably conservative interpretation using more limited data may be sufficient to select a protective and cost-effective remedy.

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*Selecting which lines of evidence to investigate requires application of the scientific method to address key site-specific questions arising from the CSM.*

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Tiered Approach. On the whole, it makes sense to approach the development of lines of evidence using a tiered or step-wise approach, beginning with the least resource-intensive tools (such as literature review, aerial photographs, and historical data collection) to identify general concepts that apply to site-specific conditions, and then proceeding to more resource-intensive tools such as field and laboratory investigations and modeling. Typically, more resource-intensive tools reduce uncertainty; however, in a world of limited resources it is necessary to negotiate a balance between effort, cost, and uncertainty.

Site managers should keep in mind that the same investigative tools may yield multiple lines of evidence in support of investigating the feasibility of MNR, other remedies, and RI/FS objectives (Table 4-1). Lines of evidence with broad utility can be collected early in the RI/FS process to inform subsequent, more specialized sampling.

TABLE 4-1. Examples of investigative tools that support multiple applications.

Tool	Applications
Analysis of organic carbon, acid volatile sulfide (AVS), and simultaneously extracted metals (SEM)	<ul style="list-style-type: none"> <li>▪ Improve accuracy of risk estimates for organic compounds and selected metals by supporting a basic assessment of bioavailability.</li> <li>▪ Investigate bioavailability reduction as a natural recovery mechanism for selected metals.</li> </ul>
Sediment coring and vertical profiling	<ul style="list-style-type: none"> <li>▪ Determine whether risk estimates based on surface sediments would apply if subsurface sediments became exposed. If not, sediment stability investigation is needed.</li> </ul>

TABLE 4-1. Examples of investigative tools that support multiple applications (continued).

Tool	Applications
Sediment coring and vertical profiling	<ul style="list-style-type: none"> <li>▪ Characterize depth of contamination to assess requirements for dredging alternatives.</li> <li>▪ Evaluate occurrence of physical isolation through burial, based on concentration profiles.</li> <li>▪ Visually identify bioturbation depths.</li> <li>▪ Estimate sediment deposition rates (particularly if geochronological parameters analyzed).</li> <li>▪ Characterize geochemical parameters influencing transformation processes or bioavailability/mobility.</li> </ul>
Model effects of statistically relevant storm events on sediment resuspension.	<ul style="list-style-type: none"> <li>▪ Identify engineering requirements for capping alternatives.</li> <li>▪ Evaluate high-energy conditions such as storms or waves and their influence on flood potential or sediment erosion.</li> <li>▪ Estimate whether naturally buried contaminants are likely to become exposed or, conversely, whether storm-related deposition is likely to augment contaminant isolation.</li> <li>▪ Estimate the likelihood and duration of geochemical changes that might release sequestered metals through oxidation.</li> <li>▪ Simulate where resuspended sediments would be deposited.</li> </ul>

⇒Refer to Chapter 7 for more information about data quality objectives.

Data quality objectives. To promote efficient and effective data collection, investigation planning should follow the data quality objectives (DQO) process (USEPA, 2000a). DQO criteria include when, where, and how to collect samples or measurements; determination of tolerable decision error rates; and the number of samples or measurements that should be collected. DQOs are qualitative and quantitative statements that define the purpose of the data collection effort, clarify what data are needed, and specify the quality of information to be obtained from the data. The DQO process clearly defines what data and information are needed to monitor remedy success in order to develop a data collection plan that will enable the field team to obtain the right type, quantity, and quality of data.

The investigation planning team should include modelers, risk assessors, and engineers to help define data use objectives and information needs. Too often, modeling and risk assessment are afterthoughts with respect to

data collection, creating inefficiency or limiting the data analyses that can be conducted.

## 4.4 Source Control

The success of any sediment remedy, including MNR, depends upon effective source control. Per USEPA’s *Principles for Managing Contaminated Sediments at Hazardous Waste Sites* (2002a), the first principle 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 sewage treatment plants, spills, precipitation runoff, erosion of contaminated soil from stream banks or adjacent land, contaminated groundwater and nonaqueous phase liquid contributions, discharges from storm water and combined sewer outfalls, upstream contributions, and air deposition.

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*The success of any sediment remedy depends upon effective source control.*

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This principle is further underscored in USEPA’s *Contaminated Sediment Guidance* (2005a). Source control should be implemented to prevent recontamination regardless of the selected remedial alternative (USEPA, 2005a). Thus, lines of evidence should be developed to identify and support the control of contaminant sources (Table 4-2).

TABLE 4-2. Lines of evidence to evaluate source control.

Evidence Type	Line of Evidence
Literature and historical data	<ul style="list-style-type: none"> <li>▪ Assemble information on historical contaminant releases, transport pathways, and source control measures, and confirm effectiveness of contaminant source control.</li> <li>▪ Review historical records, including historical aerial photographs, industry records, data on outfalls, and permitted or non-permitted releases.</li> <li>▪ Determine whether groundwater source control would address sediment and water column contaminants.</li> <li>▪ Identify background sources or sources from off-site contributors that may slow recovery.</li> </ul>

TABLE 4-2. Lines of evidence to evaluate source control (continued).

Evidence Type	Line of Evidence
Modeling	<ul style="list-style-type: none"> <li>▪ Develop a contaminant mass balance model, to determine whether known sources (e.g., storm water outfalls, groundwater, sediment contamination) account for observed concentrations in biota tissue.</li> <li>▪ Use modeling to understand historical chemical releases and chemical transport to sediments.</li> </ul>
Site-specific investigations	<ul style="list-style-type: none"> <li>▪ Conduct in-situ experiments to directly measure contaminants in entry points to sediment such as groundwater or surface water at upstream locations, outfalls, and other point or non-point sources.</li> <li>▪ Measure contaminant concentrations in upgradient sediment loads using water column, bedload, or sediment trap samples.</li> <li>▪ Use chemical forensics to associate the chemical fingerprint of sediment contaminants with that of suspected sources.</li> <li>▪ Conduct site-specific investigations as needed to verify onsite source control.</li> <li>▪ For chemicals associated with groundwater, measure on-site groundwater transport behavior and trace the source of contaminants. This also may involve measuring offshore groundwater beneath sediments in groundwater aquifers that extend offshore.</li> </ul>

Source control is not limited to primary sources but also should consider secondary sources (e.g., ongoing contaminant releases from soils or sediment in the watershed) that can persist for long periods and impact remediation rates. Further, background contamination by common urban contaminants, such as metals and PAHs (e.g., Stout et al., 2004), has the potential to limit recovery during MNR or recontaminate the sediment surface following capping or dredging remedies. While background contamination is beyond the control of site managers, it should be taken into account in projecting future risk reductions.

## 4.5 Lines of Evidence for MNR

A wide variety of tools are available to assess the occurrence, rate, and permanence of natural recovery processes and their relationship to reductions in exposure and risk. This section describes key considerations and potentially useful lines of evidence associated with each of the four natural recovery processes: chemical transformation, reduced bioavailability and mobility, physical isolation,

and dispersion. Additional information on many of the tools identified in this chapter may be found in USEPA's (2003d) compendium of sediment monitoring methods and U.S. Navy's guide for assessing sediment transport (Blake et al., 2007).

In addition to process-specific lines of evidence, it can be useful to establish the overall course of natural recovery by documenting temporal trends (e.g., Figure 4-2), such as:

- Measuring surface sediment concentrations or other relevant metrics (e.g., pore water or tissue concentrations) over time to establish time-dependent changes in chemistry, exposures, and risk.
- Surveying sediment toxicity and/or benthic community composition over time.
- Tracking recovery of fish and wildlife populations over time, where effects on these species are remedy drivers (e.g., Highlight 4-1).
- Measuring vertical contaminant concentration profiles in sediment cores to document historical changes in surface sediment chemical concentrations and to correlate those changes with temporal trends in biological receptors.

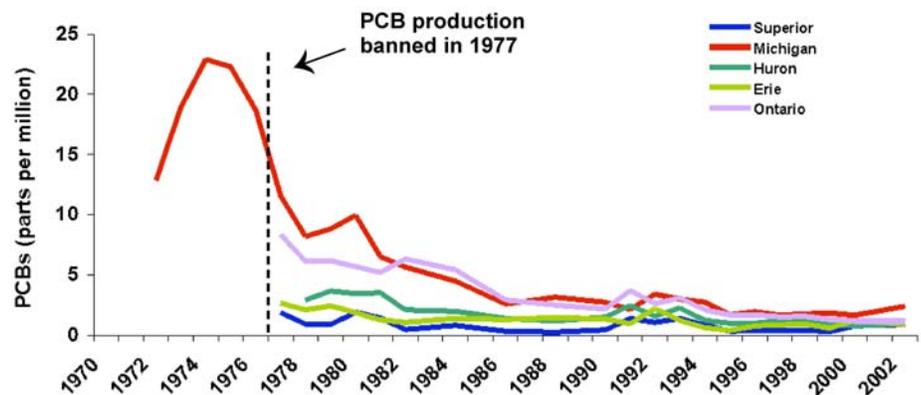


FIGURE 4-2. Temporal trends of PCB concentrations in Great Lakes open water predatory fish document historical natural recovery (Illinois-Indiana Sea Grant 2005). Concentrations declined dramatically during the decade following the PCB production ban but have tended to plateau more recently.

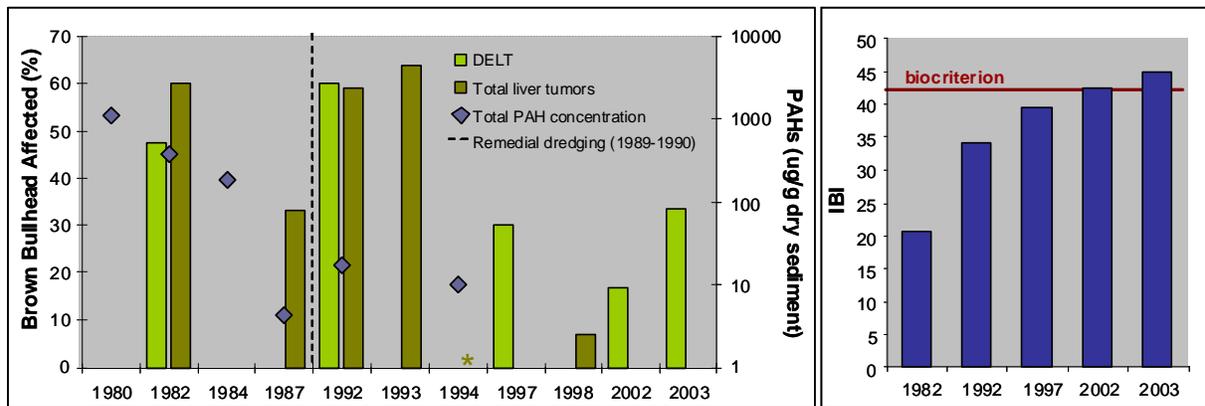
## BIOLOGICAL TRENDS OVER TIME PROVIDE LINES OF EVIDENCE FOR RECOVERY

Direct monitoring of biological receptors is a powerful tool for evaluating recovery in aquatic systems and demonstrating attainment of remedial goals. The Black River in Lorain, Ohio provides an example of natural recovery before and after dredging, using a biological endpoint monitored as evidence of risk reduction. In the early 1980s, high rates of external deformities, eroded fins, lesions, and tumors (DELT) and liver tumors in fish were associated with high levels of PAHs historically released from an upstream coke plant. The Black River was listed as impaired based on several beneficial use impairments (BUIs), including fish tumors and other deformities (Ohio EPA, 2005). The delisting criteria for this BUI include low tumor prevalence in adult brown bullhead (*Ameiurus nebulosus*) documented over a series of years. Current guidelines suggest that a 5% incidence of liver tumors is acceptable to consider the area to be in recovery (Ohio EPA, 2005). The Fish Tumors Related to Great Lakes Areas of Concern Conference Proceedings provide protocols for gross and histopathological examination of brown bullhead populations (PADEP et al., 2003).



Brown bullhead health and fish community status improved in the Black River after the coke plant closed in 1983. DELT (Ohio EPA, 2009), liver tumors (Baumann, 2000; Baumann and Harshbarger, 1998), and sediment PAH concentrations (Baumann and Harshbarger, 1998) declined until dredging of contaminated sediments near the coking plant outfall occurred in 1989 and 1990 (Black River RAP 2004). Following dredging, the prevalence of liver tumors in brown bullhead increased to levels similar to those of the early 1980s, likely as a result of PAH redistribution. By 1994, however, no instance of liver cancer was found in age 3 brown bullheads, and the percent of normal liver tissues increased from 34% to 85% between 1993 and 1994 (Baumann and Harshbarger, 1998).

The status of the overall fish community has been monitored by Ohio EPA, using the Index of Biological Integrity (IBI). The IBI evaluates the number, types, and trophic and environmental tolerance status of fish species present (Ohio EPA, 1988). The IBI index increased from 1982 to 2003, meeting the applicable state criterion by 2002 (Ohio EPA, 2009). Biological trends monitoring in the Black River provides evidence of risk reduction by natural recovery before and after dredging. In 2004, a review of the monitoring data demonstrating improvement of the IBI index and decreased prevalence of DELT and liver tumors in brown bullhead led the USEPA to approve a change in status from “impaired” to “recovery stage” for the fish tumors and deformities BUI in the Black River watershed (USEPA, 2004b).



HIGHLIGHT 4-1. Monitoring of biological endpoints as evidence of risk reduction in the Black River, Ohio.

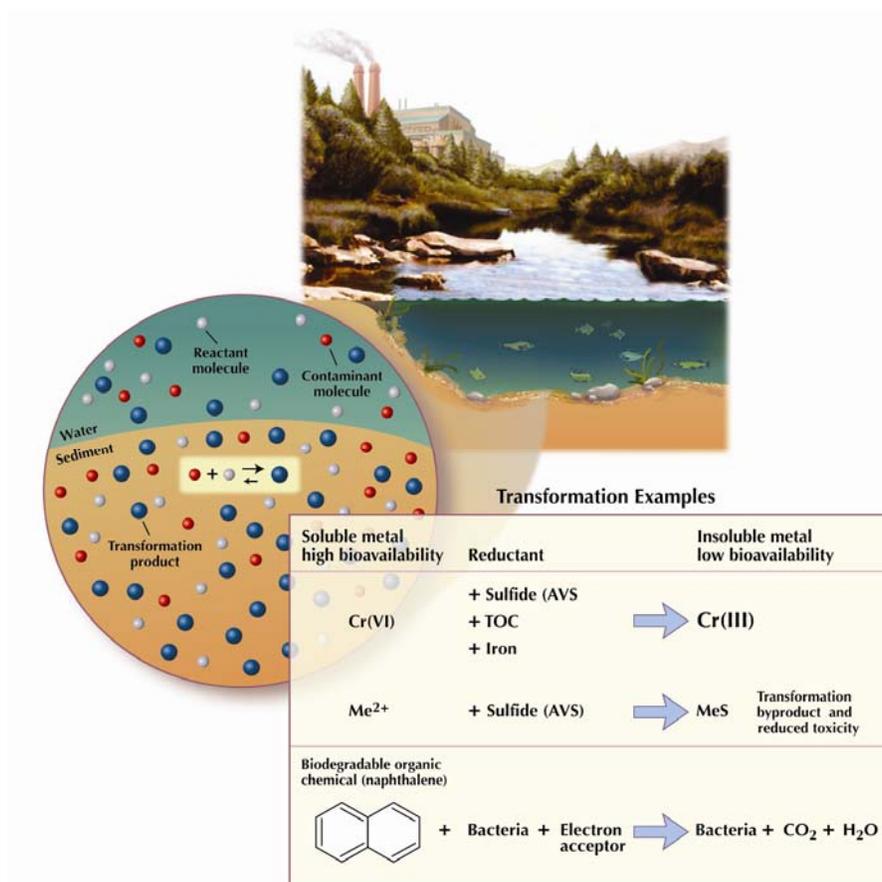


FIGURE 4-3. Chemical transformation. Note: Me<sup>2+</sup> represents a generic divalent metal.

#### 4.5.1 Chemical Transformation

⇒ Refer to Appendix B for information about particular transformation mechanisms and chemical-specific considerations.

**T**ransformation processes reduce risk when the transformation product is less toxic or less bioavailable than the parent compound. Transformation of organic compounds occurs when covalent bonds are cleaved or rearranged, resulting in the formation of a new chemical, or the complete mineralization of the chemical to its basic elements (e.g., CO<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>) (Figure 4-3). Such transformation occurs via biotic mechanisms, such as the microbial metabolism or co-metabolism of chemicals, and abiotic mechanisms, such as changes in physicochemical conditions like pH or redox potential (Magar et al., 2005a, b; Stout et al., 2001). Examples of organic contaminant transformation processes include the microbial-mediated partial dechlorination of PCBs, chlorinated solvents, and other chlorinated hydrocarbons; and the oxidative biodegradation of petroleum hydrocarbons, including some PAHs, and energetic compounds such as

G E O C H E M I C A L C O N S I D E R A T I O N S	
☆	Dissolved oxygen levels and redox potential
☆	Salinity/ionic strength/pH
☆	Sulfides (often measured as AVS)
☆	Total organic carbon
☆	Black carbon
☆	Contaminant biodegradation behavior
☆	Contaminant transformation kinetics
☆	Contaminant geochemical behavior
☆	Contaminant hydrophobicity

nitrotoluenes. Most transformations of organic compounds are not reversible.

Transformation of inorganic compounds occurs via changes in valence states and chemical bonding, which in turn affects their mobility, toxicity, and bioavailability. Chemical transformation of metals is governed by geochemical conditions. Environmental variables that govern the valence state, composition, and bioavailability of metals include pore water pH and alkalinity, sediment grain size, oxidation-reduction (redox) conditions, and the amount of sulfides and organic carbon in the sediments. Some chemical transformations of metals also may be biologically mediated. Whereas organic contaminant transformations typically demonstrate substantial permanence, inorganic metal transformations vary in their degree of reversibility. For example, chromium reduction is not significantly reversible under typical sediment conditions, whereas redox transformations of arsenic are readily reversible.

Organo metals, such as butyltins and methylmercury, form a unique group of compounds that include inorganic and organic properties. Under anaerobic, sulfate-reducing conditions, mercury methylation can occur, increasing the potential toxicity and bioavailability of mercury. In this case, transformation does not support natural recovery and in fact may increase exposure and risk. Conversely, debutylation of butyl tin compounds has been demonstrated in sediment environments, primarily under aerobic conditions, resulting in substantial risk reduction (Maguire, 2000) (Highlight 4-2).

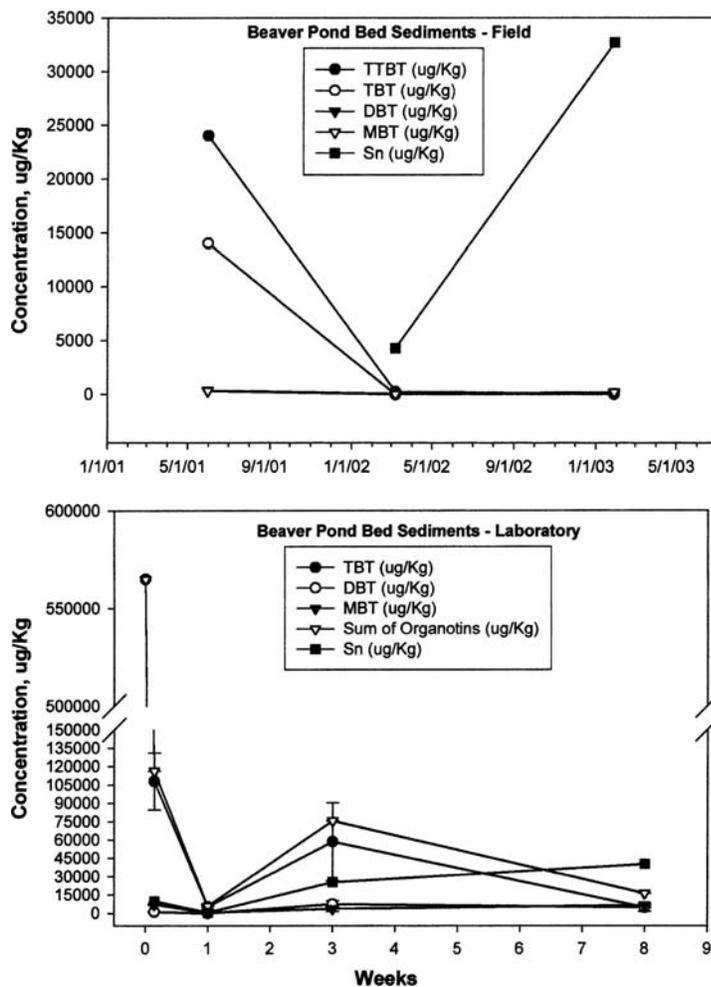
Key considerations for investigating transformation processes at any site include:

- Site conditions
- Transformation processes and toxicity
- Impact on mobility and bioavailability
- Transformation rates
- Reversibility

## BIOTRANSFORMATION OF ORGANOTIN COMPOUNDS IN A FRESHWATER SYSTEM

In 2000, an organotin manufacturer released a large quantity of organotin compounds into Red Bank Creek, a freshwater system in central South Carolina. This point-source discharge killed a large number of fish and invertebrates residing in the creek but also provided a unique opportunity to evaluate biotransformation of tributyltin (TBT) in both field and laboratory settings. Organotins are used as marine antifouling agents and in the manufacture of plastics and other products. Microbial processes successively biotransform tetrabutyltin (TTBT) via TBT, dibutyltin (DBT), and monobutyltin (MBT) to the much less toxic inorganic tin (Landmeyer, 2004).

More than 50 surface sediment samples were collected in 2000 during a remedial investigation of the creek led by the USEPA. The highest sediment concentrations of total organotin compounds, as well as TBT, in sediment were located in two depositional areas downgradient of the release—a beaver pond and Crystal Lake (farthest downgradient). Additional samples were collected from these two areas between 2001 and 2003. To evaluate organotin fate under static conditions, laboratory microcosm studies were initiated with sediment from both areas.



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Within two years after the release, concentrations of TTBT, TBT, DBT, and MBT in the beaver pond sediment had decreased by 99%, 99%, 83%, and 93%, respectively, and within three years, concentrations of TTBT, TBT, and DBT from the same locations were each less than 40 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ). In contrast, sediment concentrations of the biodegradation end products, MBT and inorganic tin, increased 89% and 87%, respectively, by the third year following the release. A similar trend was observed in Crystal Lake, although the initial concentrations were lower than in the beaver pond.

Similar to the field-based study, concentrations of TBT added to sediment (collected from the beaver pond and Crystal Lake) significantly decreased in laboratory microcosms, whereas MBT and inorganic tin significantly increased. The rate of biotransformation associated with the beaver pond was significantly higher than Crystal Lake, indicating that the organic-rich sediments of the beaver pond fostered a microbial community more acclimated to the degradation of complex organic molecules.

Highlight 4-2. Biotransformation of tributyltin to tin in a freshwater system.

Site conditions. Transformation processes may depend on the presence of specific types of microbes or physiochemical conditions such as pH, temperature, inorganic nutrients, labile or degradable carbon sources, redox, alkalinity, and organic carbon content. Lines of evidence should soundly establish that appropriate conditions for transformation exist. Some examples of contaminant-specific considerations include:

- Anoxic sediments favor the reduction of metals such as chromium and uranium, lowering their bioavailability and toxicity.
- The mobility (and thus toxicity) of divalent metals tends to decrease with increasing pH and concentrations of sulfide and organic carbon.
- Redox conditions conducive to sulfate reduction favor the formation of methylmercury, although high sulfide concentrations may in turn inhibit methylation. Aerobic conditions and strongly reducing (methanogenic) conditions also inhibit methylation. Methylmercury is more toxic and bioavailable than inorganic mercury.
- Transformation of organic compounds varies in response to redox potential. Chlorinated hydrocarbons dechlorinate under anaerobic conditions, whereas aerobic conditions favor the oxidative degradation of petroleum hydrocarbons and organotins. However, some hydrocarbons are degraded under anaerobic conditions, though typically more slowly than under aerobic conditions.
- Warm temperatures and high concentrations of degradable carbon sources encourage microbially facilitated transformation.

Transformation processes and toxicity. The relative toxicity of parent compounds and intermediate and transformation products should be established by lines of evidence, beginning with published literature and, where needed, including site-specific investigations of parent compounds and their transformation products. Some examples of contaminant-specific considerations include:

- Dechlorination of PCBs reduces chemical toxicity (lower chlorinated PCBs are generally less toxic than higher chlorinated PCBs), though environmental dechlorination is generally incomplete, resulting in the persistence of mono-, di-, and

trichlorobiphenyl congeners. Dechlorination also typically occurs progressively under anaerobic conditions, with sediment depth and age (Magar et al., 2005a, b). Hence, dechlorination may be absent or much less extensive in surface sediment.

- Lower-molecular-weight hydrocarbons (including PAHs), which tend to be more mobile, are more easily degraded than higher-molecular-weight PAHs. Thus degradation can substantially reduce the availability of low-molecular-weight hydrocarbons, though high-molecular-weight hydrocarbons tend to be much more persistent (due to their low bioavailability to biodegrading microbes).

For some compounds, like PAHs, measurement of transformation products and chemical forensics offer the most direct evidence of chemical transformation (e.g., Brenner et al., 2001; Stout et al., 2001). However, for other compounds, particularly those that are mineralized, transformation may not result in measurable byproducts. In such cases, evidence for transformation relies on inference by comparison of historical records to current contaminant concentrations, transformation processes established in the scientific literature, and chemical forensics (Murphy and Morrison, 2007; Stout et al., 2001, 2004).

Transformation products (and intermediate products) are not always less toxic or bioavailable than their parent compounds (Neff et al., 2005). The potential for mercury methylation is a common example. In such cases, transformation may hinder MNR.

Impact on mobility and bioavailability. Transformation may increase or decrease mobility and bioavailability, depending on the chemical. For example, redox transformation of most divalent metals, chromium, and certain radionuclides under anaerobic conditions reduces mobility/bioavailability. Formation of sulfide complexes is one transformation mechanism that reduces the bioavailability of divalent metals, whereas processes that cause oxidation of sulfide will tend to reverse this effect.

Transformation of organic compounds also can influence their mobility and bioavailability. Degradation of complex hydrocarbon mixtures, including PAHs, tends to reduce overall mobility because transformation results in the destruction of lower-molecular-weight relatively soluble compounds that may otherwise disperse, leaving behind less soluble and less mobile compounds. PCB dechlorination, on the other hand, increases mobility via reduced molecular weight and increased solubility.

Increased solubility and mobility do not necessarily imply increased exposure. According to USEPA (2005a), deeply buried contaminated sediment that is not within biologically active surface sediment does not necessarily contribute to site risks if they have been shown to be reasonably stable. Thus, contaminant burial should be factored into any assessment of mobility and bioavailability. For example, although PCB dechlorination to lower chlorinated congeners can increase mobility because transformation occurs in deeper sediments below the biologically active surface sediment, exposure will be retarded by overlying sediments (Magar et al., 2005a, b).

Transformation rates. Depending on the particular contaminants involved, as well as site-specific conditions, transformation processes can be very rapid (taking hours or days) or very slow (taking years or decades). Transformation rates vary according to contaminant and site-specific conditions. The rate of transformation can be determined by reviewing scientific reports and conducting site investigations (e.g., Highlight 4-2).

Reversibility. While transformations of organic compounds are typically irreversible, some metal transformation processes are reversible. For example, resuspension of anoxic sediments may result in the oxidation of the anaerobic sediments, which may cause labile minerals to dissociate to more bioavailable dissolved species. Lines of evidence (beginning with literature review) should establish the permanence of the remedy by determining the reversibility or irreversibility of transformation under site-specific conditions, including the likelihood that the site will be subject to substantially different geochemical conditions, and how the reversibility or irreversibility may affect risk reduction (e.g., Highlight 4-3). For reversible processes, lines of evidence should consider transformation kinetics, the rate of chemical release and exposure, and whether the transformation adversely affects risk.

⇒Refer to Section 4.3 for more information about selecting lines of evidence.

Table 4-3 lists lines of evidence that address the various considerations pertinent to transformation processes. Tables 4-3 through 4-6 comprise a menu of various lines of evidence that may be relevant, depending on the key questions identified in the CSM. Only a subset of these lines of evidence are likely to be needed at any given site.

TABLE 4-3. Lines of evidence to establish chemical transformation processes.

Consideration	Lines of evidence
<b>Likelihood of transformation</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>Identify established contaminant transformation pathways and biological or geochemical conditions under which they occur.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>Characterize sediment physiochemical conditions to confirm appropriate site conditions for transformation (e.g., pH, redox, presence of sulfides, acid volatile sulfide, simultaneously extracted metals, labile carbon).</li> <li>Measure the presence or absence of parent compounds and/or transformation byproducts in situ.</li> <li>Conduct laboratory studies to demonstrate the presence or absence of transformation processes, intermediate byproducts, and end products.</li> </ul>
<b>Potential of transformation to reduce risks</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>Assemble findings on toxicity, bioavailability, and mobility of transformation products.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>For poorly studied chemicals, conduct controlled experiments to directly measure toxicity of parent compounds and/or transformation products.</li> <li>Model impact of transformation on bioavailability using relevant partitioning models.</li> <li>Measure impact of transformation on bioavailability via direct in-situ or laboratory pore water or biota tissue measurements.</li> <li>Refer to Table 4-4 for additional lines of evidence related to bioavailability and mobility.</li> <li>Measure the status of biota potentially affected by COCs and their transformation products and compare to relevant background conditions (e.g., toxicity testing, benthic macroinvertebrate surveys).</li> </ul>
<b>Transformation rate</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>Assemble findings of contaminant transformation kinetics under relevant physiochemical conditions.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>Identify and measure sediment physiochemical characteristics that impact transformation kinetics.</li> </ul>

TABLE 4-3. Lines of evidence to establish chemical transformation processes (continued).

Consideration	Lines of evidence
<b>Transformation rate</b>	<ul style="list-style-type: none"> <li>▪ Conduct laboratory and/or field experiments to directly measure transformation kinetics.</li> <li>▪ Measure transformation products or metabolites to compare to original contaminant mixture.</li> <li>▪ Identify vertical or lateral profiles of parent compounds and transformation products; integrate this information with knowledge of sedimentation rates and source loading to determine transformation progress in sediments of different ages.</li> </ul>
<b>Reversibility of metal transformations</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>▪ Assemble findings on contaminant transformation pathways with respect to permanence.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>▪ Model likelihood and duration of geochemical changes that could cause transformation reversals (such as sediment erosion).</li> <li>▪ Model relative kinetics of transformations and transformation reversals.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>▪ Identify and measure sediment physiochemical characteristics with an impact on the reversibility of transformation processes.</li> <li>▪ Conduct laboratory and field experiments to detect the occurrence and extent of actual transformation reversals under relevant geochemical conditions.</li> </ul>

#### 4.5.2 Reduced Bioavailability and Mobility

**E**vidence for reduced bioavailability and mobility of many sediment-associated chemicals is often overlooked in risk assessments. Bioavailability refers to the potential for a contaminant to be absorbed by ecological receptors (e.g., plants, animals, and humans) (NRC, 2003b). The bioavailable fraction of a chemical concentration in sediment is often conceptualized as the concentration dissolved in pore water or the fraction rapidly desorbing from sediment particles. Mobility refers to the contaminant's chemical and physical stability and its ability to move in the environment. The definition of mobility can be very broad to include the surface water transport of dissolved or particulate-sorbed chemicals, dissolved pore water transport,

biological uptake and transfer between organisms, or chemical transport between multiple chemical phases (e.g., between particulate and dissolved phases).

Ongoing reductions in bioavailability and mobility are unlikely to be a primary mechanism of continuing risk reduction at most contaminated sediment sites, except where contaminant releases have occurred recently. However, bioavailability/mobility reductions may have played a significant role in past natural recovery leading to current conditions. If bioavailability has not been sufficiently addressed in the risk assessment, supplemental investigation in support of the FS may be needed for a more realistic estimate of risks that would be experienced during MNR implementation. Also, issues of bioavailability and mobility are integral to understanding the effects of other natural recovery processes. An example of an extensive investigation of chromium bioavailability in support of an MNR feasibility investigation is described in Highlight 4-3.

Of primary interest is chemical mobility between media (i.e., between solid and dissolved phases, and between sediment/aqueous phases and biota). Within the sediment bed, mobility involves the potential for chemical transport between sediment and pore water and between sediment/pore water and biota (Figure 4-4). In the water column, mobility involves the potential for chemical transport between suspended sediment and surface water and between suspended sediment/surface water and biota. In other words, the focus is primarily on intermedia chemical transport, as chemicals migrate between solid, aqueous, and biological phases. Mobility and bioavailability are interconnected, such that increases or decreases in mobility tend to correlate with increases or decreases in contaminant bioavailability.

Precipitation occurs when a chemical molecule forms bonds or weak associations with other molecules of the same chemical (crystallization or liquefaction) and the chemical comes out of solution as a solid or non-aqueous phase liquid. This may reduce aqueous solubility and contaminant mobility and bioavailability. Examples include precipitation of divalent metal hydroxides and sulfides (Di Toro et al., 2005), precipitation of Cr(III) hydroxides (USEPA, 2005b), and coalescence of high-molecular-weight PAHs into nonaqueous phase liquids (Neff et al., 2005; Pastorok et al., 1994).

For hydrophobic contaminants and some metals, sorption and other chemical bonds increase with time and age, thus decreasing contaminant mobility and bioavailability with time (Alexander, 2003). For this reason,

GEOCHEMICAL CONSIDERATIONS	
☆	Dissolved oxygen levels and redox potential
☆	Salinity/ionic strength/pH
☆	Sulfides (often measured as AVS)
☆	Total organic carbon
☆	Black carbon
☆	Contaminant biodegradation behavior
☆	Contaminant transformation kinetics
☆	Contaminant geochemical behavior
☆	Contaminant hydrophobicity

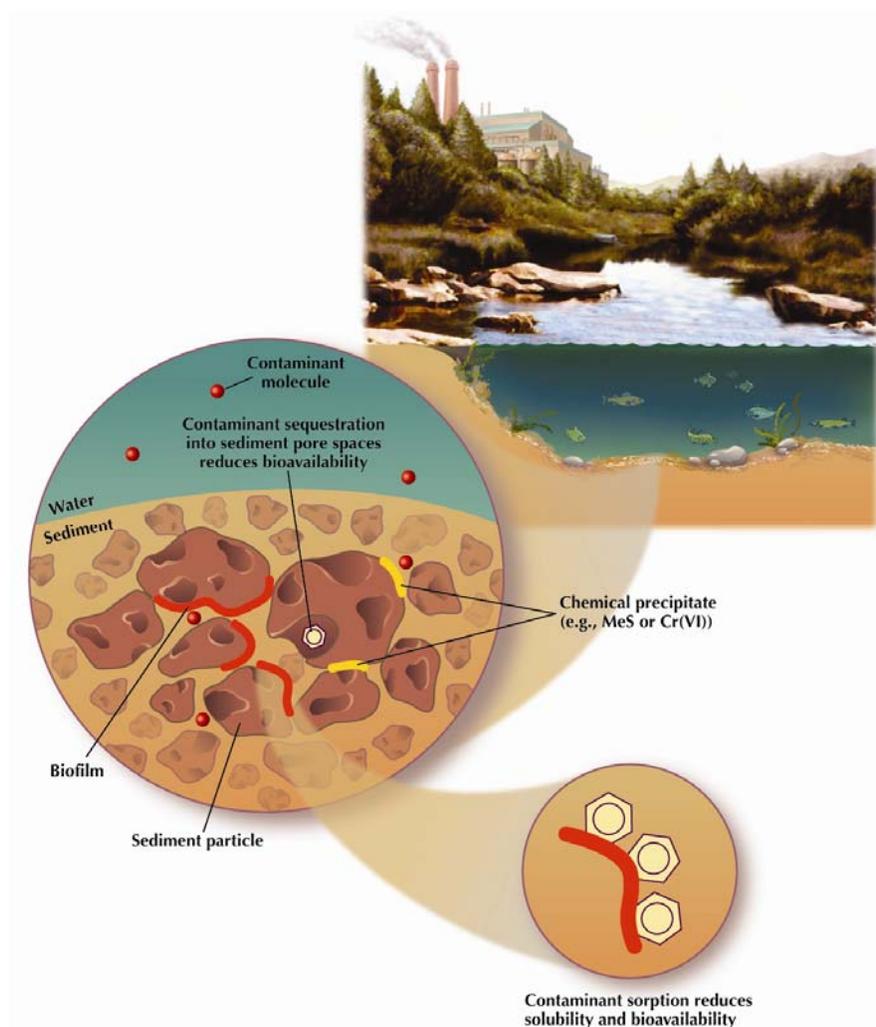


FIGURE 4-4. Processes that reduce mobility and bioavailability. Note: Me represents a generic divalent metal.

site-specific, aged sediments are preferred for biological exposure or sorption experiments in lieu of spiking clean sediment samples in the laboratory (USEPA, 2000c).

For organic contaminants, properties that most influence mobility are chemical-specific hydrophobicity, the sorbent matrix (organic carbon type), chemical concentrations, and desorption kinetics. Hydrophobicity is measured as the octanol-water partition coefficient ( $K_{ow}$ ), a measure of differential solubility of a compound in a hydrophobic solvent (octanol) and water, which predicts the solubility of hydrophobic compounds in water. In the environment, the organic-carbon partition coefficient ( $K_{oc}$ ) is a measure of the matrix-specific differential solubility of the compound

### CHROMIUM BIOAVAILABILITY IN HACKENSACK RIVER SEDIMENTS

Multiple lines of evidence were investigated to determine the bioavailability of chromium in sediments in the Hackensack River near its confluence with Newark Bay, NJ (Magar et al., 2008a; Martello et al., 2007; Sorensen et al., 2007). Chromium at the site is partly attributable to historical waterfront disposal of chromium ore processing residue. Understanding chromium bioavailability was essential to accurately estimating baseline and potential future risks in order to effectively evaluate remedial alternatives.

- **Literature review** identified key aspects of chromium geochemistry. Relevant species include Cr(VI) and Cr(III), of which Cr(VI) is much more soluble and toxic. Cr(VI) transforms rapidly to Cr(III) under reducing or mildly oxidizing conditions. Although Cr(VI) is thermodynamically favored under aerobic conditions, it is rarely formed in nature due to kinetic constraints. Cr(III) is minimally toxic in saltwater exposures.
- **Indicators of redox conditions** in surface sediment included analyses of acid volatile sulfide and sediment profile imaging. Reducing conditions (incompatible with Cr(VI)) were shown to predominate, except in a thin layer (1.7 cm on average) at the sediment surface.
- **Pore water sampling and analyses** initially targeted the upper 15 cm of sediment, with follow-up samples targeting the top, oxygenated 1 cm layer of intertidal sediments (i.e., the worst case for potential chromium oxidation). Cr(VI) was never detected, and Cr(III) was found only at low concentrations in pore water, despite whole-sediment concentrations as high as 2,090 mg/kg.
- **Cr(VI) analyses in whole-sediment** indicated detectable Cr(VI), contrary to the preceding lines of evidence. Possible explanations include analytical artifacts (Zatka 1985) and/or Cr(VI) sequestration within sediment particles (Anderson et al., 1994).
- A **sediment resuspension and oxidation test** simulated conditions during a severe weather or anthropogenic scouring event. No Cr(VI) was detected in sediment elutriate following extended aeration and mixing with water.
- **Biota tissue analyses** showed no relationship between chromium concentrations in sediment and in tissue of laboratory-exposed and indigenous invertebrates. Concentrations were within the range of those found in laboratory control organisms.
- **Toxicity tests** showed adverse effects of site sediments on amphipods but not polychaetes, although the polychaete test species is known to be particularly sensitive to Cr(VI). Effects on amphipods were associated with PAH concentrations. Tests at an upriver site affected by chromium ore processing residue demonstrated no toxicity to amphipods at total chromium concentrations up to 1,490 mg/kg (Becker et al., 2006).

Taken together, these lines of evidence demonstrated very low bioavailability of chromium in study area sediments.

HIGHLIGHT 4-3. Bioavailability of chromium in sediments in the Hackensack River.

in the presence of sediment organic carbon. Inorganic sorption is also affected by the sorbent matrix (mineralogy).

For solid-phase precipitates, chemical properties that most influence mobility are the chemical-specific solubility product ( $K_{sp}$ ), the potential for the chemical to form other chemical bonds and their respective solubility products, aqueous geochemical and physical properties (e.g., temperature, pH, alkalinity, redox conditions), and chemical concentrations.

Key considerations for investigating the natural processes associated with reduced contaminant bioavailability and mobility include:

- Sediment physiochemical characteristics
- Degree of bioavailability reduction
- Rate of reduction in bioavailability and mobility
- Reversibility
- Impact on dissolution and diffusion/advection processes
- Measuring bioavailability in the environment.

Sediment physiochemical characteristics. Sediment conditions conducive to reduced bioavailability and mobility vary by contaminant. Examples include:

- Sediments with high concentrations of organic carbon, especially black carbon (a form of carbon produced by incomplete combustion of fossil fuel and wood, forming soot, or of biomass, forming charcoals), are conducive to sorbing organic chemicals, and, to some extent, divalent metals.
- Sediments with high clay concentrations are conducive to sorbing metals.
- Sediments low in oxygen and/or high in dissolved solids (high salinity, hardness, or sulfides) favor the precipitation of low-solubility metal minerals.

Lines of evidence should establish that site-specific conditions promote sorption or precipitation for the COC. The sediment matrix plays a critical role in contaminant partitioning behavior. Recent studies on PAH partitioning at manufactured gas plant sites show that sorption to pitch is

more than an order of magnitude higher than sorption to natural organic matter; the partitioning behavior is dominated by the sorption characteristics of pitch and not by natural organic matter or black carbon (e.g., Khalil et al., 2006). A model based on whole sediment concentrations and natural organic carbon is likely to be inadequate in describing the partitioning behavior of manufactured gas plant sediments dominated by coal tar pitch, coal, coke, or soot, making carbon source identification and availability measurements prudent for these types of sediment. USEPA's equilibrium partitioning approach (USEPA, 2003a) allows for measurement of site-specific partition coefficients or direct pore water measurements to more accurately predict exposure and risk.

Whole-sediment metal concentrations alone also inadequately describe metals bioavailability and risk. Analysis of metals should be combined with measurements of AVS, SEM, pH, and organic carbon to quantify the bioavailability and risk associated with divalent metals (USEPA, 2005b; Di Toro et al., 2005).

Degree of bioavailability reduction. The balance between available and non-available contaminant fractions is dependent on matrix-specific solubilities and partition coefficients. For example, whereas chromium reduction can reduce the availability of hexavalent chromium to non-detectable levels, well below ambient water quality criteria (Martello et al., 2007), other metals may reach equilibrium between dissolved and precipitated forms with measurable levels of dissolved, bioavailable metal persisting (Di Toro et al., 2005). Organic compounds also exhibit a wide range of sorption behavior depending on the contaminant type, molecular weight and corresponding hydrophobicity, and sediment matrix (e.g., whether sorbed to natural organic carbon or various forms of black carbon). The bioavailability of hydrophobic contaminants sorbed to carbon is governed by processes that bring organisms into contact with sediment particles (e.g., ingestion) and sediment pore water (Leppänen and Kukkonen, 1998; Kukkonen and Landrum, 1994; Landrum et al., 1994). Lines of evidence should address the extent to which site-specific conditions achieve reduced contaminant bioavailability or mobility.

Rate of reduction in bioavailability and mobility. Rates vary by contaminant and per site-specific sediment characteristics. Ongoing sorption and molecular diffusion processes over years or decades can increase sequestration; however, the outcome of such aging processes may already be reflected in current conditions at sites affected by legacy contamination. Because site-specific measurement of sorption kinetics can be difficult and slow, managers are encouraged to rely on kinetics reported in the literature, as necessary.

Reversibility. Sorption and precipitation reactions may be reversible, and the conditions that lead to contaminant accumulation in sediments can result in the slow release of contaminants and their persistent mobility and bioavailability. For some chemicals, it is possible for a portion of sorbed contaminants to be irreversibly sorbed (Alexander, 2003; Tomson et al., 2003), as chemicals diffuse into the sorbed matrix and become chemically sequestered with age. However, in some cases the mechanisms that cause reduced bioavailability and mobility are reversible (Kalnejais et al., 2007; Tomson et al., 2003). Precipitation reactions of some metals, for example, may be reversible under changing redox conditions, and most hydrophobic contaminants exhibit some level of desorption. Lines of evidence should address the rates of release in relation to rates of sorption and precipitation reactions, how they influence contaminant mobility and bioavailability, and thus how risk at the site is affected.

Impact on dissolution and diffusion/advection processes. Reductions in contaminant bioavailability coincide with reduced diffusion of chemicals from the sediment to pore water. Lines of evidence that support processes limiting the movement of contaminant into the dissolved phase lend weight to predictions of reduced bioavailability and mobility.

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*There is a stronger relationship between contaminant toxicity and pore water concentrations than between contaminant toxicity and whole sediment concentrations.*

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Measuring bioavailability in the environment. Numerous studies on contaminant bioavailability and toxicity demonstrate a stronger relationship between contaminant toxicity and pore water concentrations than between contaminant toxicity and whole sediment concentrations (USEPA, 2005b, d; 2003a, b, c). Contaminant concentrations in pore water and other aqueous-phase measurements offer the most direct indication of contaminant bioavailability. A variety of methods with different advantages and disadvantages are available to sample pore water (e.g., USEPA, 2003d; 2001a), and improved techniques for pore water sampling and analysis are an area of active research (for example, see Highlight 2-1).

Alternatives to direct pore water measurements include calculation of partitioning relationships between solid and aqueous phase chemical concentrations. Development of a partitioning model requires knowledge of site-specific solid-aqueous phase partitioning relationships, chemical equilibrium kinetics, and pore water advection rates. Lines of evidence should account for contaminant- and site-specific factors that reduce bioavailability and mobility rates. Most partitioning models incorporate equilibrium partitioning, which can underestimate or overestimate contaminant solubility and bioavailability. Lack of understanding of contaminant interactions at sites and uncertainties in site-specific inputs

greatly affect the accuracy of these models. As a result, site investigations increasingly rely on direct measurement of pore water chemical concentrations (Hawthorne et al., 2007; 2006).

Table 4-4 lists lines of evidence that may be applied to address the various considerations pertinent to processes that reduce bioavailability and mobility.

TABLE 4-4. Lines of evidence to establish reduced bioavailability and mobility.

Consideration	Lines of evidence
<b>Degree of contaminant bioavailability</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>■ Assemble findings on contaminant-specific properties that influence mobility and bioavailability.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Incorporate contaminant-specific properties into equilibrium partitioning models that predict contaminant solubility, mobility, and bioavailability.</li> <li>■ Develop a site-specific equilibrium partitioning model that describes sediment- and contaminant-specific behaviors.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>■ Measure pore water concentrations in situ or in the laboratory for direct measures of contaminant bioavailability.</li> <li>■ Use biological studies to measure bioavailability, including laboratory exposure or toxicity studies, in-situ biological exposure studies, or surrogate approaches (e.g., semi-permeable membrane devices) that simulate biological exposure.</li> <li>■ Develop contaminant- and site-specific laboratory partitioning coefficients.</li> <li>■ Identify influences of chemical speciation, precipitation, or sorption on contaminant mobility and bioavailability.</li> </ul>
<b>Sorption kinetics</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>■ Assemble findings on rates of bioavailability and mobility reduction for COCs and their relevance to natural recovery.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop predictive models that incorporate kinetics.</li> </ul>

TABLE 4-4. Lines of evidence to establish reduced bioavailability and mobility (continued).

Consideration	Lines of evidence
<b>Sorption kinetics</b>	Site-specific investigations: <ul style="list-style-type: none"> <li>Conduct laboratory and field work to collect data that describe reduction rates. (Measuring sorption kinetics can be very slow and time-consuming.)</li> </ul>
<b>Reversibility</b>	Refer to Table 4-3 for information about lines of evidence to assess the potential for reversal of transformations that affect contaminant bioavailability.

### 4.5.3 Physical Isolation

Decreasing exposure to COCs reduces risk by limiting the potential for receptors (e.g., plants, animals, and humans) to come into contact with contaminants. The long-term goal of sediment remediation is to adequately reduce risks to human and ecological receptors. Insofar as contaminants associated with surface sediments contribute to human and ecological risks, natural sedimentation that reduces exposures by isolating and diluting surface sediment contaminants to concentrations will reduce risks to human health and the environment.

Physical isolation via sediment burial occurs in net depositional environments, where the rate of sediment deposition exceeds the rate of sediment scouring (Figure 4-5). Natural sedimentation occurs as a result of the erosion of watershed soils and sediments, precipitation of solids from the water column, and accumulation of the remains of aquatic biota such as plankton, algae, and aquatic macrophytes. Natural deposition of clean material can isolate and dilute contaminants in surface sediment, resulting in the long-term progressive decrease in surface sediment contaminations, leading to concentrations that approach or achieve surface sediment cleanup levels (Magar and Wenning, 2006; Brenner et al., 2004; USEPA, 2004c; Brenner et al., 2002; USEPA, 1998c).

Ironically, the same natural sediment transport mechanisms that can remediate contaminated sediment environments through natural burial were probably the cause of the initial deposition and accumulation of contaminated particles. This role of natural depositional processes emphasizes the fact that source control is an integral component of MNR and every other sediment remedy.

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*Natural sedimentation reduces exposure by isolating and diluting surface sediment contaminants.*

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*Source control should be an integral component of natural recovery and every other sediment remedy.*

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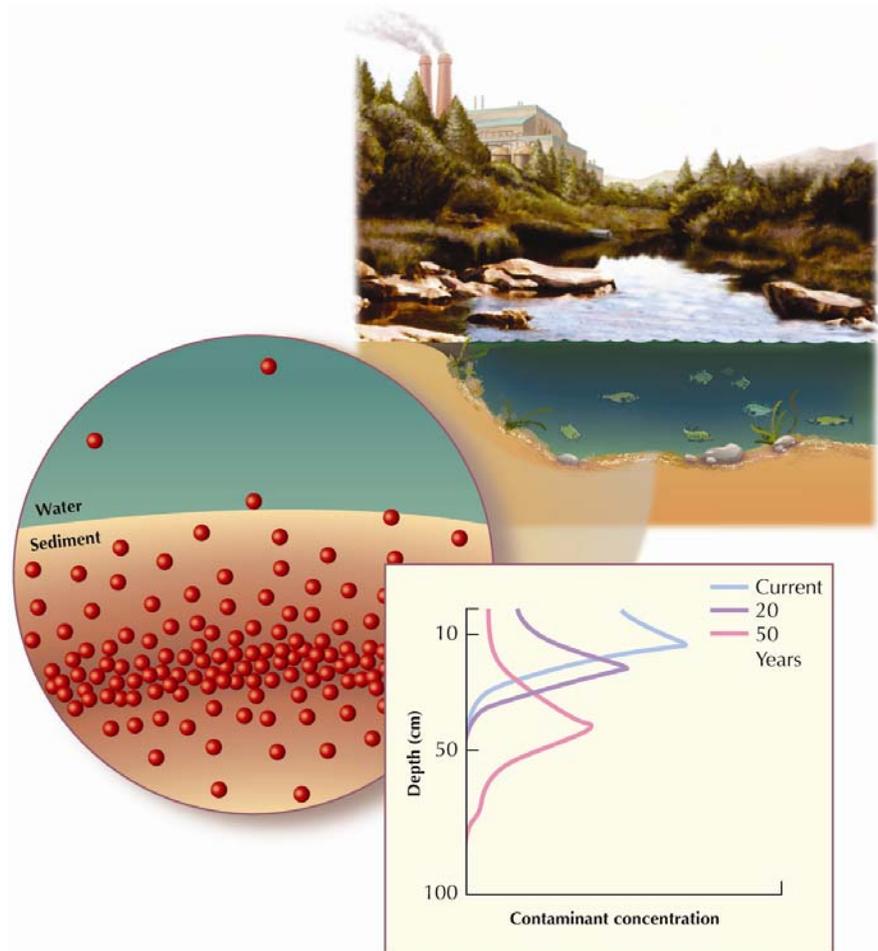


FIGURE 4-5. Physical isolation processes.

As deposited sediments contribute to isolating contaminants from biological receptors, contaminants will be diluted through a variety of mixing processes. Surface sedimentation, benthic and hydrodynamic mixing, and resuspension can contribute to the dilution of contaminated sediments with cleaner material and thus work to reduce risk by bringing about lower surface-sediment contaminant concentrations. In addition, contaminant transformation processes that are inhibited at high concentrations could be triggered as concentrations decline, further reducing risk.

Key considerations for investigating the natural processes associated with physical isolation include:

- Quality of freshly deposited sediment
- Benthic mixing (bioturbation) and hydrodynamic mixing

- Vertical cycling
- Source control
- Deposition rates
- Physical isolation via sedimentation
- Benthic bioturbation
- Impact on transformation processes and bioavailability
- Erosion potential.

Quality of freshly deposited sediment. The presence of residual soil and sediment contamination may require years or decades to flush through a watershed. Also, soil cleanup requirements at some sites are not as stringent as sediment cleanup requirements, resulting in the persistent release of low contaminant concentrations into the watershed. These issues affect the long-term success of any sediment remedy, including MNR.

Benthic mixing (bioturbation) and hydrodynamic mixing. These processes influence the rate of change in surface sediment chemical concentrations. Higher rates of mixing may lead to more rapid declines in exposure and risk, especially for contaminants that rely on mixing to enhance degradation. On the other hand, mixing also can reduce the rate of recovery by mixing older, deeper contaminated sediments into the surface layer and slowing contaminant burial. The overall effect of mixing will be governed by site-specific factors and processes.

Vertical cycling. Some chemicals—notably arsenic and mercury—exhibit vertical cycling within the sediment column, due to mobilization at redox boundaries and subsequent complexation with iron oxides in oxygenated surface sediment. While the dissolved fraction of any contaminant is subject to diffusion, the fraction of arsenic and mercury available for diffusion can change with vertical shifts in redox chemistry, either seasonally or with progressive sediment burial.

⇒Refer to Section 4.4 for more information about source control.

Source control. As noted above, freshly deposited sediments do not necessarily result in lower exposures, as when newly deposited sediments are themselves contaminated.

Deposition rates. Sedimentation rates vary according to hydrodynamics, upstream conditions, and watershed characteristics. Lines of evidence can include modeling deposition rates using watershed characteristics and water column measurements, or empirical measurements from radionuclide-based dating, bathymetric surveys, or sediment traps. Highlight 4-4 demonstrates the use of vertical contaminant profiling and radionuclide age dating to characterize the extent and rate of change in surface sediment chemical concentrations, and to determine surface sedimentation rates.

Physical isolation via sedimentation. Natural sedimentation rates should be sufficient to result in a net deposition of fresh sediment that remains intact regardless of ongoing transport and mixing mechanisms. Even when physical isolation is not complete (e.g., due to surface mixing), risk may be adequately reduced by the dilution of contaminated surface sediments with freshly deposited cleaner material. Lines of evidence typically address the historical extent of physical burial and isolation of sediment contaminants.

Benthic bioturbation. As described above, benthic mixing can impact the rate of physical isolation. Benthic bioturbation depths also help indicate how to define surface sediments (i.e., sediments to which organisms may be exposed).

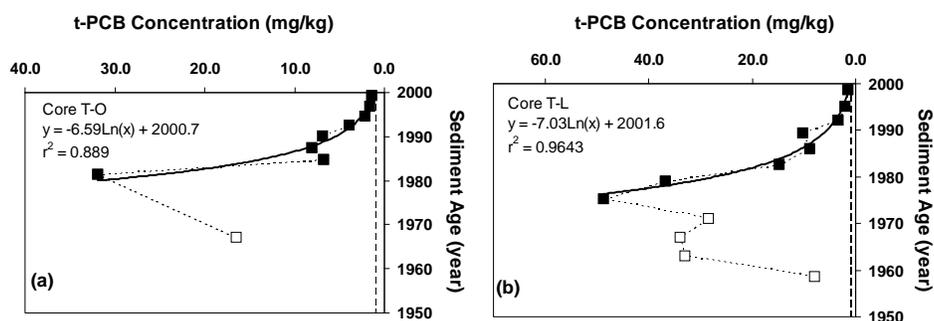
Impact on transformation processes and bioavailability. Physical isolation of sediments and the mixing of contaminated surface sediments with cleaner materials could alter physiochemical conditions (e.g., redox gradients) that promote transformation. For example, only surface sediments are oxic in many sediment ecosystems. Additional sediment layers deposited on the contaminated sediment layer may result in anoxia, decreasing the rate of chemical transformation with sediment depth for some chemicals (e.g., organotins, PAHs) and increasing it for others (e.g., PCBs). Freshly deposited sediment, after mixing with contaminated surface sediment, may result in decreased surface sediment contaminant concentrations that could enable microbial activity that might have been previously suppressed due to chemical toxicity, or could slow microbial activity that may be chemical concentration dependent (e.g., microbial activity that follows first order or Monod kinetics). Newly deposited clean sediments containing organic carbon can also, for example, sorb organic compounds reducing their bioavailability and release to surface waters from the sediment bed. Lines of evidence should consider how chemical transformation processes and bioavailability are affected by sedimentation.

## LAKE HARTWELL SURFACE SEDIMENTATION RATES AND PCB TRENDS

Lake Hartwell provides an example of surface sediment recovery following removal of a point source. 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 the Twelve-Mile Creek arm of Lake Hartwell. Sediment age dating was conducted using lead-210 ( $^{210}\text{Pb}$ ) and cesium-137 ( $^{137}\text{Cs}$ ) concentration profiles in the sediment cores (Brenner et al., 2004). PCB trends showed decreasing surface sediment concentrations since the late 1970s. The USEPA restriction of PCB use in the late 1970s and removal of upland PCB sources collectively controlled the gross contamination emanating from the Sangamo-Weston Plant and various off-site disposal areas (USEPA, 2004a).

Sediment PCB concentrations begin at a depth of approximately 100 cm below the sediment-water interface, where sediments were likely deposited at the onset of PCB use at the Sangamo-Weston plant in 1955 (USEPA, 1994). Maximum concentrations were measured at ~30–60 cm below the sediment-water interface, ca. 1970–1980. Peak concentrations were followed by a progressive decrease in surface sediment concentrations over time (or decreasing depth). Today, surface sediment concentrations approach the 1.0 mg/kg target concentration, while buried concentrations range from 40–60 mg/kg (URS, 2008; Brenner et al., 2004).

Sedimentation rates averaged  $2.1 \pm 1.5$  grams per cubic centimeter per year for 12 of 18 cores collected. Regression curves (shown below) were applied to the PCB concentration profiles to predict the amount of sedimentation required to achieve a cleanup goal of 1.0 mg/kg, stipulated in the 1994 ROD (two more goals, 0.4 mg/kg and 0.05 mg/kg total PCBs, were also identified). It was estimated that average surface sedimentation needed to meet the three goals were  $1.4 \pm 3.7$  cm,  $11 \pm 4.2$  cm, and  $33 \pm 11$  cm, respectively. Using the age-dating results, the average recovery dates to meet these goals were determined to be  $2000.6 \pm 2.7$  years,  $2007.4 \pm 3.5$  years, and  $2022.7 \pm 11$  years, respectively (Brenner et al., 2004). In actuality, the 1 mg/kg cleanup goal was achieved in surface sediments by 2007 (URS, 2008). The recovery rate was thus slightly slower than predicted, perhaps due to incomplete control of PCB releases via groundwater.



Vertical profile showing surface sediment recovery in two PCB-contaminated Lake Hartwell sediment cores. Solid symbols represent data used to generate the curves. Reprinted with permission from Brenner et al., 2004. Copyright 2004 American Chemical Society.

HIGHLIGHT 4-4. Natural recovery via sedimentation and PCB burial in Lake Hartwell, South Carolina.

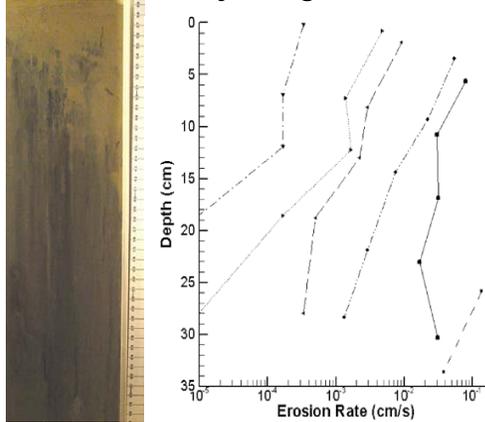
Erosion potential. Sediment erosion potential is determined by sediment properties (e.g., sediment grain size, bulk density, cohesiveness, organic content, gas content, burial depth, and age) and hydrodynamic conditions (e.g., current flow rates and wave energy during normal- and high-energy events, and as induced by anthropogenic activity) (Ziegler, 2002; McNeil et al., 1996). Erosion potential should be investigated to assess whether unacceptable risk would be created during normal and high-energy conditions, including storms, flood events, wind-wave impacts, other natural events, and human disturbances, including ship wake and propeller wash (Highlight 4-5).

Factors that can limit contaminant erosion potential include burial of contaminated sediments beneath cleaner sediments, as well as bed armoring, a natural process by which sediment erosion potential decreases over time. Armoring can occur regardless of whether the bed consists predominantly of cohesive (i.e., silt/clay) sediment or non-cohesive (i.e., sand/gravel) sediment, or a mixture of these two types. The physicochemical and transport processes that contribute to bed armoring include the consolidation of cohesive sediments with depth and over time, the background shear conditions under which sediment has been deposited (Lau and Droppo, 1999), deposition of relatively coarser sediments on the sediment bed, and the preferential erosion or winnowing of finer sediments from the surficial sediment layer (Charlton, 2008; Jones and Lick, 2001). Armoring of the sediment may occur as the result of moderate-flow events, which tend to preferentially erode finer particles from the sediment surface. The result of this process is a coarsening of the surficial sediment layer relative to the grain size distribution of underlying sediment, which tends to progressively stabilize the sediment bed from erosion during subsequent higher-flow events. Biological processes may also contribute to bed armoring through the creation of cross-linkages between organic materials and sediment inorganic particles (Gerbersdorf, 2008).

The persistence of surface armored layers is dependent on the magnitude of subsequent higher-flow events and the extent to which transport of sediment to the armored reach is supply-limited relative to its erosion potential (e.g., Vericat et al., 2005; Dietrich et al., 1989). If fine-grained sediment supply is not limited, its deposition under more quiescent conditions may result in at least a temporary fining of the surficial sediment layer prior the next flood event. Accurate understanding of site fluvial geomorphology, sediment supply potential, and watershed hydrology (e.g., Buffington and Montgomery, 1999) are needed to evaluate the extent to which bed armoring contributes to physical isolation of contaminants.

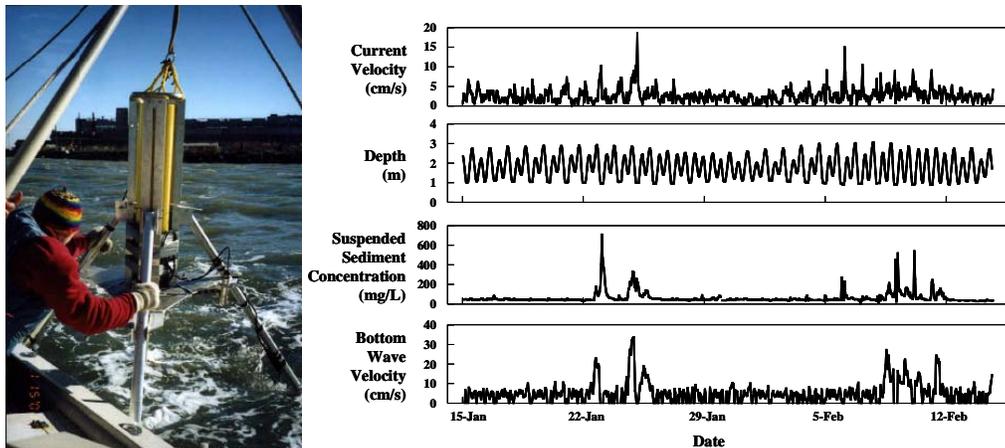
### EVIDENCE OF SEDIMENT STABILITY IN HUNTERS POINT SHIPYARD

The sediments in Hunters Point Shipyard (HPS) in southeast San Francisco are contaminated with metals, PAHs, and PCBs (NOAA, 1997). An important component of the evaluation of MNR processes for HPS was to determine whether contaminated subsurface sediments are below the depth where sediments are considered stable (Blake et al., 2007). Erosion potential is one line of evidence for understanding sediment stability and depositional conditions, and it can be determined from analysis of sediment properties and hydrologic conditions.



The Sedflume graph (left) shows measured erosion rates versus core depth at different applied shear stresses. The data show that the shear stress required to induce erosion increases with sediment depth. This characteristic is attributed to sediment consolidation and increased cohesion with depth and age. The photograph of the sediment core illustrates a vertical oxic gradient. The light brown oxic zone near the sediment-water interface suggests a 10 cm active benthic layer; deeper sediments do not experience bioturbation.

Interpretation of the Sedflume results requires an understanding of shear stresses occurring in San Francisco Bay. Measurements were collected with a Sediment Transport Measurement System equipped with a surface water amplitude meter, current meter, and turbidity, temperature, conductivity (salinity) and pressure (water depth) sensors (bottom, left). There are strong correlations between tide elevations and current velocities and between storm events (peak current velocities approach or exceed 10 centimeters per second [cm/s]), wave velocities, and suspended sediment concentrations (bottom, right). The average scouring depth during a storm in the inlet environment of HPS was estimated to be limited to several millimeters of surface sediments (up to 4 cm erosion during a typical storm event, and up to 6 cm erosion during a 25-year event), an indication that natural recovery will occur without substantial disturbance to the sediment bed (Blake et al., 2007).



HIGHLIGHT 4-5. Measurements of sediment stability in Hunters Point Shipyard, CA.

Table 4-5 lists lines of evidence that address the various considerations pertinent to processes that reduce contaminant exposure.

TABLE 4-5. Lines of evidence to establish ongoing processes that reduce exposure via physical isolation.

Consideration	Lines of evidence
<b>Occurrence and rates of sediment deposition</b>	<p>Literature and historical data</p> <ul style="list-style-type: none"> <li>■ Review literature and historical reports of sediment deposition, rates, and geochronology information.</li> <li>■ Review literature and historical reports of hydrodynamic conditions and sediment transport.</li> <li>■ Review historical bathymetric and profile analyses to qualitatively or quantitatively determine historical deposition rates.</li> <li>■ Review historical dredging records to quantify the amount of sediment removed routinely, for comparison with estimated sediment deposition rates.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop models to characterize and predict sedimentation and contaminant burial, including net deposition rates, bioturbation, diffusion, hydrodynamic mixing, geochronological age dating.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>■ Vertically profile contaminant concentrations via coring and segmenting at appropriate intervals.</li> <li>■ Perform geochronological isotope analyses (e.g., <sup>210</sup>Pb and <sup>137</sup>Cs) to determine historic deposition rates and to develop an understanding of sediment stability in depositional environments.</li> <li>■ Analyze parameters such as bulk density and grain size analyses, chemical forensics and fingerprinting, or mineralogical characterization in sediment cores to understand changes in sediment and contaminant characteristics with sediment depth and time.</li> <li>■ Perform dendrogeomorphic analyses (based on tree root exposure) to establish sedimentation rates.</li> <li>■ Perform geophysical analyses (bathymetry, sidescan sonar, or subbottom profiling) to characterize sediment bed properties, establish baseline conditions, and contribute to hydrodynamic modeling.</li> </ul>
<b>Characteristics of freshly deposited sediments</b>	<p>Refer to Table 4-2 for lines of evidence to identify ongoing contaminant sources and/or verify source control.</p> <p>Additional lines of evidence include:</p>

S E D I M E N T C H A R A C T E R I S T I C S	
☆	Grain size
☆	Bulk density
☆	Cohesiveness
☆	Organic content
☆	Burial depth
☆	Age
☆	Bioturbation

TABLE 4-5. Lines of evidence to establish ongoing processes that reduce exposure via physical isolation (continued).

Consideration	Lines of evidence
<b>Characteristics of freshly deposited sediments</b>	<p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop models that account for current sediment characteristics and demonstrate the impact of deposition on contaminated surface sediments.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>■ Analyze chemical and partitioning characteristics of recently deposited sediments.</li> </ul>
<b>Benthic bioturbation and hydrodynamic mixing</b>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>■ Assemble findings on benthic community characteristics (habitat usage, burrowing depths, bioturbation rates).</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Model benthic mixing and hydrodynamic mixing to demonstrate the impact of sedimentation and mixing on surface sediment concentration changes with time.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>■ Collect surface grab samples to characterize the benthic community, including background locations.</li> <li>■ Use sediment profile imagery to identify surface sediment redox zones, bioturbating animals, and maximum site-specific bioturbation depths.</li> <li>■ Perform isotope analyses to characterize surface sediment bioturbation depths. This can be done by evaluating asymptotic changes in <sup>210</sup>Pb or <sup>137</sup>Cs profiles or by viewing the presence or absence of beryllium-7 (<sup>7</sup>Be) in surface sediment.</li> </ul>
<b>Sediment Stability</b>	<p>Literature and historical data:</p> <ul style="list-style-type: none"> <li>■ Assemble information on site-specific sediment transport processes.</li> <li>■ Assemble sediment core data, identifying signs of depositional behavior, including historical contaminant trends and geochronological trends.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop models that account for current velocities and sediment shear strength behavior.</li> <li>■ Model sediment transport potential by integrating surface water hydrodynamic shear forces and sediment shear strength properties.</li> </ul>

TABLE 4-5. Lines of evidence to establish ongoing processes that reduce exposure via physical isolation (continued).

Consideration	Lines of evidence
<b>Sediment Stability</b>	Site-specific investigations: <ul style="list-style-type: none"> <li>▪ Conduct experiments to directly measure sediment critical shear strength.</li> <li>▪ Characterize hydrodynamic conditions under normal and high-energy events (include storms, winds, prop wash, and other events, as appropriate).</li> </ul> Measure sediment bed bathymetry over time using high-resolution multibeam techniques.

#### 4.5.4 Dispersion

**D**ispersion encompasses a range of natural processes that tend to move contamination from higher to lower concentration regimes (downgradient). Dispersion must be gauged carefully with respect to MNR effectiveness because it may result in broader exposure, albeit at lower concentrations, rather than eliminating exposure pathways (USEPA, 2005a). On the other hand, it must be recognized that dispersion processes are active at almost every site and thus must be considered within the MNR remedy both for the direct effects they may have on exposure and for the manner in which they may interact with and influence other natural recovery mechanisms. Dispersion may be a mechanism by which contaminants move from higher energy areas to depositional areas, where they may then undergo other recovery processes (Highlight 4-6). Also, dispersion may be an important mechanism accounting for past reduction in contaminant exposures. As such, understanding dispersion processes can be important to predicting how exposures are likely to decrease in the future.

Dispersion of contaminants occurs as a result of physical sediment resuspension, movement of dissolved chemicals via surface water currents or groundwater advection (emergence of groundwater to surface water), and simple chemical diffusion (Figure 4-6). Dispersion is rarely an isolated process. Instead, it is usually part of a dynamic process of resuspension at the sediment bed surface. The continuous introduction of increasingly clean sediment following source control combined with dynamic deposition, resuspension, and surface sediment mixing can contribute to the long-term dilution of surface sediment contaminant concentrations and corresponding reductions in biological exposures.

Physical processes may bury, mix, dilute, or transfer contaminants to another medium. Physical processes such as sedimentation, erosion,

diffusion, dilution, bioturbation, advection, and volatilization may reduce contaminant concentrations in surface sediment and thus reduce risk associated with the sediment (USEPA, 2005a). However, some of these mechanisms may move contaminants off site over a wider area or to another medium (e.g., via groundwater or surface water). An MNR strategy should evaluate the nature and magnitude of exposures and risks where contaminants disperse and/or deposit.

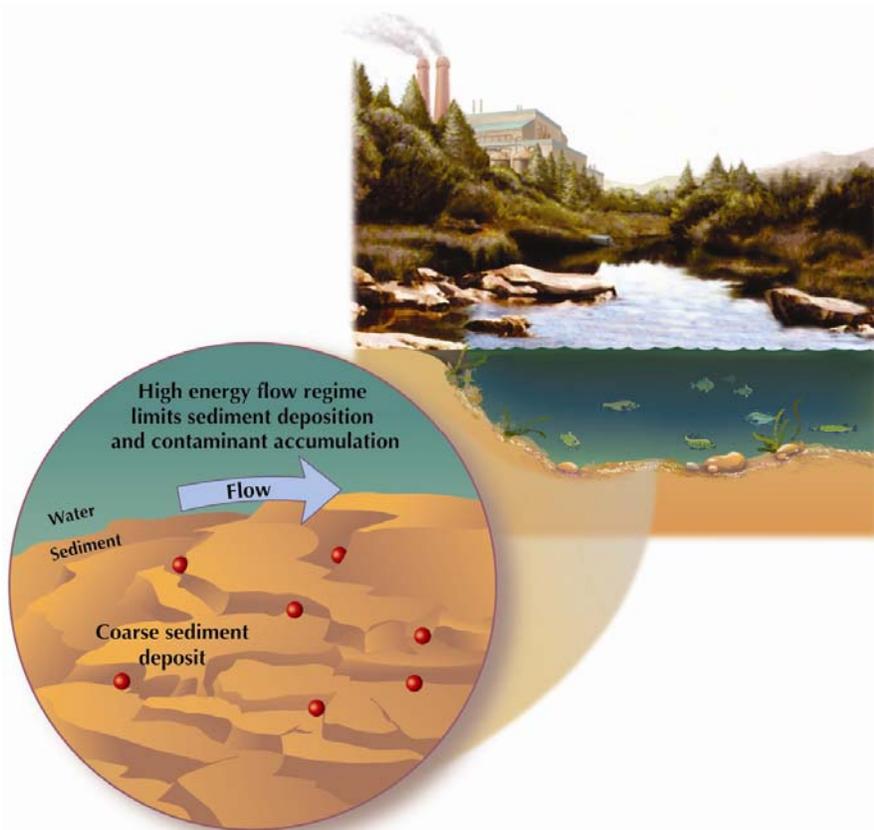


FIGURE 4-6. Dispersion and transport processes.

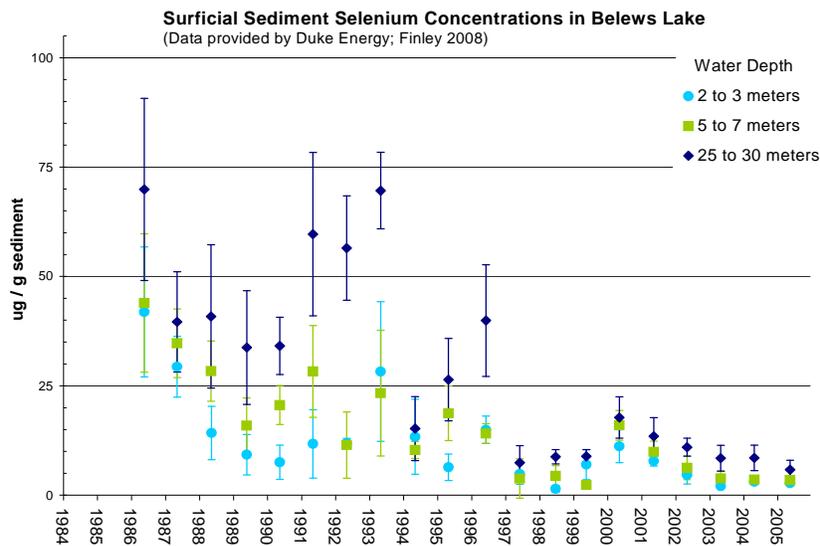
Whether sediment transport or chemical diffusion or advection contributes to reduced surface sediment exposures depends on the site physicochemical conditions and contaminant mobility. Sediment transport is most relevant to areas of relatively high hydrodynamic energy where contaminated sediment particles do not accumulate. Such areas may include rapidly flowing portions of rivers, ports and harbors or rivers where ship traffic persistently resuspends sediment particles and prevents sediment accumulation, or areas with episodic flows that also persistently suspend settled particles, limiting or preventing sediment

### SEDIMENT FOCUSING IN BELEWS LAKE, NC

Belews Lake was created in 1974 to supply cooling water for a Duke Energy power plant. The company disposed of its fly ash in disposal basins that overflowed selenium (Se) -laden effluent directly into Belews Lake. Two years after leachate began contaminating the lake with Se, 18 fish species had disappeared, leaving only two fish species in the lake (Horne, 2004). In 1984, the ash disposal was modified to prevent further contamination (ACAA, 2007). Monitoring by Duke Energy has shown a gradual decline in Se levels since source control began. Se concentrations remain above background levels, but benthic species diversity and fish community characteristics indicate contamination from the power plant is no longer impacting fauna in Belews Lake (NCDWQ, 2001).

Fish consumption advisories reflect the recovery of Belews Lake. The 1988 fish consumption advisory included all species, while the 1996 advisory included only common carp, redear sunfish and crappie (NCDWQ, 1996). In 1999, selenium concentrations were not detected in surface water. Concentrations in benthic macroinvertebrates had decreased compared with previous samples but remained above background levels. Selenium concentrations in fish tissue had declined below concentrations causing human risk. The fish consumption advisory was lifted in 2000 (NCDWQ, 2001).

Belews Lake’s recovery can be attributed to sediment focusing (Finley and Garrett, 2007). Focusing occurs when sediment accumulation is greater in deep areas of a lake or reservoir than in the shallows due to sediment resuspension by peripheral wave action, as well as sliding and slumping on steep slopes (Hilton, 1985). Belews Lake has steep slopes and low sedimentation rates that are indicative of sediment focusing (Pers. Comm., K.A. Finley, April 2008). Additionally, Duke Energy has observed depth-dependent Se concentrations in surface sediments collected from depths between 2 and 30 m, indicating higher rates of trace element decline in shallow areas than in deeper sediments (Coughlin et al., 2006). In Belews Lake, Se has been dispersed from bioactive shallows to deep, anoxic waters. Anoxia in deep areas of the lake induces transformation of Se to less bioavailable forms while limiting biological exposure.



HIGHLIGHT 4-6. Natural recovery through contaminant dispersion and transformation in Belews Lake.

P H Y S I C A L D I S T U R B A N C E S	
☆	Natural scour and erosion due to currents, tides, and waves
☆	Storm events
☆	Anthropogenic disturbances, such as propeller wash and vessel traffic
☆	Release and offsite transport
☆	Groundwater efflux
☆	Formation and release of gas bubbles

accumulation. In areas subject to erosion and off-site sediment transport, it may not be possible to identify natural recovery processes using sediment cores to characterize vertical contaminant profiles, historical contaminant releases, and reduced surface sediment exposures. Instead, geostatistical sampling can be used to monitor changes in surface sediment contaminant concentrations with time.

Chemical diffusion, in some cases augmented by groundwater advection, is most relevant to relatively mobile chemicals where soluble transport can contribute to dilution. For example, under aerobic groundwater transport conditions, divalent metals are relatively soluble and mobile. Under reducing conditions, chemical reduction and precipitation can result in their accumulation in sediment, while diffusion and advective transport, particularly under aerobic conditions, can result in reduced sediment contaminant concentrations or can minimize the net sediment accumulation of contaminants via sorption and precipitation. Other relatively soluble contaminants transported via groundwater with low affinity for sediment may behave similarly, such as low-molecular-weight volatile organic compounds. Groundwater migration should consider the relative hydraulic gradient of groundwater transport through sediment. Where contaminant accumulation is associated with the deposition of fine grained sediment, low hydraulic conductivity and correspondingly low transmissivity commonly prevail, limiting the potential for groundwater transport through the sediment bed.

For dissolved contaminants transported via surface water or groundwater advection, it may be reasonable to expect that once the surface water or groundwater sources are controlled, concentrations will dissipate in sediments, leaving only a sorbed or precipitated fraction behind. Following source control, advective processes can continue to desorb or dissolve sediment-bound contaminants, reducing long-term sediment exposures. Therefore, many relatively soluble groundwater contaminants are not commonly addressed as sediment contaminants. Chloroethenes, gasoline releases, and some metals, for example, are generally best addressed by controlling groundwater advective transport.

Key considerations for investigating the natural dispersion processes associated with reduced exposure include:

- Hydrodynamic processes
- Sedimentation processes, including deposition, erosion, and diffusion
- Groundwater transport processes

- Impact on processes that reduce bioavailability and mobility
- Downgradient risks.

Hydrodynamic processes. Hydrodynamic flows and current velocities entering and exiting the site and surface water elevations are important for predicting hydrodynamic behavior under a range of dry and wet weather conditions. Measurement of current velocities and corresponding shear forces informs the understanding of sediment transport potential. Given sufficient information about the hydrodynamics of the system, hydrodynamic shear stress can be quantified mathematically (Ziegler, 2002).

Sedimentation processes, including deposition, erosion and diffusion. Sediment suspension and deposition processes and rates are highly interconnected. Natural sedimentation processes can reduce dispersion by diluting and physically isolating contaminated sediments. Lines of evidence should determine net in-situ sediment deposition, and erosion rates. Lines of evidence to assess sediment stability—such as sediment physical characteristics and settling properties, hydrodynamic conditions, and benthic activity—also should be used to evaluate suspension and dispersion rates. Further, if contaminant transport is predicted, lines of evidence should be developed to understand where and at what concentrations they will deposit.

Groundwater transport processes. Groundwater transport is generally slow in consolidated, cohesive, fine-grained sediment, limiting the potential for contaminant transport via groundwater advection. Thus, in most contaminated sediment environments, groundwater transport is not characterized in detail. However, for relatively soluble contaminants, particularly groundwater contaminants such as gasoline and chlorinated solvents, an understanding of advection processes may be used to calculate the release of chemicals to the water body. Impacts of groundwater advection on dispersion of more persistent sediment contaminants tend to be captured by other lines of evidence such as bathymetric surveys that identify groundwater upwelling areas, pore water chemistry that characterizes surface sediment dissolved chemical concentrations, and surface water sampling of chemicals and sediment loads.

Impact on processes that reduce bioavailability and mobility. Site-specific lines of evidence are required to establish the particular effects of dispersion on contaminant sorption and precipitation processes, and the degree to which these processes contribute to reduced exposures and corresponding risk reductions.

Downgradient risks. Where dispersion is contemplated as an ongoing natural recovery process, resulting exposures and risks to downstream areas and other receiving water bodies must be evaluated. Risk reductions in the source area should be weighed against risks downstream. Effects on water quality and tissue residues along the pathway of dispersing contaminants should be considered, as well as risks in the areas of ultimate contaminant deposition.

Table 4-6 lists lines of evidence that address the various considerations pertinent to processes that reduce contaminant exposure.

TABLE 4-6. Lines of evidence to establish dispersion processes.

Consideration	Lines of evidence
<p><b>Hydrodynamic conditions</b></p>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>■ Assemble site-specific findings on hydrodynamic conditions.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop hydrodynamic models to capture the flow dynamics and the energy regime of the site, to support advective transport calculations and sediment transport characterizations.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>■ Measure bathymetry to establish the morphology of the site, which controls the energy regime experienced and boundary flow conditions.</li> <li>■ Measure water elevations upstream and downstream of the site to establish hydrodynamic boundary conditions; evaluate normal flow conditions, storms, diurnal flows, tidal or seiche conditions. (Local tidal gauges are often useful for long-term data.)</li> <li>■ Measure flow velocities to establish site-specific velocities in deep and relatively shallow areas.</li> <li>■ Measure near-bed current velocities to establish flow conditions at the sediment-water interface.</li> </ul>
<p><b>Sedimentation processes including deposition, erosion, and transport in the water column</b></p>	<p>Literature review:</p> <ul style="list-style-type: none"> <li>■ Assemble site-specific findings on sediment contaminant-specific fate and transport considerations.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>■ Develop sediment transport models to simulate sediment erosion, deposition, and transport, to determine sources and sinks of sediment contaminants.</li> <li>■ Develop a sediment mass balance model to examine</li> </ul>

TABLE 4-6. Lines of evidence to establish dispersion processes (continued).

Consideration	Lines of evidence
<p><b>Sedimentation processes including deposition, erosion, and transport in the water column</b></p>	<ul style="list-style-type: none"> <li>▪ inputs and outputs of sediment at major boundaries of the system.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>▪ Characterize fluvial morphology and examine sediment bed forms to characterize depositional and erosional behaviors.</li> <li>▪ Conduct geochronological sediment core profiles to examine historical deposition rates, or lack thereof.</li> <li>▪ Measure vertical sediment contaminant profiles to determine whether persistent historical deposits exist.</li> <li>▪ Measure sediment loads and corresponding contaminant conditions entering and exiting site boundaries to understand contaminant fate and transport.</li> <li>▪ Measure sediment stability using sediment flumes that directly measure sediment shear strength and analytically compare with hydrodynamic shear forces.</li> </ul>
<p><b>Groundwater advection and contaminant transport</b></p>	<p>Literature review and historical data:</p> <ul style="list-style-type: none"> <li>▪ Assemble findings to establish the potential impact of groundwater advection on contaminant transport.</li> <li>▪ Identify site-specific studies that describe near-shore groundwater transport behavior.</li> </ul> <p>Modeling:</p> <ul style="list-style-type: none"> <li>▪ Incorporate results of site-specific investigations to assess the relative importance of groundwater advection to the transport of sediment contaminants.</li> <li>▪ If warranted, develop a groundwater transport model to describe contaminant transport.</li> </ul> <p>Site-specific investigations:</p> <ul style="list-style-type: none"> <li>▪ For mobile contaminants, measure groundwater flux rates, and use measured or estimated partitioning to establish desorption rates and corresponding aqueous concentrations and exposures.</li> <li>▪ Measure site-specific hydraulic conductivity values in consolidated sediment to calculate groundwater transport rates through the sediment bed.</li> <li>▪ Use bathymetry to identify potential groundwater breakthrough areas that could convey the majority of groundwater, bypassing much of the sediment bed; this is particularly relevant to navigationally dredged areas where historical dredging may have cut into an underlying aquifer.</li> </ul>

## 4.6 Process Interdependencies and Modeling Considerations

The four major natural recovery processes are interrelated, and no single process occurs unaccompanied by another. Sedimentation and contaminant burial are directly related to erosion potential and the potential for off-site contaminated sediment transport; moreover, off-site transport at one location is likely to result in sedimentation and accumulation of sediments at a downstream location. Sedimentation/burial and sediment suspension processes also can influence chemical transformation kinetics, as transformation is often controlled by geochemical characteristics such as redox potential, pH, and temperature. All processes are integrally related to contaminant mobility, and all four influence contaminant exposure, bioavailability, and risk.

Diagnostic modeling of contaminant transport behavior can greatly facilitate understanding the complex relationships among the multiple physical, chemical, and biological processes that influence contaminant bioavailability. Hence, modeling is strongly recommended as a tool to understand these relationships. As always, the scope, the level of detail and cost of the models all should be commensurate with the magnitude and complexity of the site. Direct measurement of contaminant bioavailability can establish existing exposure and risk levels and supply corroborating evidence for models. Ideally, modeled relationships mimic concentrations measured in the environment to explain contaminant behavior and kinetics.

## 4.7 MNR Lines of Evidence Checklist

The following checklist identifies considerations for developing lines of evidence to evaluate the feasibility of MNR. Note that the extent of investigation of each potential natural recovery process will be site-specific, depending on the relative importance of each process and the complexity of the site.

CHECKLIST 4-1. Lines of evidence considerations.

***In view of the decisions currently under consideration within the project:***

***1. Have sources at the site been sufficiently controlled to support effective natural recovery? Consider the following components:***

- Historical sources of chemical inputs to the site.
- Potential for ongoing sources.

- Background conditions including hydrodynamics that may act to recontaminate the site or limit the rate or extent of site recovery.
- Uncertainty related to ongoing source control or elevated background conditions, and how these conditions will influence the effectiveness of MNR as a remedy relative to other remedies, including capping and dredging.

**2. Do historical data show decreasing exposures over time? Consider the following components:**

- If available, determine whether historical data suggest that exposures and/or tissue concentrations are decreasing over time.

**3. What evidence exists of chemical transformation at the site? Consider the following components:**

- Literature regarding relevant chemical transformation processes and relative toxicity of transformation products.
- The extent to which ancillary chemistry such as redox reflects conditions that support the potential for chemical degradation or transformation at the site.
- Site-specific chemical degradation and/or forensics studies to identify transformation processes and byproducts, if necessary to reduce uncertainty and validate literature-reported processes and rates.
- Potential for reversal of chemical transformation reactions (e.g., for metals) due to plausible changes in physicochemical conditions.
- Update the CSM for this process and, if applicable, incorporate relevant data into the natural recovery model for the site.

**4. What evidence exists for reduced chemical bioavailability and mobility at the site? Consider the following components:**

- Literature and historical data regarding bioavailability and mobility of relevant site COCs and conditions.
- COC and site-specific conditions and controlling factors that are most likely to influence bioavailability and mobility at the site.
- Site-specific evaluations of chemical bioavailability, such as pore water analyses, organic carbon data, and/or in situ/laboratory toxicity or chemical bioaccumulation studies, if necessary to reduce uncertainty and validate historical and literature-reported estimates.
- Potential for reversal of chemical sequestration due to plausible changes in physicochemical conditions.
- Update the CSM for this process and, if applicable, incorporate relevant data into the natural recovery model for the site.

**5. What evidence exists of physical isolation of contaminants at the site? Consider the following components:**

- Literature and historical hydrodynamic, bathymetric, chemical, or sediment transport data to determine if depositional processes are likely to result in contaminant burial and risk reduction at the site.
- Sediment cores for vertical contaminant profiles during site investigation to provide initial evidence of contaminant burial.
- Evaluate sediment core profiles (e.g., contaminant profiles and/or radiological profiles such as <sup>210</sup>Pb and <sup>137</sup>Cs) to identify the occurrence and frequency or severity of historical sediment erosion events.

- Temporal trends in surface sediment contaminant concentrations, if sufficient historical data are available.
- Carry out additional site-specific assessment, including sediment age dating, sediment traps, and sediment stability measurements, if necessary to reduce uncertainty and validate historical and literature-reported estimates.
- Hydrodynamic modeling to evaluate site-specific sediment transport, deposition, and erosion processes.
- Characterization of sediment stability through hydrodynamic modeling, direct measurement of sediment shear strength, and/or sediment transport modeling. Consider sediment stability under normal and high-energy hydrodynamic events. Also evaluate wind or other forces that can influence flow conditions and bottom shear stress.
- Update the CSM for this process and, if applicable, incorporate relevant data into the natural recovery model for the site.

**6. What evidence exists of natural recovery via chemical or sediment dispersion processes? Consider the following components:**

- Evaluate literature and historical hydrodynamic, bathymetric, chemical, or sediment transport data to determine if dispersion processes are likely to result in risk reduction at the site.
- Incorporate spatial mapping of contaminant deposits into the site investigation to provide initial evidence of contaminant dispersion.
- Carry out additional site-specific assessment such as sediment age dating, sediment traps, and sediment stability measurements, if necessary to reduce uncertainty and validate historical and literature-reported estimates.
- For sites with evidence of lateral contaminant dispersion, identify likely downstream depositional areas and associated risk.
- For mobile contaminants, evaluate water-borne pathways of dispersion such as tidal pumping or groundwater advection.
- Update the CSM for this process and, if applicable, incorporate relevant data into the natural recovery model for the site.

**7. To what extent do process interactions influence natural recovery? Consider the following components:**

- Evaluate the updated CSM to determine whether and which process interactions are likely to influence recovery at the site.
- Carry out evaluation of process interactions using the natural recovery model for the site, if necessary to accurately predict recovery and reduce uncertainty in MNR remedy effectiveness.

**8. How effectively will natural recovery processes reduce risks? Consider the following components:**

- Over what time scale natural recovery processes such as sedimentation and chemical degradation will manage risk.
- Rate and magnitude of risk reduction achieved by MNR compared to that achieved by engineered remedies such as capping or dredging.
- Reasonably anticipated future events, such as navigational dredging, removal of dams or other structures, or major storms that have the potential to affect natural recovery processes or natural recovery rates.

- ❑ Modeling exercises, as appropriate, to understand the effect of reasonably anticipated future events on natural recovery processes at the site.

## 5 Numerical Models

*Numerical models in the context of MNR, model types and complexity, management issues, and good-practice guidelines*

Numerical models can help answer sediment management questions, such as: What is the extent of historical and future contaminant migration? Do offsite contaminant sources negatively impact the site and the proposed remedy? How vulnerable are buried sediments to episodic scour events? What is the potential for natural recovery processes to reduce contaminant exposures, and over what time frame? How will proposed remedies affect physical environmental conditions?

Model development should be based on a CSM for the site, starting simply and adding complexity as needed. This progression commonly begins with a hydrodynamic model that describes the flow of water in the system, followed by models that describe sediment transport, chemical transport, and biological uptake. Managing model complexity in this manner facilitates more reliable forecasts by carefully and progressively incorporating and constraining process rates and process coefficients based on physical principles and direct field measurements.

Model development goes hand-in-hand with CSM development, with the numerical model evolving as the CSM evolves. Model development involves identifying and incorporating site-specific processes and parameters that are important to understanding current site behavior and predicting long-term risk. Modelers should consider changes in site-specific processes over time, such as changes in sediment loading due to erosion control, or changes in contaminant partitioning behavior due to weathering.

A critical assessment of uncertainty in model projections is important for effective decision making. Considerations related to regulatory and community acceptance include model transparency, successful applications at other sites, and (where appropriate) peer review.

**T**o evaluate MNR feasibility, information about source control and site-specific processes, including the ongoing fate and transport processes driving recovery, are captured in the CSM. Numerical modeling involves incorporating the underlying pathways and relationships documented in the CSM—as well as supporting lines of evidence demonstrating historical trends—into a quantitative, mathematical model that captures the response of the system to natural processes (USEPA, 2008b; NRC, 2007b; Dekker et al., 2004).

CHAPTER CONTENTS	
☆	Evaluating MNR with Numerical Models
☆	Determining Model Complexity
☆	Key Elements and Constraints
☆	Model Uncertainty
☆	Selecting a Modeling Framework
☆	Numerical Modeling Checklist

## 5.1 Evaluating MNR with Numerical Models

Showing the degree to which observed risk reductions can reasonably be expected to continue into the future is important in determining whether MNR will be an effective sediment management alternative. A well-constructed numerical model can perform this function, capturing site-specific physical, chemical, and biological processes that contribute to understanding present and future risk attenuation and natural recovery. Numerical models are used to evaluate processes that influence future levels of recovery and the time required for recovery.

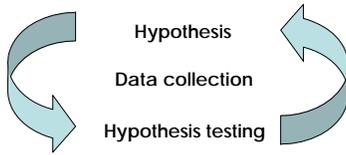
In addition to prediction, the numerical model serves at least three other distinct purposes that may aid in evaluating MNR, including (Martin and McCutcheon, 1999; Chapra, 1997; Thomann and Mueller, 1987):

- Hypothesis testing
- Data synthesis
- Directed data gathering.

During CSM development, various hypotheses about site behavior are developed and may be tested by the numerical model using measured or literature-based site parameters. The model plays a diagnostic role as questions are asked about contaminant distribution, the degree of sediment deposition or erosion in response to a particular event, or the fate and transport of chemicals in the aquatic environment and food chain. Over time, as more data are gathered, the questions asked necessarily become more specific, integrative, and often more complex. How has contaminant distribution changed over time? What have the net effects of sediment deposition and erosion been with time? How do biota contribute to mixing of the sediment bed and biomagnification in higher trophic levels? More complex questions call for testing hypothesized outcomes against an integrated picture of site behavior constrained by different lines of evidence across different media. Numerical models, used to integrate multiple physical, chemical, and biological processes, effectively become a hypothesis testing framework. Important processes are highlighted and less important processes screened out, in concert with continual CSM refinement.

Data synthesis and review are often overlooked functions of numerical models. Modeling and data management functions are complementary; increasingly, models are developed within a database framework. Models facilitate a higher level of data review than is typically possible with a

EVALUATING HYPOTHESES (HILL 1965)	
☆	Co-occurrence
☆	Temporality
☆	Specificity of cause
☆	Evidence consistency
☆	Evidence coherence



project database, by allowing large amounts of data to be considered in terms of consistency and conformity to the expected physical behavior of the system. These data include (but are not limited to) contaminant concentrations in sediment, water, and biota; external solids and contaminant loads; decay and sorption rate coefficients; hydrodynamic conditions; sediment transport, including sediment bed stability and deposition and scour potential; and biological uptake and biomagnification. This data synthesis function is particularly relevant to MNR because of the broad range of lines of evidence that are often involved and the reliance on underlying natural processes for remedy success.

Models add an important level of data review by placing physical constraints on the range of acceptable data. The data management and review function is typically assigned to a project database with built-in quality assurance functions and geographic information system capabilities. By incorporating a level of review that goes beyond the project database, a model has the potential to highlight problems not revealed by typical data quality assurance and control practices. Further, the modeler trying to calibrate a model with unrealistic values is compelled to resolve issues raised by suspect data.

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*Models add an important level of data review by placing physical constraints on the range of acceptable data.*

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Models also play a role in directing the collection of future data. For real-world systems in which fate and transport processes driving recovery are complex and variable, simple extrapolation of historical trends may not be appropriate. The process of calibrating a well-constructed model to environmental data generates feedback about the relative importance of system parameters for achieving long-term recovery goals, contributing to the efficiency of data gathering campaigns. At each stage of site investigation, the model can be used to identify gaps in the knowledge of the site and can help to identify places where further sampling will have the most beneficial effect. Models also assist with directed data gathering by helping to determine whether the financial and resource costs of data collection justify the benefits (i.e., anticipated reduction of uncertainties, leading to more confident prediction of future conditions).

## 5.2 Determining Model Complexity

**S**ediment sites are subject to many different types and degrees of contamination and can be exposed to a broad range of meteorological and hydrodynamic conditions. For example, contaminated sediments may be located in rivers, lakes, bays and estuaries, or dam impoundments and may be impacted by tidal or seiche effects, high flows due to spring runoff, wind-generated waves and

currents or by human activities such as dam and lock maintenance, boat traffic, or navigational dredging. Model complexity generally depends on the overall complexity of the system being studied and the needs of decision making in regard to model accuracy. The goal of this section is to present a simplified process for identifying and selecting the level of model complexity that is most appropriate for a particular site and set of management questions.

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*Model development is based on the CSM and proceeds in parallel with CSM refinement, starting simply and adding complexity as needed.*

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A common obstacle to model selection is the perception that a complete, site-wide, multicompartiment, and multicontaminant model needs to be developed at the outset of a project. Much more typically, model development is based on the CSM and proceeds in parallel with CSM refinement, starting simply and adding complexity as needed. This building of complexity often proceeds sequentially through the major compartments of the system, starting with water, then considering solids and sediments, then contaminants associated with solids in the water, and finally considering biota and biota-related contaminant partitioning and accumulation. This approach allows for a progressive understanding of the system to be developed with the opportunity to create limited models that go only as far as is needed to elicit meaningful answers to management questions as they develop. For example, a basic understanding of hydrodynamics and sediment stability can offer a great deal of insight into the way a site functions and the potential effectiveness of a proposed remedy, even in the absence of a contaminant fate and transport model.

Figure 5-1 classifies different modeling approaches in progressively more complex tiers. The first tier includes simple empirical and statistical models useful for detecting statistically significant trends in contaminant exposure, exploring and testing for correlations between environmental variables (e.g., river discharge, temperature, water column contaminant concentrations, contaminant levels in biota), and making limited projections of future system behavior. Simple statistical models are inherently limited in their ability to predict future conditions. Such models typically are “fits” to available historical and contemporary data, and as such are unconstrained by the physics of the system being simulated. Using statistical empirical trend analyses to extrapolate a fitted model beyond a relatively short period will produce erroneous predictions in a system whose drivers are subject to change with time.

The second tier builds on the first by using observations about trends and correlations, combined with process understanding, to further develop the conceptual model of the system. By exploring different dependencies and

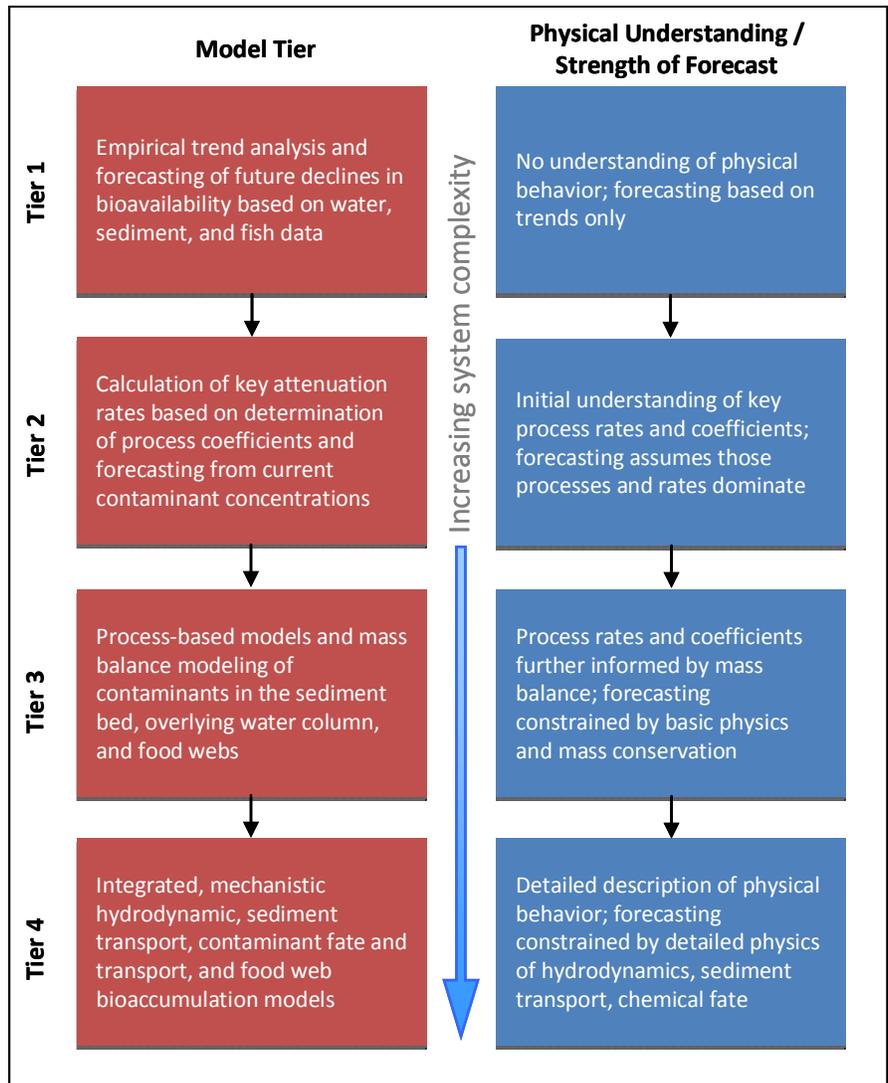


FIGURE 5-1. Tiers of increasing model complexity.

drawing inferences from them, conclusions can be reached about the behavior of the system and the likely factors driving ongoing exposure. For example, it may be possible to identify trends in fish contaminant concentrations over time, and link these trends to known differences in feeding habits of the fish species or changes in surface sediment contaminant concentrations, thus determining the degree to which different fish species are affected by contaminant trends in the sediment bed. Similarly, measured historical trends in water column or sediment bed contaminant concentrations can be linked to known contaminant mass transport processes such as surface water or groundwater flows, natural sedimentation processes, ongoing primary or secondary sources, or contaminant transformation processes. Such observations superimpose general knowledge of the physical behavior of contaminated sediment

systems on site-specific empirical observations and begin the process of quantifying process coefficients and rates, which leads to a more formal numerical model.

Tier 3 (process-based and/or mass-balance) modeling involves organizing knowledge of different system compartments (e.g., surface water hydrodynamics, solids characteristics, and contaminant concentration distributions in solids and biota) into a quantitative framework that measures fluxes into and out of these compartments and associated rates of accumulation within each compartment. This imposition of mass balance and physical process limitations places a constraint on models that is absent in the lower tiers and makes it possible to answer quantitative questions that are critical to an MNR evaluation, such as:

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*The imposition of mass balance and physical process limitations on the model makes it possible to answer quantitative questions that are critical to an MNR evaluation.*

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- What is the rate of accumulation of solids in the sediment bed?
- What is the rate of suspended solids and contaminant export downstream?
- To what extent does erosion of the banks contribute to the solids and contaminant mass balance?
- How will exposures change over time in response to natural recovery processes?

An example of a Tier 3, one-dimensional mass balance model of phenanthrene (a PAH) for the surface sediment layer at two locations in Pearl Harbor (Chadwick et al., 2006) is shown in Figure 5-2. For Site A, the results suggest a system dominated by the settling of particle-bound phenanthrene, while Site B indicates a system in which inputs from settling and advection are roughly balanced by losses from degradation. In these scenarios, the contaminated flux via sedimentation at Site A is greater than the losses due to contaminant degradation, whereas at Site B, contaminant losses due to degradation are greater than the contaminant flux via sedimentation. Thus, MNR at Site A would benefit from increased source control, while conditions at Site B are more immediately amenable to MNR.

The complexity of the site, the scope of decisions being made, and the specific management questions being asked may necessitate a more detailed modeling evaluation, often to improve understanding of specific components of the system. A Tier 4 model is an extension of the Tier 3

mass-balance model that incorporates more detailed, fine-scale and multidimensional hydrodynamics; a more mechanistic description of sediment transport and sediment bed handling; a more mechanistic description of contaminant partitioning, transformation, and other fate and transport and bioaccumulation processes; and other supporting modeling evaluations such as simulation of wind-wave dynamics, localized bed or bank erosion, and extreme event modeling (Erickson et al., 2004).

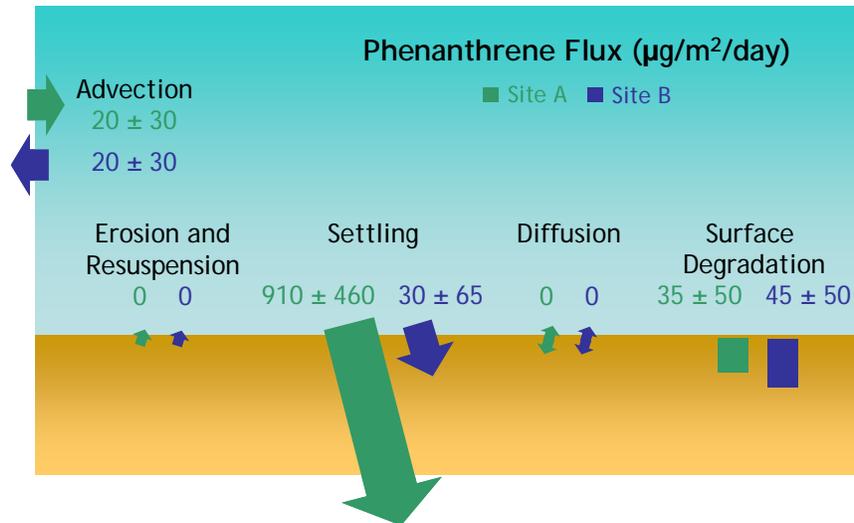


FIGURE 5-2. One-dimensional mass balance model.

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*How does each refinement of the model contribute to a better understanding of sediment management questions?*

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A Tier 4 model is shown in Figure 5-3 (Chadwick et al., 2007). In this application, a three-dimensional model was developed to examine the linkage between upstream sources in an urban-industrial watershed that drained to San Diego Bay. The model generated potential depositional footprints for particles and associated contaminants for estimation of watershed source control requirements. Tier 3 and Tier 4 models provide increasingly detailed descriptions of processes affecting MNR and have correspondingly higher requirements for supporting data. The need for data support is discussed further in Section 5.3.

While the foregoing examples focus on hydrodynamic and sediment transport models, fish bioaccumulation models also vary greatly in their complexity. Statistical associations between organic carbon normalized sediment contaminant concentrations and lipid normalized biota concentrations, e.g., biota-sediment accumulation factors (BSAFs) are the simplest. These represent the relationship between contaminants in sediment and biota at the time and under the conditions measured.

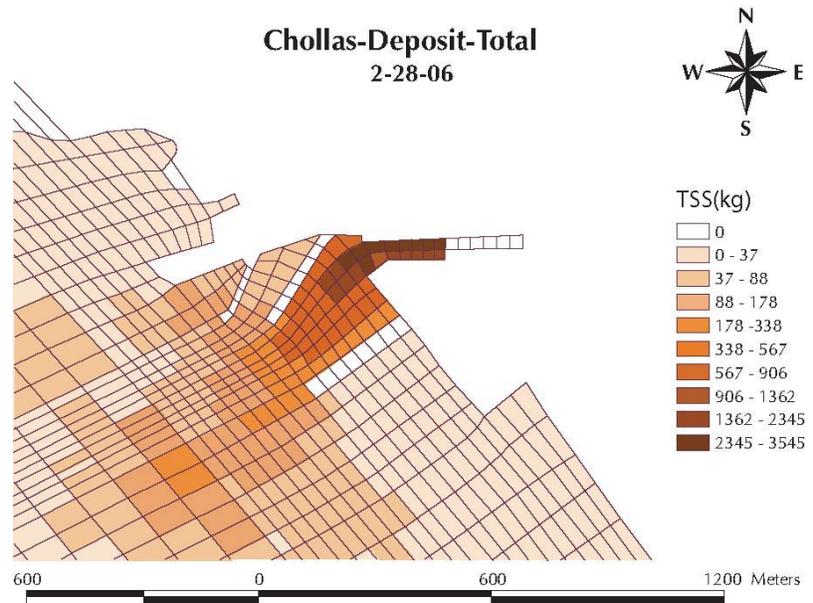


FIGURE 5-3. Depositional footprint for particle releases from the Chollas Creek watershed to San Diego Bay.

Because BSAFs are not considered to be predictive for future, post-remediation conditions, more complex kinetic food web models may be needed to predict ecological responses to natural recovery processes over time. Food web bioaccumulation models incorporate contaminant exposure and uptake pathways (water and diet) along with elimination (e.g., excretion and metabolism) and dilution (growth) pathways to estimate biota concentrations. Simpler steady state applications assume contaminant equilibrium among model compartments while dynamic (time-varying) applications can use linked hydrodynamic, sediment transport, and contaminant transport models to vary environmental contaminant concentrations over time. Dynamic models modify fish tissue concentrations over time on the basis of their exposures, uptake, and elimination. With the increasing complexity comes a greater reliance on estimated and site-specific measured model parameters that describe biologic and chemical process phenomena in organisms. Where model parameters are unavailable or cannot be measured directly, these models can be “trained” to depict current conditions by calibrating their output to measured fish tissue concentrations and validating their predicted output using an independent fish tissue data set not included in the calibration data set. The appropriate level of model complexity will depend upon the decisions to be made, the strength of data to support modeling, and the time frames and future conditions to be evaluated. When limited empirical data and site-specific information is available on the biological relationships being modeled, simpler approaches are often better; greater

model complexity cannot compensate for incomplete site characterization.

Taking the progressive approach described above requires a continual assessment of “how much model is enough?” or, more specifically, how each additional refinement of the model contributes to a better understanding of the lines of evidence to the management questions that are being asked. Table 5-1 illustrates how these questions could be addressed at a typical contaminated sediment site. The model complexity (vertical axis) and range of management questions (horizontal axis) combine to form a matrix of possible outcomes, progressing from no answers to answers that offer qualitative guidance, to quantitative answers supporting management decision making. This matrix outlines a useful process for the planning of any contaminated sediment assessment project: developing a list of likely management questions to be addressed over the life of the project, outlining a progression of modeling or other analytical efforts to be developed to address management questions, and thinking about the degree of specificity that might emerge.

Table 5-1 is useful to construct and evaluate early in a project as a basis for discussing how models would be developed and where modeling effort might be focused. The matrix helps guide how modeling is to be conducted, how models will be used to answer specific questions, and the expectations of models at each stage of the project. Highlight 5-1 discusses how models of varying complexity were used in investigations of the Fox River in Wisconsin.

In addition to the potential complexity of the site, determination of model complexity is also governed by resources—the resources available to conduct a project, and the resources at risk due to the scope of the decisions being made. Figure 5-4 illustrates a commonly observed relationship between a model’s utility or reliability and its complexity (DePinto et al., 2002).

At a certain level of model complexity (and corresponding resource investment in modeling effort), there is a point of diminishing returns. Just short of this point, on the “knee” of the curves shown in Figure 5-4, there is an optimal point, where the model offers the most economical blend of utility, reliability, and complexity. The two curves represent different levels of resources that might be typical of different modeling efforts. In an environment in which data for model calibration and validation are relatively abundant (and the stakes related to a decision are high), a higher level of model reliability may justify greater complexity and dollars spent (Point B). Such a model typically addresses a more complex set of management questions than can be addressed at operating

SITE - SPECIFIC PROCESSES	
☆	Water column advection
☆	Air deposition
☆	Sediment bed dynamics
☆	Solid-water partitioning
☆	Hydrodynamics
☆	Sediment geochemistry
☆	Deposition/burial
☆	Geomorphologic changes
☆	Watershed solids loading
☆	Erosion/resuspension
☆	Biodegradation
☆	Algal production
☆	Diffusion
☆	Contaminant weathering
☆	Contaminant transformation
☆	Groundwater advection
☆	Volatilization
☆	Bioaccumulation
☆	Bioturbation

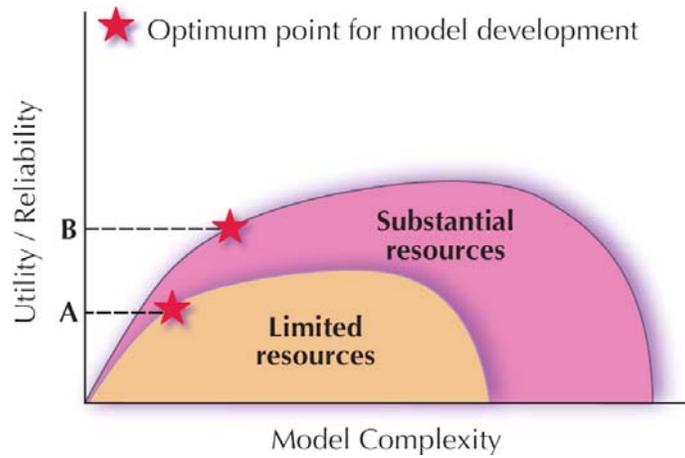


FIGURE 5-4. Trade-offs between model utility and complexity.

Point A. For example, if two remedies, such as dredging or MNR, cannot be distinguished from one another in terms of risk reduction, costs, and other objectives due to uncertainties associated with future projections, the potential cost differences between these remedies may argue forcefully for additional modeling investment to reduce project uncertainties. In an atmosphere of more limited resources (with less costly consequences), a lower operating point (A) may be appropriate.

The right side of the curve in Figure 5-4 shows that beyond a certain threshold, additional complexity actually begins to degrade the utility of the model. Many engineers, scientists, and site managers can recall a modeling effort that became so cumbersome and lacking in transparency that the model lost its value as a tool for decision making. An overspecified model—one with more processes and coefficients than can be constrained with the available dataset—usually does not offer guidance useful for decision making.

### 5.3 Key Elements and Constraints

Regardless of the level of modeling complexity selected, some basic rules apply for ensuring that the model is true to the data and able to predict future behavior with a reasonable level of certainty. A well-constrained model includes the elements described in this section, which can be considered as guidelines for best practices (Glaser and Bridges, 2007; Pasqual et al., 2003; Martin and McCutcheon, 1999; Chapra, 1997):

TABLE 5-1. Framework for relating model development to management questions.

Key: Qualitative prediction Screening-level quantitative prediction Quantitative prediction

		← <b>Increasing Model Complexity</b> →					
		Water		Water + Solids		Water + Solids + Contaminants	Water + Solids + Contaminants + Biota
Model		<i>Simple Statistical Hydrodynamic</i>	<i>Detailed Numerical Hydrodynamic</i>	<i>Hydrodynamic with Particle Transport</i>	<i>Mechanistic Sediment Transport</i>	<i>Contaminant Fate and Transport</i>	<i>Contaminant Bio-Uptake and Accumulation</i>
<b>Technical Benefits</b>		Direction of flow Factors governing hydraulics at the site	Direction and magnitude of flow	Pathway of suspended sediment transport	Pathway and degree of suspended sediment transport	Pathway of dissolved and sediment-associated contaminant transport	Degree of exposure, partitioning, and accumulation of contaminants in biota
<b>Management Questions and Related Model Output</b>	<b>Contaminant Migration</b> What are the historical extent and future risks of off-site migration? Do multiple sources affect the site? Will remediated areas be recontaminated?	Hydraulic connection of site areas with historical release area	Clearer links between sources and depositional areas Potential for resuspension of site contaminants	Potential sediment transport pathways	Extent to which sources have contributed/will contribute to on- or off-site sediment accumulation	Extent to which sources have contributed/will contribute to on- or off-site contaminant accumulation and water column loads	Extent to which sources have contributed/will contribute to contaminant uptake and bioaccumulation
	<b>Extreme Weather Effects</b> How will extreme weather events affect buried contaminants and the proposed remedy?	Systems's historical response to hydrological events	Likelihood that resuspension and disruption of remedy will occur	Likelihood that sediment deposition or scour will occur Pathway of sediment transport following resuspension	Degree of sediment deposition or scour Pathway of sediment transport following resuspension	Degree of sediment deposition or scour Pathway of sediment and contaminant transport following resuspension	Degree of sediment deposition or scour Implications for exposure and bioaccumulation
	<b>Historical Dredging</b> How has historical dredging affected site contamination and sediment?	--	--	Pathway of sediment transport following resuspension due to dredging	Pathway of sediment transport following resuspension Changes in sediment stability due to dredging	Pathway of sediment and associated contaminant transport following resuspension Changes in sediment stability due to dredging	Pathway of sediment transport and associated contaminant transport and bioaccumulation Changes in sediment stability due to dredging
	<b>MNR Evaluation</b> What is the potential for natural recovery at the site due to deposition of clean sediments?	--	Likely depositional areas	Depositional pathways	Degree of sediment accumulation	Degree of sediment accumulation Effect of deposition on concentrations in surficial and buried sediments	Degree of sediment accumulation Effect of deposition on body burdens in biota
	<b>Remedy Comparison</b> How will proposed remedies affect environmental conditions off site?	--	Effect on circulation patterns, flow velocities important to aquatic life	Effect on circulation patterns, flow velocities important to aquatic life	Effect on circulation patterns, flow velocities, sediment deposition or scour important to aquatic life	Effect on circulation patterns, flow velocities, sediment/ contaminant deposition or scour	Effect on circulation patterns, flow velocities, deposition or scour, aquatic, human, and wildlife exposures

## NUMERICAL MODELING OF THE LOWER FOX RIVER IN SUPPORT OF CSM DEVELOPMENT AND REMEDY SELECTION

Numerical models were used throughout the Lower Fox River/Green Bay, Wisconsin, investigation for insight into river and bay hydrodynamics, sediment transport, and contaminant transport. Models were developed for both the historical behavior of the river and prediction of future changes in contaminant levels and associated risk. Models also explored current conditions, building understanding of the function of present-day river hydrodynamics, sediment bed dynamics, solids loadings and transport, and contaminant transport and sequestration.

Over the duration of the Fox River investigation, models were progressively refined to generate answers to increasingly specific questions about river behavior, contaminant transport, physical and chemical stability of in-place contaminants, and the viability of alternative proposed remedies. Some examples of models used on the Fox River are as follows:

*Hydrodynamic models:* Several different hydrodynamic models were developed for different purposes, including simple one-dimensional steady-state models, one-dimensional dynamic models, and more detailed 2- and 3-dimensional models of areas of interest within the Fox River/Green Bay system. Hydrodynamic models quantified the relatively slow hydrodynamics of Little Lake Butte des Morts, the upstream most operable unit (OU1), the relatively fast moving riverine hydrodynamics of OU2 and OU3, the relatively slow hydrodynamics where the river transitions to Green Bay and Lake Michigan downstream of DePere Dam (OU4), and the large-lake hydrodynamics of Green Bay itself (OU5) (e.g., LimnoTech, 2002a; Jones et al., 2001; DePinto et al., 1993).

*Simple statistical and process models of solids loadings:* In order to develop an understanding of the magnitude, seasonality, and long-term trending of solids loads to the lower Fox River and Green Bay, simplified models of solids loadings were developed using a variety of methods. These models included statistical approaches (e.g., Beale's Unstratified Ratio Estimator (BURE), linear regression models), spreadsheet-based primary production models, and simplified watershed runoff models (e.g., LimnoTech, 1999).

*Sediment and Contaminant Transport Models.* Models were developed by both the potentially responsible party (PRP) group and the Wisconsin Department of Natural Resources, using a period of relatively intensive data collection in the late 1980s and 1990s as a calibration period, and forecasting future recovery for several decades (LimnoTech 2002a). While the PRP group and regulatory agency models differed in their predictions of the rate of long-term recovery, the models helped to establish common elements in the conceptual models of the two groups. The models established the four operable units as distinct in terms of transport characteristics and served as a framework for discussions about the degree to which sediment transport, erosion, deposition, and burial contributed to contaminant movement or stability in each reach.

The ROD issued in 2003 and amendments in 2007 and 2008 were strongly influenced by the conceptual model development and numerical modeling that accompanied it. The varying hydrodynamic and sediment transport characteristics of the different Fox River reaches made a strong case for unique approaches to each reach, including the selection of an MNR alternative for OU2 and OU5 (Shaw, 2006; USEPA, 2003e; WDNR and USEPA, 2003).

- Data support, including measurement of relevant loads, rates, partitioning, and physical coefficients.
- Consideration of relevant temporal and spatial scales.
- Simulation of key processes.
- High-quality, transparent calibration.
- Model confirmation/validation.
- Understanding of major sources of uncertainty.
- Stakeholder acceptance and peer review.

Data support. Fundamentally, a model must be well-supported by data. The quality and representativeness of the dataset supporting a model is as important as the structure and quality of the model itself; higher data quality and greater representativeness reduce model uncertainty, as described in Section 5.4. The dataset used to develop a model can include many different environmental variables and uses that support the CSM elements described in detail in Chapter 4. The specific measurements and spatial and temporal extent of measurements are highly site-specific but will often include information on the magnitude and type of solids transported through the system, the characteristics of the sediment bed, and the sources, sinks, and transport characteristics of contaminants of interest.

Consideration of relevant temporal and spatial scales. Ideally, numerical model development goes hand-in-hand with CSM development, and the model evolves—with the CSM—as understanding of the system changes. Possibly the most significant component of model development is identifying and incorporating site-specific processes and coefficients that are relevant to the use and reliability of the model for predicting long-term risk. This requires a level of confidence (informed by system understanding) that future conditions and operative processes will be similar to conditions and processes encountered during model calibration, or that the model sufficiently represents changing processes to account for the future.

A commonly encountered example of such a changing system is a river with a history of high solids loading in the 1960s and 1970s, and then a decreased solids loading rate as watershed erosion controls increased in the 1980s and 1990s. A model representing such a system would need to be calibrated to data obtained during the loading period, with a well

supported representation of the solids and contaminant sourcing, water column transport, and sediment deposition processes operative during more recent loading periods, including present-day and future conditions. A description of system performance in more recent time periods would require a representation of the system's changing solids loads, long-term sequestration of buried materials, vulnerability of buried materials to short-term resuspension under extreme flow conditions, and likely changes in erosional or depositional areas of the river. Over time, as the sediment bed consolidates and as gross solids transport processes decrease in importance, diffusion processes, chemical sequestration, and contaminant decay may also become increasingly relevant to the long-term recovery prediction.

Simulation of key processes. Models supporting MNR evaluations often are used to predict long-term reductions in exposure due to processes that operate on annual and even decade-long scales, as well as very short-term changes to the sediment bed that occur in response to extreme meteorological or anthropogenic events, ranging from ship traffic and propeller wash to dam removal or other structural changes to the river. Ultimately, a model may need to incorporate the combined effects of changes in contaminant loadings, biological and chemical degradation, and natural transport and mixing processes that occur over a wide range of spatial and temporal scales.

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*Model confirmation and validation increase confidence in predictions of site behavior.*

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Model calibration. Calibration involves identifying important metrics of model performance, usually as points of comparison with data, and varying input parameters until an optimal fit to the predetermined set of calibration metrics is achieved. Less common but equally important is model confirmation or validation, in which a calibrated model is compared with an independent data set to evaluate the model's predictive capacity for a dataset independent of the calibration data. By testing model robustness, model confirmation and validation increase confidence in the ability to predict site behavior outside of the temporal or spatial domain under which the model was calibrated.

Stakeholder acceptance. Building stakeholder acceptance is another key element of good modeling practice. The use of models that are well-known and have an established track record of applications on sites familiar to the regulatory and stakeholder community makes it much easier to develop confidence in the validity of model predictions. The likelihood of stakeholder acceptance can be increased by encouraging technical interactions between all parties at an early stage of model development, preferably before the work of model selection, construction, and calibration and validation is complete.

For large systems where considerable resources are devoted to model development, scientific peer review by a qualified group of experts can ensure a high level of technical rigor, which in turn increases confidence in model conclusions. Peer review fosters openness and transparency, which promotes greater technical understanding of the model and in turn increases the likelihood of public and regulatory acceptance of model results.

## 5.4 Model Uncertainty

All models are to some degree uncertain in that they provide an incomplete representation of the reality they attempt to portray. It is important to recognize model limitations, and—to the extent possible—categorize and quantify uncertainties presented by such limitations. Figure 5-5 summarizes the major sources of analytical modeling uncertainty, composed of both deterministic and nondeterministic components.

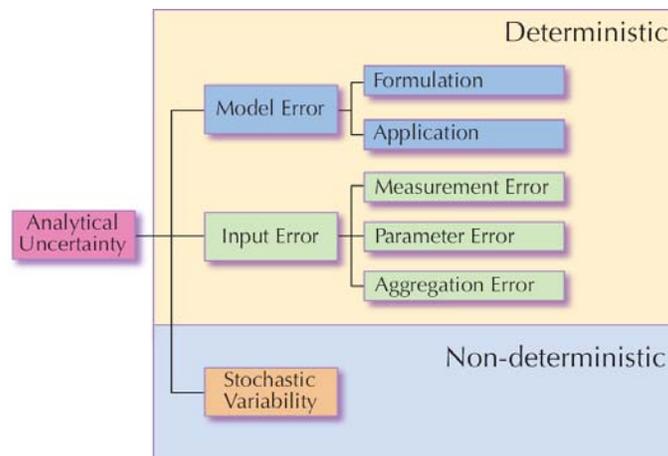


FIGURE 5-5. Components of analytical uncertainty.

Deterministic components of uncertainty include error in the model itself (both the formulation and application of the model) and errors in the inputs that drive the model (error in measurement, errors in parameter estimation, and errors in the aggregation [averaging] of inputs across temporal or spatial scales). Nondeterministic uncertainty includes sources of uncertainty that are inherent to natural systems and are not controllable (stochastic variability in environmental parameters and spatial heterogeneity).

Numerical models should recognize, categorize, and—to the extent possible—quantify sources of uncertainty. This is of particular importance in predictive models, which make projections of future

behavior that may extend for long periods of time, resulting in increased uncertainty. Validation—or comparison of a model to an independent dataset—increases confidence in the ability to predict site behavior outside of the temporal or spatial domain under which the model was calibrated. Another tool for understanding model uncertainty is the sensitivity analysis, in which model sensitivity to different parameters is explored and related to the uncertainty in the measurement of the parameters themselves. Sensitivity analyses can be performed by thoughtfully constructing “bounding” simulations that use parameter sets representing reasonable upper and lower bound conditions. Stochastic and Bayesian analytical tools are valuable for exploring model uncertainty, and tools for response-surface modeling such as PEST (Doherty, 2004) are finding greater application in the uncertainty analysis of environmental models.

Consideration of model uncertainty requires more than just an understanding of the variability in input parameters. Also important is the interrelationship between parameters and model sensitivity to those interrelationships. This factor (parameter covariance) is often neglected, but can have a very significant impact on the validity of model uncertainty analyses. A model uncertainty analysis that varies parameters without considering these interrelationships almost always results in unrealistic combinations of parameters and correspondingly unrealistic model behavior.

Modeling uncertainty is particularly important when projecting complex interactions of environmental processes over long periods, as is the case when evaluating and comparing the risk-reduction performance of alternative remedies. A critical assessment of uncertainty in these projections enables risk managers to make more effective remedy selection and implementation decisions.

## 5.5 Selecting a Modeling Framework

**E**nvironmental modeling encompasses a broad range of contaminants, media, environmental conditions, and endpoints, and the modeling frameworks available are similarly wide-ranging. Technical criteria to consider in selecting a modeling framework or approach are necessarily specific to the characteristics of the site being modeled and the management questions of interest, and fundamentally relate to the model’s ability to capture major processes identified in the site’s CSM as critical for an evaluation of MNR and other remedial alternatives.

The list of available tools for modeling is continually evolving. Models commonly used for contaminated sediment sites (characterizing hydrology/hydrodynamics, sediment transport, water quality and contaminant transport, and exposure assessment) have been developed by academic researchers, independent code developers, and government agencies including USEPA, U.S. Army Corps of Engineers (USACE), U.S. Geological Survey (USGS), and the National Oceanic and Atmospheric Administration (NOAA). Some of the available and more widely used tools for modeling of hydrodynamics, sediment transport, contaminant transport and biological uptake are listed in Appendix C, with a brief description and summary of the supporting agency or developer (adapted from LimnoTech, 2002b). The quality of available models and the levels of documentation and support vary widely, and should be considered when selecting a model. Technical support, modeling forums, and downloadable code for many of the models listed in Appendix C are available online (Table 5-2). A short list of nontechnical criteria to consider during model selection includes:

- Whether a modeling system is already available for the site
- Model transparency
- Widespread use
- Regulatory acceptance
- Cost.

TABLE 5-2. Modeling resources.

Resource	Details
U.S. Army Corps of Engineers	<a href="http://www.hec.usace.army.mil/">http://www.hec.usace.army.mil/</a> <a href="http://www.erdc.usace.army.mil/">http://www.erdc.usace.army.mil/</a>
EPA Watershed and Water Quality Technical Support Center	<a href="http://www.epa.gov/athens/wwqtsc/">http://www.epa.gov/athens/wwqtsc/</a>
USGS National Research Program Modeling Support	<a href="http://water.usgs.gov/nrp/models.html">http://water.usgs.gov/nrp/models.html</a>
USGS Surface Water and Water Quality Models Clearinghouse	<a href="http://smig.usgs.gov/SMIC/SMIC.html">http://smig.usgs.gov/SMIC/SMIC.html</a>
EPA Center for Exposure Assessment Modeling	<a href="http://www.epa.gov/ceampubl/">http://www.epa.gov/ceampubl/</a>
USGS Fort Collins Science Center (Habitat Evaluation/Suitability Software)	<a href="http://www.fort.usgs.gov/Products/Software/">http://www.fort.usgs.gov/Products/Software/</a>

If a modeling system already exists for the site (e.g., for previous applications) considerable effort may be saved in continuing the use of that model, both in the terms of implementing the model and in garnering acceptance for model results. Consideration should be given to the similarities and differences between the previous and current requirements and applications. Working with models already in widespread use may help reduce potential distrust. In general, models that are well known, based on generally acknowledged process equations and solution methods, and that have a good track record of past applications are viewed with more confidence.

Model transparency, widespread usage, and regulatory acceptance criteria address the problem of treating models as “black boxes” containing mysterious algorithms. To combat this perception, and increase confidence in model results, models should be well-documented and the model code should be open to inspection by reviewers. Detailed documentation is even more important when allowing access to the model’s code is not possible. Confidence also increases when a model is familiar to and accepted by the parties relevant to remedial decisions. The models listed in Appendix C generally fall into this category, though Appendix C is not an exhaustive listing of such models.

Technical support for the model should also be available. Additionally, creative and intuitive visualization of model output is essential for communicating model results within project teams, other organizations and the public.

## 5.6 Summary

**M**odels can simulate many aspects of contaminated sediment systems relevant to remedy selection and remedy performance. Modeling can support the understanding of hydrodynamics, sediment transport, wind-wave and wind-current interactions, extreme events (e.g., high-energy wind and rain events), contaminant fate and transport, bioaccumulation in fish and terrestrial biota, and fish consumption and bioaccumulation in humans.

A well-conceptualized, well-constrained model with adequate supporting data can effectively support sediment remedy decision making, including the determination of whether part or all of a site would be amenable to MNR. Such a decision is not based on one model but on the conclusions indicated by many lines of evidence. Several of those lines of evidence, however, may be captured in various numerical models.

Ultimately, a model is most useful if it provides a means for realistically comparing the relative benefits of different remedial alternatives. The model's level of conceptual representation, scale, and spatial resolution should be such that the model can provide a meaningful and fair comparison of different cleanup alternatives being considered, and a sound argument for site recovery if MNR is identified as a component of the remedy.

## 5.7 Numerical Modeling Checklist

The following checklist summarizes considerations for selecting and applying models in the evaluation and implementation of MNR.

CHECKLIST 5-1. Modeling considerations.

***In view of the decisions currently under consideration within the project:***

***1. Is the set of decision-relevant questions motivating the modeling effort sufficiently comprehensive and specific? Consider the following components:***

- Whether the CSM contains sufficient resolution concerning natural processes relevant to evaluating risks and the performance of alternative remedies.
- Review and discuss, within the project team and relevant stakeholders, the set of questions informing the scope of the modeling effort.
- Establish a plan for guiding interaction between the project team, stakeholders, and model developers throughout the modeling effort.

***2. Will the selected numerical model appropriately capture the relevant natural recovery processes identified in the CSM? Consider whether the model satisfies the following attributes:***

- The model provides adequate mathematical representation of MNR-relevant processes (as outlined in Chapter 4).
- The degree of model complexity corresponds to the complexity of the CSM.
- The degree of model complexity is appropriate for the resources available and the level of site management decisions being made.

***3. Does the numerical model represent appropriate temporal and spatial domains for natural recovery processes at the site? Consider whether the model satisfies the following attributes:***

- The model is constructed at a sufficiently fine scale to represent relevant processes.
- The spatial domain of the model is large enough to capture major processes such as watershed loading or tidal forcing that may affect recovery.
- The model has been calibrated over a sufficient time interval and range of conditions to effectively constrain model behavior and to reliably predict recovery.

**4. Is the model well-supported by and integrated with data from natural recovery lines of evidence? Consider the following components:**

- Whether sufficient data exist to constrain the relevant rate, partitioning, and process coefficients used as model input.
- Model calibration to relevant physical and chemical data.
- Model validation against an independent data set.
- Data requirements for model implementation, calibration and validation during the evaluation of MNR lines of evidence.

**5. Is there a clear understanding of model uncertainty? Consider the following components:**

- Sources of error in input terms and model implementation.
- If sensitivity analysis or formal model uncertainty analysis have been used correctly to quantify uncertainty in model outputs.
- The degree to which model uncertainty could influence the ability of the model to support the assessment of remedy effectiveness.

**6. Does the model meet the requirements for acceptability by multiple parties in an MNR evaluation? Consider the following components:**

- Clear documentation of the algorithms applied in the model and transparency in model implementation, calibration and validation.
- Record of successful applications of the modeling framework.
- Regulatory acceptance of the model framework.

**7. Does the model provide the tools for evaluation of MNR as a remedy? Consider whether the model satisfies the following attributes:**

- The intended model provides answers to relevant site management questions.
- The model is capable of long-term predictions with a manageable and mutually acceptable degree of uncertainty.
- The model is capable of assessing the importance of future changes to the system, such as long-term changes in solids loads, changing site hydrology, or increased frequency of extreme events.
- The model is capable of representing a change in long-term recovery processes such as shifting from short-term burial to long-term chemical decay.
- The model provides support for development and adaptive refinement of a long-term monitoring plan.
- Model results are used to further inform the CSM for natural recovery at the site.

## 6 MNR and the Remedy Selection Process

*Remedy selection criteria, implementation risks, and residual risks*

USEPA and DoD regulations, policy, and guidance provide the framework for evaluating MNR as a remedial alternative. Most DoD cleanup is conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Under CERCLA, remedial alternatives are assessed based on the nine NCP criteria for health and environmental protection, compliance with regulatory requirements, short-term and long-term effectiveness and permanence, reduction of toxicity, mobility and volume, implementability, cost, and state and community acceptance.

Particular advantages of MNR include the opportunistic use of natural processes to reduce risk, the lack of environmental risks associated with remedy construction, and the absence of construction costs (although site characterization and monitoring costs can be substantial). A thorough assessment of remedy-related risks for various remedial alternatives is key to ensuring that remedy selection includes all relevant aspects of potential risks and risk reduction. Multiple lines of evidence are necessary to establish the expected permanence of an MNR remedy in order to achieve remedy acceptance.

Responsible parties may elect to incorporate habitat restoration elements in the remedy selection process, to improve overall environmental benefits, increase community acceptance, or offset natural resource damage liability (where applicable). MNR generally allows for preserving desirable natural habitat qualities, due to the lack of remedy-related habitat damage generally associated with constructed remedies.

Case studies of MNR evaluation in the remedy selection process indicate that MNR has been selected, often in conjunction with dredging, isolation capping, or thin-layer capping, for several reasons. Frequently, MNR is selected because it is expected to reduce risks and be cost-effective. Preservation of valued and sensitive habitat types and infeasibility of alternative technologies are additional reasons for inclusion of MNR in selected remedies.

**R**isk management decision making should consider the net risk reductions afforded by a full range of sediment management strategies, including source control, institutional controls, and remediation via MNR, capping, and environmental dredging (USEPA,

CHAPTER CONTENTS	
☆	Policy Resources for Remedy Selection
☆	RAOs, Remedial Goals, and Cleanup Levels
☆	MNR in the CERCLA Feasibility Study Process
☆	Comparative Net Risk Evaluation
☆	Interaction of Remedy and Restoration
☆	MNR Case Studies
☆	Summary

⇒Refer to Chapter 2  
for additional  
discussion of risk  
management  
concepts.

2005a; 1998a). In determining the appropriate remedy for a site, project managers should evaluate and compare the effectiveness of in situ (e.g., capping and MNR) and ex situ (e.g., dredging) alternatives to achieve desired risk reduction under actual site conditions. Combined remedies also should be considered, particularly at complex sites. Remedy selection should consider not only risk reduction associated with existing human and ecological exposure, but also the minimization of risks introduced by implementing a remedy.

## 6.1 Policy Resources for Remedy Selection

The policy of USEPA has been and continues to be that there is no presumptive remedy for contaminated sediment sites, regardless of the contaminant or level of risk (USEPA 2005a; 1998a). This policy recognizes that there is no universal best remedy technology for contaminated sediment sites. The physical, chemical and biological conditions and processes operating in water bodies are highly variable among contaminated sediment sites. These conditions and processes will determine the nature of the risks at a site, as well as how effective a remedy will be in reducing risks. Data concerning these conditions and processes will be used to develop evidence to support conclusions about the remedy effectiveness and other performance criteria. In the absence of such site-specific evidence, it is incorrect to presume that any remedy, whether it be removal of contaminated sediments via dredging, capping or MNR, would satisfy the multiple objectives relevant to decision making at the site (USEPA, 2005a). Evidence supporting remedy selection should consider all relevant remedy selection criteria.

Since 1986, the DoD has used the Defense Environmental Restoration Program (DERP) to restore environmentally impacted properties at active installations, Base Realignment and Closure (BRAC) installations, and Formerly Used Defense Sites in the United States and its territories. Within DERP, the Installation Restoration Program primarily addresses sites impacted by hazardous substances, whereas the Military Munitions Response Program focuses on unexploded ordnance and military munitions waste. The DoD chiefly relies on the environmental restoration process developed by USEPA under the CERCLA (Figure 6-1).

As a matter of DoD policy, environmental response actions are typically conducted in accordance with the provisions of CERCLA, its implementing regulation, the NCP (CFR 300.430; NCP, 2008), the USEPA Sediment Guidance (USEPA, 2005a), and related Executive Orders 12580 and 13016. However, cleanup may proceed under Resource Conservation and Recovery Act (RCRA) authority or state-led

programs in some cases, such as where an installation has sought a RCRA permit for managing hazardous waste (DoD, 1998). General environmental policies are outlined in the DoD’s Environmental Restoration Program Instruction 4715.7 (DoD, 1996). These policies relate to DoD’s commitment to environmental cleanup, compliance with legal requirements and program goals, developing partnerships with USEPA and other regulatory agencies, promoting public participation, supporting innovative technologies and process improvements, and supporting community reinvestment at BRAC sites. These policies have been implemented throughout the services.

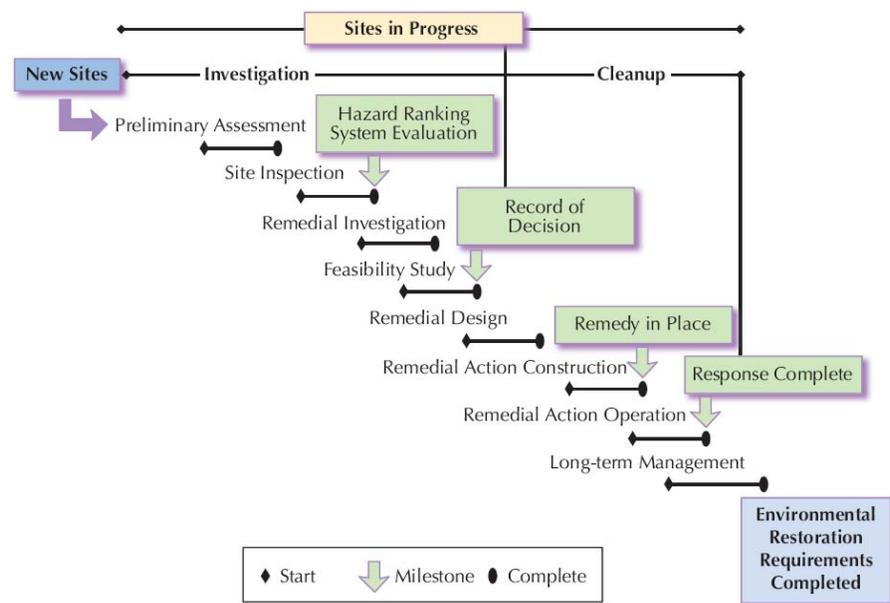


FIGURE 6-1. DoD CERCLA environmental restoration process phases and milestones.

MNR is one of the major remedial approaches described in USEPA’s *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (2005a). That guidance and several related resources are identified in Table 6-1. DoD’s restoration program and consideration of MNR is compatible with USEPA regulations, policy, and guidance, particularly with regard to sediments. A U.S. Army memorandum (U.S. Army, 1995) establishes that:

...natural attenuation must be considered as a candidate remedy for contaminated sites either alone or in combination with active engineered measures. An engineered remedial action will not be approved unless

data exists to prove that natural attenuation is inappropriate for a site cleanup.

Similarly, U.S. Navy (2002) policy on sediment site investigation and response actions states:

Natural Recovery/Natural Attenuation of sediments and/or a combination of other cleanup alternatives should be considered. Establishing potential remedial alternative objectives early will allow the collection of specific data (type of samples) during the remedial investigation or feasibility study.

TABLE 6-1. Sediment remediation resources.

Resource	URL
NRC 2007a: <i>Sediment Dredging at Superfund Megsites: Assessing the Effectiveness</i>	<a href="http://www.epa.gov/superfund/health/conmedia/sediment/pdfs/dredging.pdf">http://www.epa.gov/superfund/health/conmedia/sediment/pdfs/dredging.pdf</a>
USEPA 2005a: <i>Contaminated Sediment Remediation Guidance for Hazardous Waste Sites</i>	<a href="http://www.epa.gov/superfund/health/conmedia/sediment/guidance.htm">http://www.epa.gov/superfund/health/conmedia/sediment/guidance.htm</a>
USEPA 2002a: <i>Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites</i>	<a href="http://www.epa.gov/superfund/policy/remedy/pdfs/92-85608-s.pdf">http://www.epa.gov/superfund/policy/remedy/pdfs/92-85608-s.pdf</a>
NRC 2001: <i>A Risk-Management Strategy for PCB-Contaminated Sediments</i>	<a href="http://www.nap.edu/catalog.php?record_id=10041#toc">http://www.nap.edu/catalog.php?record_id=10041#toc</a>
USEPA 1988: <i>Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA</i> , Interim Final	<a href="http://www.epa.gov/superfund/policy/remedy/pdfs/540g-89004-s.pdf">http://www.epa.gov/superfund/policy/remedy/pdfs/540g-89004-s.pdf</a>
U.S. Navy 2003: <i>Implementation Guide For Assessing and Managing Contaminated Sediment at Navy Facilities</i>	<a href="http://web.ead.anl.gov/ecorisk/related/documents/rev_fin_Imple_Guide_for_Sediment_1.pdf">http://web.ead.anl.gov/ecorisk/related/documents/rev_fin_Imple_Guide_for_Sediment_1.pdf</a>
U.S. Air Force 2005: <i>Performance-Based Management Guidance</i>	<a href="http://www.afcee.brooks.af.mil/products/techtrans/pbm/PBMguidance.asp">http://www.afcee.brooks.af.mil/products/techtrans/pbm/PBMguidance.asp</a>

The *Management Guidance for the Defense Environmental Restoration Program* (DoD, 2001) provides specific direction for DERP implementation. The Defense Environmental Network and Information Exchange (DENIX) assembles policy, guidance, annual reports, and publications issued by all DoD agencies. Many of these resources can be accessed on the Internet (Table 6-2).

TABLE 6-2. DoD policy and related resources.

Resource	URL
DENIX	<a href="http://www.denix.osd.mil">http://www.denix.osd.mil</a>
DERP	<a href="https://www.denix.osd.mil/portal/page/portal/denix/environment/cleanup/DERP">https://www.denix.osd.mil/portal/page/portal/denix/environment/cleanup/DERP</a>
CERCLA	<a href="http://www.epa.gov/superfund/policy/cercla.htm">http://www.epa.gov/superfund/policy/cercla.htm</a>
40 CFR Part 300.430	<a href="http://www.access.gpo.gov/nara/cfr/waisidx_02/40cfr300_08.html">http://www.access.gpo.gov/nara/cfr/waisidx_02/40cfr300_08.html</a>
Environmental Restoration Program Instruction 4715.7	<a href="http://www.dtic.mil/whs/directives/corres/pdf/471507p.pdf">http://www.dtic.mil/whs/directives/corres/pdf/471507p.pdf</a>
Executive Orders 12580 and 13016	<a href="http://www.archives.gov/federal-register/executive-orders/1987.html">http://www.archives.gov/federal-register/executive-orders/1987.html</a>
Management Guidance for DERP	<a href="http://www.nao.usace.army.mil/projects/Environmental%20Projects/fuds/DERP_SEPT2001.PDF">http://www.nao.usace.army.mil/projects/Environmental%20Projects/fuds/DERP_SEPT2001.PDF</a>

## 6.2 RAOs, Remedial Goals, and Cleanup Levels

**B**efore a remedy can be selected, the RAOs, remedial goals, and sediment cleanup levels must be defined. RAOs for contaminated sediment focus on reducing human health and ecological risks (USEPA, 2005a). To be most useful, RAOs should be risk-based, and specify the receptors to be protected, the level of protection to be achieved, and the pathway of exposure.

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*Timescales for MNR to achieve remedial goals may be longer than those for other remedies (although this is not always the case).*

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Remedial goals specify the measurement endpoint to be used, the level of protection to be achieved for that endpoint, and the time frame for achieving protection and may include cleanup levels that establish target values for sediment COC concentrations. Remedial goals are site-specific and are generally developed through a consensus process among stakeholders.

A common difference between remedial goals for MNR and other remedies is the time frame involved. Whereas MNR, capping, and dredging can achieve similar outcomes, timescales for MNR to achieve remedial goals may be longer than those for other remedies (although this is not always the case). At sites where natural recovery already has been underway for decades, the timescale for MNR should consider the time since the original release. In some cases, sites may be close to achieving remedial goals after years or decades of natural recovery.

## 6.3 MNR in the CERCLA Feasibility Study Process

The remedial alternatives analysis—or FS under CERCLA—formally compares remedial alternatives in preparation for selection, design, and implementation of a contaminated sediment remedy. The comparison of potential remedies involves three sequential phases:

- Identification and development of alternatives
- Remedy screening
- Detailed analysis of remedial alternatives.

In the development and screening of remedial alternatives, DoD policy, consistent with the NCP (CFR 300.430), requires that the short- and long-term aspects of three evaluation criteria—effectiveness, implementability, and cost—be considered.

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S C R E E N I N G  
C R I T E R I A

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☆ Effectiveness

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☆ Implementability

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☆ Cost

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Effectiveness focuses on the degree to which an alternative reduces toxicity, mobility, or volume; minimizes residual risks; affords long-term protection; complies with applicable or relevant and appropriate requirements (ARARs); and minimizes short-term impacts. Natural recovery processes can effectively address risks via transformation, reduced bioavailability, natural sedimentation, or dispersion, without incurring short-term risks commonly associated with implementing dredging and capping.

Implementability focuses on the technical feasibility and availability of the technologies each alternative would employ and the administrative feasibility of implementing each alternative. MNR implementation is simpler because its sole active remedial component is monitoring to identify trends and quantify the rate of improvement to achieve risk-reduction goals. Alternatives that are not technically or administratively feasible or that would require equipment, specialists, or facilities that are not available within a reasonable period of time may be eliminated from further consideration.

Cost is a third important factor and typically includes the costs of construction and long-term costs to operate, maintain, and monitor the alternatives. While MNR site investigations and long-term monitoring can be expensive, MNR typically is less costly than capping or dredging implementation (Magar and Wenning, 2006; Magar, 2001). During the

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*While MNR site investigations and long-term monitoring can be expensive, MNR typically is less costly than capping or dredging.*

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remedy screening phase, alternatives achieving effectiveness and implementability similar to that of another alternative—but at greater cost—may be eliminated.

After the initial screening stage, a detailed analysis of alternatives representing viable approaches to remedial action is conducted. Under CERCLA, this analysis is based on nine evaluation criteria specified by the NCP. The first two are “threshold requirements” that each alternative must meet in order to be eligible for selection:

1. Overall protection of human health and the environment
2. Compliance with ARARs (unless a specific ARAR is waived).

The next five are “balancing criteria” where trade-offs among the criteria are considered:

3. Long-term effectiveness and permanence
4. Reduction of toxicity, mobility, or volume through treatment
5. Short-term effectiveness
6. Implementability
7. Cost.

The last two are “modifying criteria” to be considered in remedy selection:

8. State acceptance
9. Community acceptance.

The comparative analysis is conducted for each sediment remedy alternative under consideration and emphasizes relative performance against the established criteria (USEPA, 2005a). The criteria are described below in the context of evaluating MNR as a remedial alternative.

Protectiveness of human health and the environment is a risk-based criterion that evaluates how well the remedy reduces or eliminates risk to human and ecological receptors. As with other remedies, pre- and post-remedy risks can be evaluated for MNR using predictive modeling to evaluate the long-term risk reduction achieved by MNR. Protectiveness

NCP CRITERIA	
☆	Protection of human health and the environment
☆	Compliance with ARARs
☆	Long-term effectiveness and permanence
☆	Reduction of toxicity, mobility, and/or volume
☆	Short-term effectiveness
☆	Implementability
☆	Cost
☆	State acceptance
☆	Community acceptance

is reinforced by long-term monitoring of sediment, chemical, geochemical, and biological conditions. Long-term monitoring reduces remedy uncertainty and builds community and regulatory confidence in the protectiveness of the MNR remedy.

Determining ARAR compliance involves establishing whether the remedial alternative adheres to policies established by federal, state, and local government and agency entities, such as state and federal requirements promulgated under various Clean Water Act programs. MNR, like other remedies, is expected to comply with ARARs. Chemical-specific ARARs may be achieved via any of the four major processes that contribute to reduced mobility and exposure. MNR has no active components that may impact water quality and aquatic ecology.

Assessing long-term effectiveness establishes the likely permanence of the remedy under consideration. Factors include the effectiveness of source control, long-term physical and geochemical stability of the remedy under normal and high-energy natural or anthropogenic events, and its long-term ecological integrity.

Predicting the long-term effectiveness of the risk reduction offered by MNR often relies on analysis of issues such as resuspension potential, contaminant fate and transport, the reversibility of chemical transformation processes, and the projected site conditions that are responsible for reduced exposure, bioavailability, and risk. These are addressed and communicated within the CSM and elucidated via predictive modeling and empirical lines of evidence. As with all such evaluations of long-term effectiveness, the uncertainty of the estimates should be evaluated and communicated.

Predicting reduction of toxicity, mobility, or volume through treatment requires analysis of physical, chemical, and biological processes associated with contaminant fate and transport. Similar to many in situ and ex situ remediation approaches, MNR does not have a specific “treatment” component. For MNR, this criterion addresses the mechanistic performance of the natural recovery processes, a key focus of the MNR lines of evidence developed from the CSM. Mobility and toxicity reduction can be achieved via natural biological and geochemical processes that reduce chemical bioavailability and toxicity. Natural sedimentation provides further reductions in chemical mobility, and leads to reduced contaminant concentrations in surface sediment via natural dilution and burial.

Change in contaminant toxicity, mobility, and volume is both site- and chemical-specific—site-specific because physical, chemical, and biological processes differ from site to site and among different ecosystems and chemical-specific because different chemicals exhibit different tendencies toward transformation and toxicity reduction. Many lines of evidence (e.g., chemical fingerprinting, hydrodynamic modeling, and ecological studies) may be employed for this criterion.

Assessment of short-term effectiveness determines how quickly the remedy will achieve meaningful results, and highlights short-term risks associated with remedy implementation. Identification of short-term risks includes an evaluation of potential impacts to the community, site workers, and the environment during remedy execution.

In most cases, the short-term effectiveness of MNR remedies involves current conditions related to contaminant exposure and risk and the expected time to achieve acceptable risk levels. MNR has minimal or no short-term risks to the community or site workers associated with remedy implementation. Because MNR does not involve on-site construction activities, this alternative is unlikely to increase short-term risks to human health and the environment.

Evaluation of remedy implementability explores factors such as design complexity, construction challenges, availability of tools, and the administrative feasibility of implementing a remedy. It incorporates an assessment of the technical difficulties associated with construction and operation of the remediation system, the reliability of the chosen technologies, and the ease of long-term remedy maintenance and monitoring. Evaluation also may include an assessment of the ability to obtain necessary permits, treatment, storage and disposal services, and the availability of equipment and labor to implement all facets of the remedy.

For MNR, remedy implementability involves evaluating the lines of evidence in order to determine its potential effectiveness. Establishing implementability calls for showing how the various lines of evidence can be used to measure and predict the risk-reduction effectiveness of natural recovery processes. Once these lines of evidence are established during the RI/FS, MNR generally is implementable, with few apparent implementability constraints. Long-term monitoring is reliable, with well-established industry practices and methods. Monitoring for triggers of contingency actions can be established to respond readily to changes in baseline conditions; such actions could include increased monitoring

⇒Refer to Chapter 7  
for additional  
discussion of  
long-term monitoring.

to verify the change, data evaluation, and development of an appropriate response, as needed.

Remedy costs are estimated with as much accuracy as possible for capital, operation, and maintenance. FS costs are considered accurate to within +50 to -30% and are calculated as present value for comparison of alternatives (USEPA, 2000d).

Unlike dredging and capping, no construction effort is needed in MNR, so capital costs for MNR are negligible. Most costs for MNR are associated with development of the RI/FS when building a CSM that describes and quantifies MNR processes. Remaining costs are associated with long-term monitoring to ensure that MNR processes are functioning as predicted and to assess attainment of risk-based RAOs, event-based monitoring following natural or anthropogenic events that could potentially threaten to disrupt natural recovery processes, and the implementation of institutional controls.

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*Transparency of the remedy selection process, facilitated by the CSM and associated lines of evidence, can increase community acceptance.*

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Community acceptance explores issues and concerns the general public may have regarding each remedial alternative. Though introduced in the FS, community acceptance is addressed in detail in the ROD once community comments on the FS and proposed plan are received.

For in situ remedies, such as MNR and capping, initial community acceptance may be lower than for dredging because MNR does not involve an engineered removal of contaminants from the system. It should be noted, however, that no remedy technology can remove all contaminants from a sediment site. For dredging, there are substantial uncertainties concerning effectiveness; short-term and long-term risks resulting from resuspension releases, and residuals; and disruption to the community during construction (Bridges et al. 2008; NRC, 2007a). These considerations may ultimately influence or reduce community acceptance of dredging. Transparency of the remedy selection process, facilitated by the CSM and associated lines of evidence, can increase community acceptance of the selected remedy.

Regulatory acceptance evaluates the technical and administrative issues and concerns that government agencies may have regarding each remedial alternative. As with community acceptance, this criterion is evaluated to the extent possible in the FS and is addressed in detail in the ROD once agency comments on the FS and proposed plan are received.

MNR has gained regulatory acceptance at several contaminated sediment sites across the country. Experiences with MNR and data from monitoring activities at these sites will provide opportunities to address

uncertainties that pose challenges for implementing MNR. USEPA (2005a) views MNR as an effective and permanent remedy when the conditions at the site are compatible with attributes of the remedy. While MNR, capping, or dredging—and other innovative remedies—should be evaluated using the same criteria, it is to be expected that nonremoval remedies will generally undergo an evaluation that gives particular attention to processes and uncertainties associated with long-term risks. However, carefully designed and implemented monitoring programs provide the scientific means for addressing uncertainty to verify whether acceptable risk reduction is achieved.

## 6.4 Comparative Net Risk Evaluation

⇒ Refer to Chapter 2 for more information about comparative risk evaluation.

**R**isk assessment during the RI/FS evaluates baseline conditions to establish whether the level of risk requires corrective action. If corrective action is needed, alternatives may be systematically compared in the remedy selection process as directed in the NCP. An important component of evaluating remedy protectiveness and effectiveness is the comparison of overall or net risks associated with each remedial alternative (USEPA, 2005a).

The comparison of relative risk reduction, relative risk increase, or static risk conditions, provides information for decision making that might not otherwise be available. Comparisons of net risk should be performed to determine the relative risk reduction afforded by each remedy alternative and the direct risks that may be associated with remedy implementation. These comparisons, combined with an evaluation of costs, support the selection of an appropriate remedy for a site. The goal is to meet risk-reduction goals at the most reasonable cost, while minimizing negative impacts to the natural environment and minimizing short-term risks to human health and the environment associated with remedy implementation (Magar et al., 2008b).

This section discusses two basic types of risks—contaminant risks and implementation risks. Contaminant risks relate to contaminant exposures and how they are modified during and following remedial operations, while implementation risks are other risks to workers, the community, or the environment posed by the remedy (Wenning et al., 2006).

### 6.4.1 Projecting Contaminant Risk Trajectories

**P**rojections for contaminant risk reduction can be modeled using site-specific hydrology, hydrodynamic, and hydrogeology data; sediment geophysical and contaminant properties; fate and

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#### IMPLEMENTATION RISK ISSUES

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- ☆ Protection of the community

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- ☆ Protection of workers

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- ☆ Environmental impacts

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- ☆ Time to achieve RAOs

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transport mechanisms; and ecological inputs. The models or assessment tools used will depend on the size and complexity of the site, type of risk evaluated, the manner in which exposure occurs, and the types of chemical transformation processes that may occur over time. For example, prediction of the risk of exceeding species-specific critical body residues might involve the prediction of surface water concentrations and creating food chain models of the hypothetical changed conditions following a sediment remedy.

Remedy evaluation should explicitly consider the uncertainties associated with such projections. Indeed, a number of groups have called for research to improve modeling capabilities and reduce uncertainties in risk projections to support remedy comparisons (Bridges et al., 2008; NRC, 2007b, 2001). Uncertainties in predicting future effectiveness and risks are inherent in all remedial approaches, and the presumption that MNR is fraught with greater uncertainty than constructed remedies such as capping and dredging is not always correct. In an MNR remedy, uncertainty can be reduced over time through monitoring.

#### 6.4.2 Remedy Risks and MNR

**R**emedy risks associated with MNR primarily relate to 1) the continued exposure to contaminants during the MNR period and 2) the risk that assumptions about modeling of MNR are incorrect and, in the short- or long-term, exposures either will not decline or will increase due to unforeseen or mischaracterized events. Otherwise, MNR has few implementation risks beyond those associated with accompanying monitoring programs.

Contaminant risk associated with MNR also relate to continued exposures during the MNR period. As a result, the time required to achieve remedial goals is a key factor in comparative net risk evaluations of remedies, including MNR. Remediation efforts must meet cleanup goals within a “reasonable timeframe”; defining what is “reasonable” for remediation is a site-specific task (USEPA, 2005a, 2001b). At many sites, risk goals may already have been achieved, for example where surface sediment concentrations already approach cleanup levels defined by the remedial goals. At other sites additional time may be required (years to decades) for natural processes to sufficiently reduce surface sediment concentrations. The acceptability of MNR depends on the overall magnitude of the baseline risk, the amount of time that would be required to meet remedial goals, and the uncertainties associated with predictions about natural recovery process rates and rates associated with constructed remedies. In performing a comparative net risk evaluation,

evidence concerning these aspects of MNR are compared to factors germane to the constructed remedies under consideration.

### 6.4.3 Remedy Risks for Constructed Remedies

Implementation risks, such as those posed by extensive dredging and the transportation of construction and waste materials, must be evaluated carefully and weighed against any anticipated long-term risk reduction (Table 6-3). In the context of human health, remedy implementation risks include unanticipated injuries (or even fatalities) to workers and nearby residents during cleanup (Wenning et al., 2006). Economic risks include costly delays associated with substantial remedy modifications or abandonment of an incomplete remedy (Church, 2001). For ecological health, implementation risks can include the removal, destruction, or modification of aquatic and terrestrial habitats, as a result of the dredging process or activities associated with staging, transport, and disposal of materials—these risks are particularly important considerations, when high-value habitats are involved.

Contaminant risks associated with sediment dredging projects often are considered on two time scales—during remedy implementation and post-implementation (Table 6-3). Adverse risks may be evident during the active remedy phase primarily due to resuspension of contaminated sediments and release of contaminants from sediments or pore water to the water column (Bridges et al., 2008; Palermo et al., 2008). After remedial action is complete, longer term contaminant risks may persist as a result of residual contamination, transport of releases beyond the project area, or a new sediment physical-chemical equilibrium that alters ecological exposure conditions and can adversely affect aquatic biota either by direct toxicity or by increasing residues of bioaccumulative chemicals via the food chain (Bridges et al., 2008; Wenning et al., 2006). Where remedy activities are focused on deeper deposits with higher concentrations of contaminants or different geochemistry than surficial deposits, increases in water column exposure can be more severe. Therefore, when evaluating MNR against other alternatives, the effectiveness of natural processes should be considered under both current (implementation, or active remedy) conditions and long-term (residual) conditions.

For dredging, engineering and operational controls can be taken to limit contaminant releases during operations (though typically with trade-offs regarding cost and efficiency), or areas can be drained and excavation can occur in the dry (Bridges et al., 2008; Palermo et al., 2008).

IMPLEMENTATION RISK ELEMENTS	
☆	Construction accidents
☆	Transportation accidents and spills
☆	Water quality impacts of resuspended sediments
☆	Dispersion and deposition of resuspended sediments
☆	Water quality impacts of sediment dewatering effluent
☆	Air emissions from sediment handling
☆	Short- or long-term habitat degradation
☆	Quality-of-life impacts
☆	Carbon footprint

TABLE 6-3. Residual and implementation risks.

Type of Risk	Source of Risk	Measure of Risk
<i>Implementation Risks</i>		
Construction or transportation accidents	Construction and remediation operations	Accident rates
Temporary loss of aquatic habitat	Physical removal of benthic macro-invertebrate community and habitat	Habitat recovery time
Temporary (or permanent) loss of riparian habitat	Construction of access roads or staging areas in riparian zone	Habitat recovery time
Temporary impacts of sediment suspension and contaminant release on water quality and sediment recovery	Dredging or capping	Predicted dispersion and deposition rates; water quality testing; post-remediation monitoring
Air emissions	Dredging; dewatering and stabilization; transportation and disposal	Health risk to sensitive receptors; odors; carbon emissions
Public quality of life issues	Restricted use of a resource; vehicle traffic; odors; noise	Time for loss of amenity; truck volumes on local roads; air quality monitoring
Continued contaminant risks during remedy implementation	Time required to achieve remedial goals	Projected risk reduction trajectory over time
<i>Residual Risks</i>		
Long-term contaminant risks	Dredging and recontamination; insufficient source control	Residual deposition away from remediation area (potentially even chemicals unrelated to target compounds) and recontamination of remediated or MNR areas
Long-term habitat degradation	Incomplete recovery of channel morphology; long-term channel incision; slow or incomplete recovery of riparian tree cover	Effectiveness of post-remedy aquatic and riparian habitat restoration

However, even best-management practices cannot contain 100% of chemical contamination, particularly once desorbed and partitioned into the aqueous phase. Because some risks will be time-dependent, remediation can be planned to minimize these risks by, for example, avoiding dredging during wildlife breeding seasons and during high-water-flow conditions. Of course, these issues are of greatest concern for dredging projects, of modest concern for capping projects, and of no concern for the MNR remedy. Another alternative is to limit dredging by using combination remedies that include in situ remedies, such as MNR or capping, in areas of the site where those remedies provide effective means for managing exposures and risk.

Over the long term, post-remedy risks are determined primarily by changes in the exposure field, influenced by the bioavailability, concentration, and exposure area resulting from residuals and redistributed contaminants. The ability to predict changes in bioaccumulation and other risks depends not only on the ability to describe the post-remedy exposure field but also the degree to which pre-remedy modeling accurately reflects the relationship between sediment, water, and food chain exposures and actual bioaccumulation. Because many sediment management projects identify both short-term and long-term risk reduction goals, it is important for risk evaluations to consider both short- and long-term environmental changes and corresponding risks.

⇒Refer to Chapter 4  
for more information  
about source  
control.

Understanding and characterizing uncontrolled/ongoing sources and urban/industrial background chemical concentrations is essential to recognizing and assessing their contribution to long-term sediment recovery for all sediment remedies. Urban background concentrations can be significant for a variety of chemicals (e.g., PAHs) (Stout et al., 2004) and will affect long-term residual risks.

The potential for long-term habitat degradation due to remedy implementation also should be considered. Just as constructed remedies often are not completely effective in removing or containing contamination, restoration efforts may not completely restore habitat that is disrupted through remediation, or recovery may proceed very slowly (e.g., regrowth of forested wetland). Efroymsen et al. (2008a, b) describe an innovative application of habitat valuation methods to inform remedy comparisons in portions of the U.S. Department of Energy's Oak Ridge Reservation. Their approach, which includes both habitat characteristics and habitat use by various organism types, has the potential to promote thorough consideration of the natural resource benefits and detriments of remedial alternatives.

## 6.5 Interaction of Remedy and Restoration

Increasingly, ecological restoration is being integrated into remedy analyses and decision making to enhance ecological value beyond simply controlling contaminant transport and exposure. For example, bank and shoreline stabilization actions implemented for source control purposes can incorporate significant habitat enhancement measures (e.g., shoreline armoring at the Asarco site on Commencement Bay, Washington) (NOAA, 2006) that include the use of deep rooted native plants. Where functioning habitats exist, MNR may be a restoration-friendly alternative, because it does not incur short- or long-term construction-related habitat damage. On the other hand, major restoration actions such as dam removal or habitat reengineering may be incompatible with MNR if physically isolated contaminants would become exposed and mobilized.

While USEPA cannot mandate supplemental habitat restoration under CERCLA, responsible parties can elect to include restoration elements as part of, or in addition to, remedial actions. Reasons to consider restoration during the remedy selection process include:

- Increasing overall environmental benefits
- Promoting community acceptance
- Offsetting natural resource damage (NRD) liabilities, where applicable.

Implementation of MNR can either decrease or increase NRD liability, depending on site-specific considerations. Specifically, the lack of remedy-related habitat damage will tend to decrease liability, whereas if MNR results in increased time to ecosystem recovery compared to other remedial alternatives, NRD liability will tend to increase. In the latter case, early implementation of restoration actions can help to offset damages estimated to accrue during the recovery period.

The implications of habitat restoration for overall protectiveness of an MNR remedy also merit consideration. Habitat quality and quantity often are more limiting than chemical effects with respect to fish and wildlife populations. However, if habitat restoration were to attract larger numbers of organisms to an area where contaminant exposures are high (e.g., resulting in reproductive failure), a population sink could be created during the natural recovery period. Also, increased attractiveness of restored aquatic habitat for fishing could create a need for increased

institutional controls to limit human exposures where bioaccumulative chemicals are of concern.

## 6.6 MNR Case Studies

Appendix A includes more than a dozen case studies of sites for which MNR was evaluated and selected as the approved remedy or remedy component. At most of the sites, the evaluation of MNR feasibility was based on empirical investigation of site conditions, followed by modeling to interpret the data and predict achievement of remedial goals and cleanup levels. Natural recovery timelines usually ranged from 5–30 years, and costs associated with MNR usually were orders of magnitude lower than those associated with dredging and capping. The primary reasons for selecting MNR in these cases included:

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*In more than a dozen case studies, costs associated with MNR were orders of magnitude lower than for dredging or capping, and—where monitoring data were sufficient to judge—MNR was usually considered successful.*

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- Ability of MNR to achieve RAOs within an acceptable time period and at a reasonable cost
- Preservation of valuable habitat that would otherwise be destroyed by capping or dredging
- Infeasibility of capping or dredging, or their inability to achieve better results than MNR.

Remedy selection at the case study sites is summarized in Table 6-4.

TABLE 6-4. Summary of remedy selection at case study sites.

Site	Description
Bellingham Bay, Whatcom Waterway, Bellingham, WA	Multiple lines of evidence documented ongoing physical isolation of mercury-contaminated sediments. Remedies were compared using Washington's semiquantitative multicriteria ranking method. The selected remedy includes dredging, capping, and MNR components.
Bremerton Naval Complex, Bremerton, WA	The investigation of physical isolation processes supported the selection of EMNR as well as dredging to address PCB- and mercury-contaminated sediments. The remedy relies on MNR to address post-dredging residual concentrations.
Commencement Bay, Nearshore/Tideflats, Tacoma, WA	Documented natural recovery processes include physical isolation, chemical transformation, and dispersion of sediments containing numerous contaminants. The selected remedy includes source control, institutional controls, dredging, isolation capping, EMNR, and MNR components. In the Sitcum Waterway subarea, MNR was selected to address post-dredging residuals.

TABLE 6-4. Summary of remedy selection at case study sites (continued).

Site	Description
Elizabeth Mine, Stratford and Thetford, VT	Qualitative evidence indicates that physical isolation and dispersion processes are occurring. MNR was selected as the most cost-effective and least damaging option for wetland and stream resources. However, recovery is not expected until acid mine drainage can be controlled.
Hackensack River, Jersey City, NJ	Lines of evidence supporting MNR included low risks due to chromium transformation and associated low bioavailability, as well as physically stable depositional sediments. A detailed comparative risk evaluation informed the comparison of remedial alternatives. The negotiated remedy in this case entails dredging, capping, and MNR components.
James River, Hopewell, VA	One of the earliest examples of MNR; pioneered the use of sediment age dating to demonstrate recovery via physical isolation. Kepone concentrations in fish fell below the action level by the late 1980s. The very large size of the affected area contributed to selection of MNR.
Ketchikan Pulp Company, Ward Cover, Ketchikan, AK	MNR was selected for portions of the site where physical conditions made capping and dredging infeasible. Physical isolation of sediments containing ammonia, sulfide, and 4-methylphenol was the primary process reducing benthic toxicity.
Koppers Co., Inc., Barge Canal, Charleston, SC	Subaqueous capping was initially selected to address PAH-contaminated sediment in the Barge Canal. However, investigations during the remedial design phase demonstrated significant natural recovery through sedimentation, and the remedy was changed to MNR.
Lavaca Bay, Point Comfort, TX	Measured sedimentation rates supported physical isolation as the dominant natural recovery process. Hurricane scour modeling evaluated potential sediment erosion and mercury redistribution during future hurricane events. The selected remedy includes source control, dredging, EMNR, and MNR.
Lower Fox River/ Green Bay, WI	MNR was selected for operable units where capping and dredging are not implementable. Constraints include shallow bedrock and high dispersion potential in Operable Unit 2 and an excessive volume of low-level contaminated sediment in Green Bay. Physical isolation and dispersion are predicted to reduce PCB risks over a period of decades.
Mississippi River Pool 15, Scott County, IA	Temporal trends of decreasing PCB concentrations in sediment and fish and low human and ecological risks supported the selection of source control and MNR to address localized shoreline contamination.

TABLE 6-4. Summary of remedy selection at case study sites (continued).

Site	Description
Sangamo Weston/ Twelve-Mile Creek/ Lake Hartwell, Pickens County, SC	Physical isolation rates were such that natural recovery was expected to achieve protectiveness as fast as dredging alternatives. Release of sediment from upstream impoundments accelerated sedimentation. Although surface sediment PCB concentrations have declined as predicted, fish tissue levels remain elevated, suggesting incompletely characterized and controlled exposure pathways.
Wyckoff/Eagle Harbor, Puget Sound, WA	MNR was selected for a portion of the site where habitat preservation (i.e., preservation of eel grass beds) outweighed the potential benefits of sediment removal or capping. Physical isolation processes were expected to effectively address PAH-contaminated sediment in this area.

In almost every case where long-term monitoring is sufficient to evaluate remedy success, the results indicate appropriate progress toward remedial goals. Although none of the sites have achieved closure, the Koppers Barge Canal site may be nearing cessation of monitoring in the subarea where MNR has been implemented. As noted in Table 6-4, only the Lake Hartwell case study suggests mixed results for MNR.

## 6.7 Summary

Comparisons of baseline risks with risk reduction measures and evaluation of the time to achieve risk-based goals require relatively realistic ecological and human health risk projections for each remedy alternative. A thorough assessment of remedy-related risks for various remedial alternatives is key to ensuring that remedy selection includes relevant aspects of potential risks and risk reduction. Multiple lines of evidence are used to establish the expected performance of an MNR remedy in order to achieve remedy acceptance.

After remedial action objectives and site- and media-specific cleanup levels are established, potential remedies are compared and evaluated per the NCP. In selecting a remedy, advantages and limitations of each remedial approach are considered and trade-offs among the approaches are balanced on the basis of the nine NCP remedy evaluation criteria. Comparative net risk evaluations that consider the short- and long-term risk related to remedy implementation and risks related to contaminant exposures are useful in this process.

## 7 Natural Recovery Monitoring and Remedy Success

*Process steps for developing a monitoring plan; physical, chemical, and biological techniques; and evaluating remedy success.*

Long-term monitoring is used to confirm that exposure pathways and risks have been managed adequately, such that the remedy achieves stable and permanent protection of human and ecological receptors. The monitoring plan addresses the RAOs established in the ROD. Corresponding remedial goals and cleanup levels determine the site-specific monitoring objectives.

Baseline monitoring establishes current conditions for comparison with future chemical concentrations and related risks, and for monitoring the performance of natural recovery processes. Baseline monitoring generates data to refine the CSM, identify factors that could influence recovery success, and establish a statistical baseline for measurement endpoints.

Long-term monitoring provides data to determine recovery rates, verify source control, and evaluate trends. Long-term monitoring verifies that natural recovery processes are sufficient to meet cleanup levels within an acceptable time frame. Long-term monitoring also includes monitoring of remedial goals by quantifying recovery trends. Monitoring objectives typically correspond to key endpoints identified as risk drivers during the RI/FS.

Establishing an effective monitoring plan requires consideration of contingencies in the event that MNR does not achieve success within an acceptable time frame. At sites where remedial goals and cleanup levels have been achieved, pathways to site closure or long-term monitoring for remedy permanence are evaluated.

**M**onitoring is a fundamental component of the MNR remedy. Monitoring is conducted to assess remedy performance and effectiveness in achieving sediment remedial goals and in reducing human health and ecological risks (NRC, 2007a; USEPA, 2005a). Monitoring environmental remediation recognizes that uncertainty is inherent to any cleanup activity and must be managed through data collection (USDOE, 1999; 1997). Verification of natural recovery performance through monitoring reduces uncertainty by demonstrating whether contaminated sediment exposure pathways and

CHAPTER CONTENTS	
☆	Monitoring Framework
☆	Considerations for Monitoring Program Design
☆	Baseline Monitoring
☆	Long-term Monitoring
☆	Adaptive Site Management for MNR
☆	MNR Performance Checklist

associated risks are adequately managed and whether the remedy results in stable and lasting protection of human and ecological receptors (USEPA, 2005a). Long-term monitoring plans are designed to confirm conceptual and quantitative models of the effectiveness of natural recovery over time and to verify that recovery levels achieve risk-based goals.

## 7.1 Monitoring Framework

The general framework for monitoring of all remedies at contaminated sediment sites is structured around four measures of remedy effectiveness (USEPA, 2005a):

- Short-term remedy performance (e.g., Have the sediment cleanup levels been achieved?)
- Long-term remedy performance (e.g., Have the sediment cleanup levels been reached and maintained for at least 5 years, and thereafter as appropriate?)
- Short-term risk reduction (e.g., Do data indicate a reduction in fish tissue levels, a decrease in benthic toxicity, or an increase in species diversity or other community indices?)
- Long-term risk reduction (e.g., Have the remedial goals in fish tissue been reached or has ecological recovery been accomplished?)

As part of MNR, these goals are met via the following monitoring activities:

- Baseline monitoring establishes baseline conditions for the future trajectory of contaminants and related risks, as well as the baseline for performance of natural recovery processes. Baseline data should establish conditions to support comparisons to future data sets and model predictions (USEPA, 2005a). Baseline monitoring also can facilitate comparisons of current conditions with conditions in the past, demonstrating historical recovery.
- Long-term monitoring evaluates the effectiveness of the remedy in achieving human or ecological risk-based remedial goals and cleanup levels. Long-term monitoring may reconfirm and evaluate natural recovery processes identified during the RI/FS (Figure 7-1a). Following the attainment of remedial goals, monitoring frequency may be reduced. Monitoring should

continue until the ongoing stability and permanence of the remedy is confirmed or until sufficient data have been collected such that the permanence of risk reduction afforded by natural recovery is certain (Figure 7-1b). Long-term monitoring may take more or less time than initially expected; adaptive site management will determine the time frame for long-term monitoring.

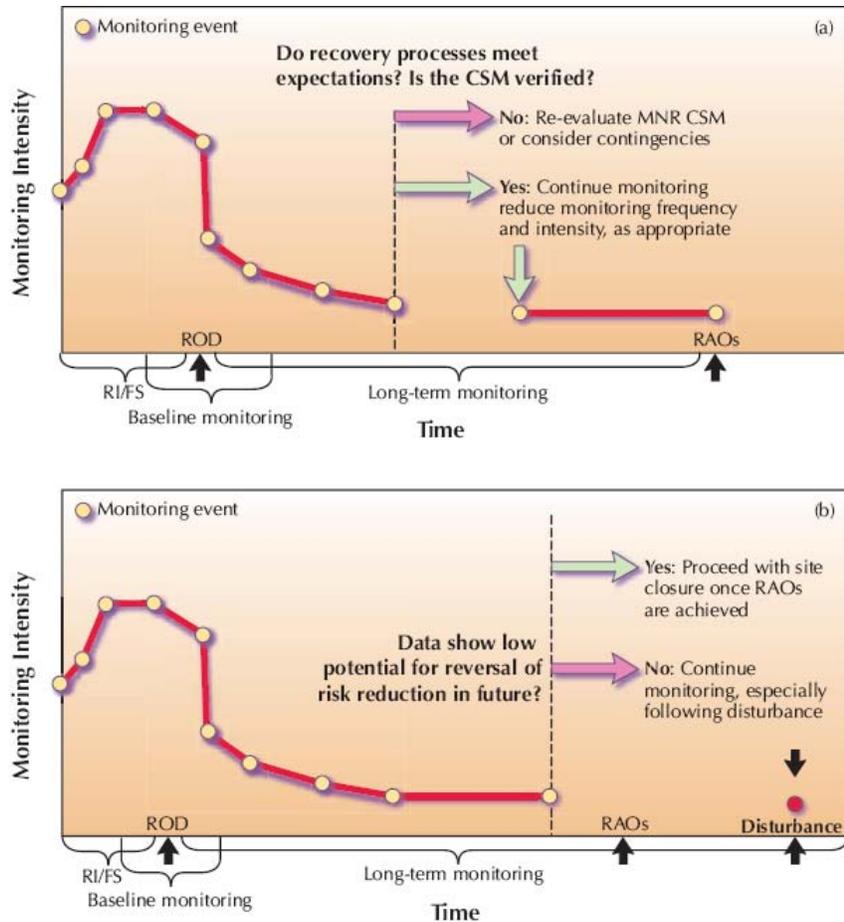


FIGURE 7-1. Timeline and adaptive management decision framework for long-term monitoring (a) prior to and (b) following achievement of RAOs.

## 7.2 Considerations for Monitoring Program Design

Fundamental to establishing a clearly defined MNR monitoring plan is an understanding of the remedy’s physical, chemical, and biological processes that are relied upon to achieve remedial goals and cleanup levels. The monitoring plan should address the risk-based

DATA QUALITY OBJECTIVES PROCESS	
☆	State the problem
☆	Identify the goals of the study
☆	Identify information inputs
☆	Define the boundaries of the study
☆	Develop the analytical approach
☆	Specify performance or acceptance criteria
☆	Develop the plan for obtaining data

RAOs established in the ROD, which are translated into remedial goals and sediment cleanup levels (USEPA, 2005a). Data collection should be conducted with an understanding of how the data will be used and how they contribute to a validation of remedy performance and success.

A long-term monitoring plan that is developed according to the DQO process (USEPA, 2000a) can produce the most useful and cost-effective data for verifying MNR remedy success. The DQO process clearly defines the data and information needed to monitor remedy success; thus, the DQO process informs the development of a data collection plan that will enable the field team to obtain the right type, quantity, and quality of data. DQO criteria determine when, where, and how to collect samples or measurements; tolerable decision error rates; and the number of samples or measurements that should be collected. Specific elements of the monitoring plan design process (USEPA, 2005a; 2004d) are discussed below, with particular focus on MNR remedies.

**Identify Monitoring Objectives.** Determine monitoring objectives by analyzing the relationship of the monitoring elements to the remedial goals. For MNR, monitoring objectives should generally target performance of key natural recovery processes (i.e., through process-specific lines of evidence) and attainment of remedial goals. Although natural recovery will have been established during the RI/FS, natural recovery performance may need to be verified over a much longer period of remedy implementation, especially if key site conditions change with time.

*Example: Determine if site-specific physical isolation processes continue to be sufficient to meet remedial goals.*

**Develop Monitoring Plan Hypotheses.** Monitoring plan hypotheses are testable assertions about the relationship between the remedy and its expected outcomes, and may be articulated as a statement or a question. In the case of MNR, monitoring plan hypotheses should relate the effectiveness of key natural recovery processes to achieving remedial goals and cleanup levels.

*Example: The sediment deposition rate is sufficient to achieve surface-sediment concentration goals within a predetermined time frame.*

**Formulate Monitoring Decision Rules.** Decision rules guide the interpretation and adaptation of monitoring elements with respect to the monitoring objectives. A decision rule is generally a conditional statement that defines the circumstances that would cause the decision maker to continue, stop, or modify the monitoring activity or remedial

⇒Refer to Section 7.5 for information on adaptive site management.

action. Decision rules for MNR relate to remedial goals and cleanup levels. One essential component of these decision rules consists of contingency strategies for situations where performance is not as expected, remedial goals or cleanup levels are not achieved, or data do not resolve the underlying trend with sufficient certainty. In these cases, decision rules should support alternative strategies, designs, and measurements. Establishing decision rules with targets and time frames for remedial goals and cleanup levels is an essential component of an adaptive site management framework.

*Example: If lines of evidence conflict, give greater weight to the line of evidence that is more closely related to RAOs (e.g., if fish tissue contaminant concentrations are declining despite lower sediment deposition than predicted, the site may still be progressing toward remedial goal attainment).*

Design the Monitoring Plan. The monitoring plan is designed based on the plan hypotheses and decision rules. The plan identifies data needs, monitoring elements (e.g., methods, frequency, duration), and data analysis methods. Baseline and long-term monitoring often incorporate multiple lines of evidence, relying on multiple monitoring elements to reduce uncertainty, while recognizing the need to maintain cost-effectiveness (Magar and Wenning, 2006).

Critical considerations for long-term monitoring elements include careful collection and analysis procedures so that natural recovery processes are not altered significantly by the monitoring itself. Long-term monitoring should focus on validating and refining the CSM and identifying trends toward recovery. Therefore, long-term monitoring can be scaled down compared to data collection during the RI/FS stage, which focuses on establishing multiple lines of evidence that natural processes are occurring and are reducing risk.

The recently developed Navy online Interactive Sediment Remedy Assessment Portal ([www.israp.org](http://www.israp.org)) links remedy-specific and goal-specific monitoring needs with appropriate monitoring tools and approaches (SPAWAR and ENVIRON, 2009). This tool is intended as an aid in monitoring plan design; it highlights key issues associated with site-specific monitoring, provides remedy-specific recommendations for sediment monitoring programs, and facilitates comparison of effective monitoring tools.

USEPA (2005a) identifies the following questions for designing a long-term MNR monitoring plan:

- What is the purpose of the monitoring?
- Are detection limits adequate to meet the purpose of the monitoring?
- How will factors such as local conditions or habitats influence the natural recovery process and monitoring data?
- Are potentially confounding factors well understood?
- How often should monitoring take place and for how long?
- Can the monitoring data be readily placed into electronic databases and shared with others?
- Who is responsible for reviewing the monitoring data?
- What are the methods and triggers for identifying trends in the results?
- What are the most appropriate methods for analyzing the monitoring data (e.g., statistical tests, other quantitative analyses, or qualitative analyses)?
- If statistical analysis is planned, will there be sufficient data to support it?
- Is there agreement on what actions will be taken based on the possible results of the monitoring?
- How will the results be communicated to the public, and who is responsible for this communication?

*Example: Monitoring elements that supply lines of evidence for a sedimentation hypothesis include bathymetric mapping, sediment stability measurements, geochronology assessment, chemical and geophysical profiling, and sediment sampling. Many of these elements may be captured during the RI/FS to support an MNR remedy. Long-term monitoring may include a subset of measurements, such as bathymetric mapping and surface sediment chemistry monitoring, to verify ongoing net deposition and declining surface sediment concentrations with time.*

Monitoring Data Analysis. This step includes collection and analysis of data, evaluating analytical results, addressing deviations from DQOs, and quantifying uncertainty. Monitoring and analysis methods should be

documented clearly in the monitoring plan, which should include strategies to address precision, accuracy, representativeness, completeness, and comparability of data.

*Example: Monitoring data are analyzed to determine sedimentation rates and changes in surface sediment contaminant concentrations in order to assess the progress toward attainment of cleanup levels.*

Establish the Management Decision. Monitoring results, decision rules, and uncertainties are evaluated to determine the progress toward remedial goal attainment, support decisions regarding changes in monitoring or remedial strategies, and communicate findings to stakeholders. Management decisions should be supported by and consistent with the CSM. Long-term monitoring guides decisions and expectations regarding the rate of recovery, attainment of remedial goals and cleanup levels, and permanence of the remedy after disturbance and changes in site conditions.

*Example: If monitoring data, analysis, and decision rules support the predicted attainment of surface-sediment concentration goals within the expected time frame, this could support a decision to reduce monitoring frequency and maintain support for the MNR remedy.*

### 7.3 Baseline Monitoring

**B**aseline monitoring conducted during the RI/FS process (or immediately thereafter) establishes baseline conditions for the future trajectory of contaminants and related risks, as well as the baseline for performance of natural recovery processes. The accurate characterization of current conditions and processes during the RI/FS supports both the remedy selection process and the quantification of progress toward remedial goals. However, RI/FS and baseline sampling are designed with different objectives. Thus, RI/FS data may not provide a sufficient basis for comparison to long-term monitoring results, and additional baseline sampling may be needed. Site characterization during the RI/FS generally encompasses sampling to develop the CSM, determining the nature and extent of contamination, assessing risks to human health and the environment, and evaluating the feasibility of remedial alternatives. Baseline data should establish pre-remedy conditions to support statistically valid comparisons to future data sets and model predictions (NRC, 2007a; USEPA, 2005a). Historical data may also contribute to establishing baseline conditions (e.g., Figure 7-2).

Statistical considerations. The CSM and baseline monitoring comprise a framework and statistical basis for evaluation of site conditions and attainment of remedial goals and cleanup levels. Statistical analysis can help to quantify and mitigate uncertainties associated with monitoring results. Detection of a statistical trend requires a statistical test of a hypothesis, typically expressed as a null hypothesis of “no effect” – zero trend, or no significant change in concentration over a particular period of monitoring (Devore, 1987).

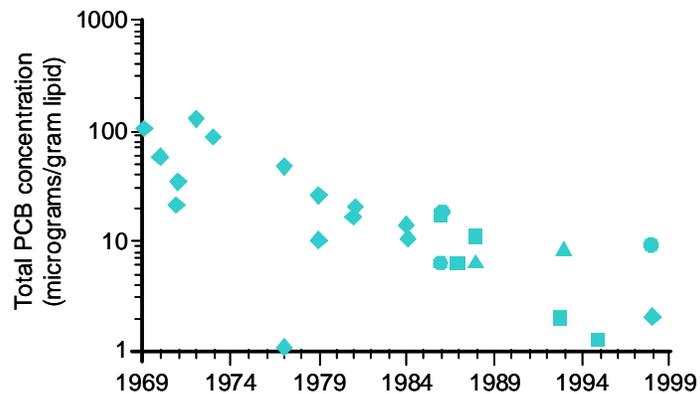


FIGURE 7-2. Temporal trends in PCB concentrations in four species of fish from the lower Delaware River, 1969-98. Symbols represent different species of fish (adapted from Rivamurray et al. 2003).

The null hypothesis is subject to two different types of error: the rejection of the null hypothesis when it is actually correct (Type I error) and the failure to reject the null hypothesis when it is incorrect (Type II error). This second type of error can confound evaluation of recovery in a monitored system. The statistical power of a particular test is defined as the probability of avoiding such an error, or more simply, the probability that the test will lead an investigator to detect a trend when one actually does exist (Murphy and Myors, 1998).

The up-front calculation of statistical power necessary to discern a particular trend has direct implications for sampling design. The designer of the long-term monitoring plan can specify a requirement that an environmental trend be detectable at a particular level of probability (e.g., 80%), and then calculate the number of samples required to obtain this level of power. This enables the creation of a test that is statistically defensible, while efficiently limiting sampling to the level needed to reach the required level of confidence (USEPA, 2008c). However, a high level of statistical power is not always feasible if an excessively large number of samples would be required. For fish tissue monitoring, analysis of composite samples can help limit the total number of analyses required by reducing variability (USEPA, 2008c). However,

the decision to composite samples should be considered carefully to ensure that important information is not lost through the process.

## 7.4 Long-Term Monitoring

**L**ong-term monitoring for MNR identifies recovery trends, refines the CSM, verifies attainment of remedial goals and cleanup levels, and confirms remedy permanence (USEPA, 2005a; 2002a). Long-term monitoring should target representative areas, including those potentially most susceptible to slowing or reversal of natural recovery processes. Additionally, source control monitoring is an important component in the long-term monitoring strategy, as recovery can be halted or reversed if source control is insufficient.

The key objective for long-term monitoring is to determine progress toward attainment of remedial goals and cleanup levels. Typical trends that give evidence of MNR success can include:

- Long-term decreasing trend of contaminant levels in higher trophic-level biota (e.g., Figure 7-3).
- Long-term decreasing trend of water column or sediment contaminant concentrations.
- Long-term decreasing trends of surface-sediment pore water chemical concentrations or toxicity. At sites where surface sediment chemical concentrations are at or below cleanup levels, but buried sediment concentrations exceed cleanup levels, monitoring may focus on maintaining the status quo.

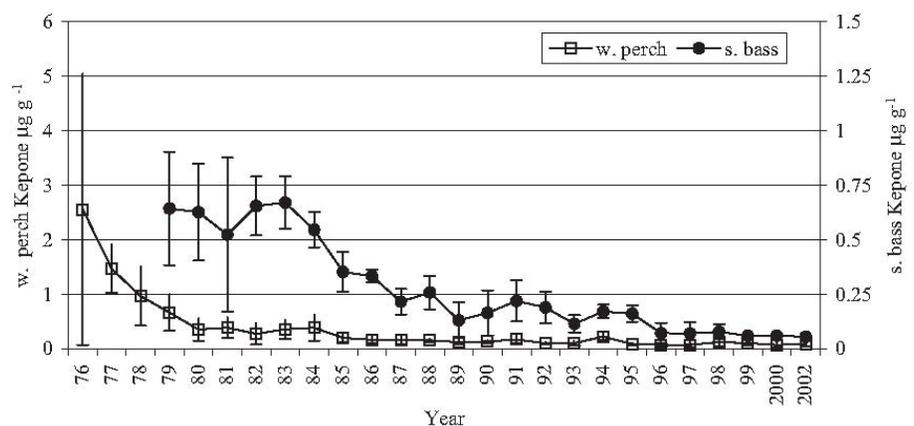


FIGURE 7-3. Long-term decreasing average Kepone concentrations in white perch and striped bass in the James River, VA. Reprinted from Luellen et al. (2006), with permission from Elsevier.

The first step of developing a long-term monitoring strategy involves the translation of RAOs from the ROD to measurable remedial goals and cleanup levels (Table 7-1). Remedial goals and cleanup levels are standards by which to evaluate measurable or otherwise observable aspects of the sediment site and thereby indicate the progress of the site toward meeting the RAOs (Thom and Wellman, 1997). While Table 7-1 focuses on risk-based remedial goals, in some cases risk-based target concentrations may be unachievable because they are lower than locally applicable background or baseline concentrations. In such cases, remedial goals may focus on achieving conditions comparable to reference areas.

Monitoring elements should be measurable and provide direct feedback on performance of the system with respect to meeting remedial goals and achieving cleanup levels. Monitoring elements may include direct measurement of risk reduction (e.g., chemical concentrations in biota tissue or biological effects), or indirect measurements of risk reduction (e.g., surface sediment, pore water, or surface water concentrations). Indirect measurements are more often conducted than direct measurements of risk, and are frequently the basis for risk-based cleanup levels; direct measurements of risk are expressed as remedial goals. Highlight 7-1 describes a monitoring program focusing on toxicity to benthic organisms; Highlight 7-2 features a monitoring program focusing on contaminant bioaccumulation.

Long-term monitoring often continues after remedial goals have been achieved. Low-frequency, disturbance-based monitoring is generally implemented when data confirming the permanence of the remedy is insufficient or highly uncertain. This monitoring should target specific times, locations, processes, and measurements that verify permanence of the remedy and risk reduction. Monitoring elements may be implemented after potential sediment disturbance, such as a hurricane, in order to verify low-risk conditions remain at the site. Typically, after a predetermined number of disturbance-based monitoring events have occurred, stakeholders will evaluate whether the data indicate that the remedy is permanently protective of human and ecological health. When the remedy is confirmed to be permanent, the site can proceed to closure.

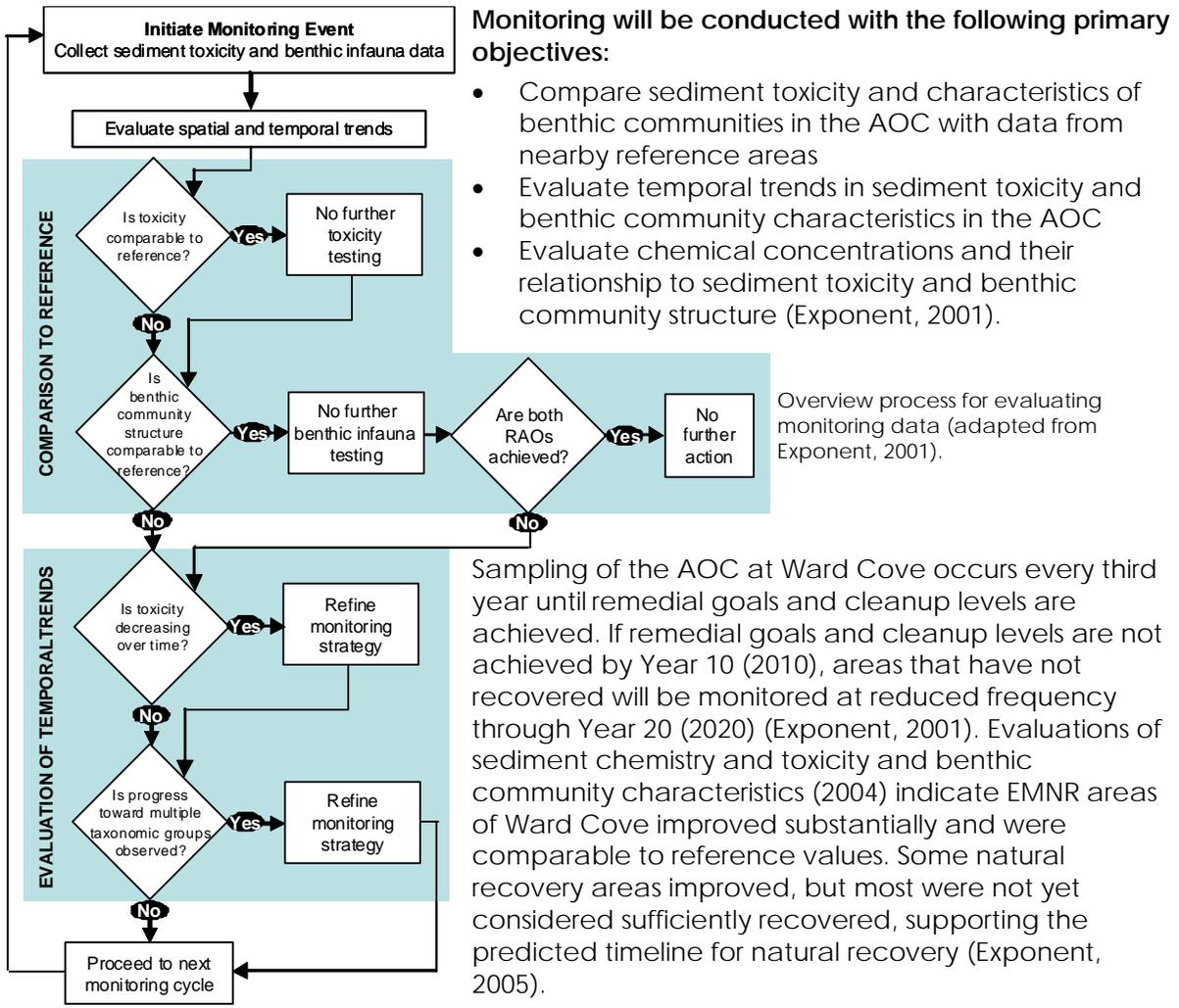
TABLE 7-1. Example translation of RAOs to measurement endpoints, remedial goals, and cleanup levels.

RAOs	Measurement Endpoints	Remedial Goals	Cleanup Levels
Reduce contaminant concentrations in fish and shellfish to levels protective of human health	Concentrations of contaminants in fish and shellfish	Average or 95% upper confidence limit (UCL) concentrations in fish and shellfish are below human health risk-based target concentrations	95% UCL or spatially weighted average concentration (SWAC) in surface sediment or pore water is at or below levels predicted to achieve remedial goals
Reduce surface-sediment contaminant concentrations to levels below human health risk-based target concentrations for direct contact	Concentrations of contaminants in sediment	Surface sediment SWAC or 95% UCL is less than human health risk-based target concentrations	Surface sediment SWAC or 95% UCL is less than human health risk-based target concentrations
Eliminate toxicity of surface sediments	Growth, reproductive, and survival endpoints in sediment toxicity tests	No statistically significant differences in sediment toxicity between reference and site locations	Surface sediment SWAC (or other statistic) is at or below levels predicted to achieve remedial goals
Enhance recolonization of surface sediments to support a healthy marine benthic infauna community	Species diversity, richness, abundance of key invertebrate species	No statistically significant differences in macroinvertebrate community metrics between reference and site locations	Surface sediment SWAC (or other statistic) is at or below levels predicted to achieve remedial goals
Reduce contaminant concentrations in fish to levels protective of piscivorous wildlife	Concentrations of contaminants in fish Reproductive and population endpoints in wildlife species	Average or 95% UCL concentrations in fish are below risk-based target concentrations No statistically significant differences in wildlife population endpoints between site and reference areas	Surface sediment SWAC (or other statistic) is at or below levels predicted to achieve remedial goals
Ensure with high confidence that future high-energy events will not result in unacceptable risks	Relationship between weather events and: Sediment core vertical profiles of contaminant concentrations Bathymetric surveys Contaminant concentrations in surface sediment	Statistically relevant extreme weather events will not cause more than a target amount of sediment erosion, on an aerial and depth basis	

### LONG-TERM MONITORING FOR TOXICITY IN WARD COVE, AK

The Marine Operable Unit in Ward Cove, Alaska, received pulp mill discharges from the Ketchikan Pulp Company between 1954 and 1997. The COCs at the site (ammonia, sulfide, and 4-methylphenol) are by-products from the decomposition of organic matter in pulping effluent. While these chemicals are neither persistent nor bioaccumulative, they are toxic to the benthic community in surface sediments.

The RAOs aim to reduce toxicity of surface sediments and enhance recolonization of surface sediments by a healthy benthic community that will serve as a diverse food source to larger invertebrates and fishes. An area of concern (AOC) of approximately 80 acres was defined based on chemical concentrations and/or toxicity levels (determined by amphipod and echinoderm tests) exceeding minimum cleanup levels. The selected remedy achieves RAOs through a combination of EMNR, navigational dredging, and natural recovery. The thin-layer placement serves as habitat for benthic communities. Naturally recovering areas, where capping is impracticable, will become suitable habitat primarily through natural accumulation of clean sediments and decay of toxic constituents. Natural recovery of benthic communities is estimated to take 8 to more than 20 years (USEPA, 2000e).



HIGHLIGHT 7-1. Monitoring recovery of benthic communities at the Ketchikan Pulp Company Superfund Site.

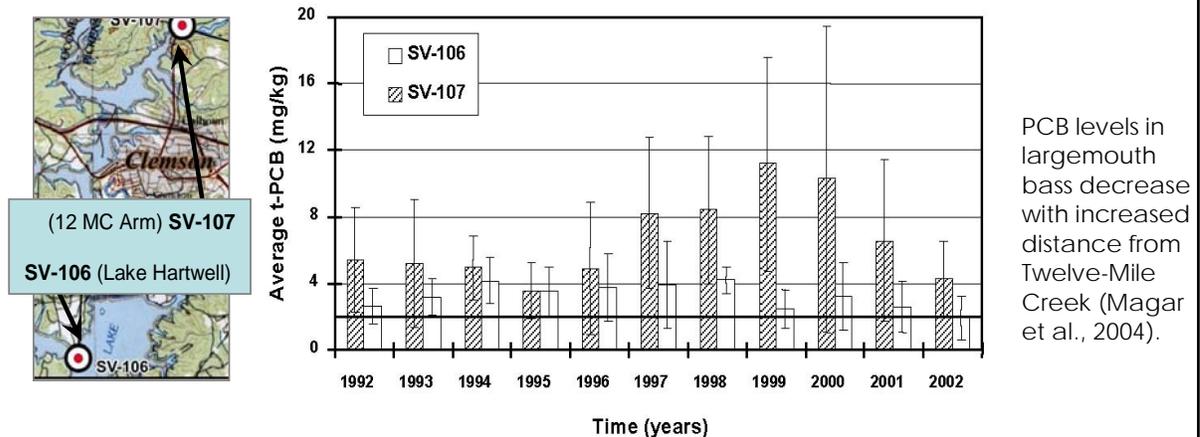
## MONITORING PCB BIOACCUMULATION IN LAKE HARTWELL

Deposition of cleaner sediment is reducing surface sediment PCB concentrations in the Twelve-Mile Creek arm of Lake Hartwell (Highlight 4-4). Aquatic bioaccumulation modeling conducted in 1993 predicted PCB concentrations would decline in all components of the aquatic food chain, with mean concentrations in largemouth bass fillets falling below the 2.0 mg/kg U.S. Food and Drug Administration (FDA) tolerance level by Year 10 (in 2003) or Year 12 for 10-year-old fish (USEPA, 1994). The majority of the surficial sediments in the Twelve-Mile Creek Arm were predicted to achieve the 1 mg/kg cleanup level between 2007 and 2011 (USEPA, 2004a).

PCB monitoring supports modifications to fish advisories and modeling activities, and confirms that the MNR remedy, combined with ongoing fish advisories, remains protective of human health and the environment. PCB concentrations are measured in surface sediment samples, caged freshwater clams (*Corbicula*) exposed for 28 days, forage fish (gizzard shad/blueback herring, threadfin shad, and bluegill), and game fish (largemouth bass, channel catfish, and hybrid bass) (USEPA, 1994).

Results of the second 5-year review demonstrate steadily declining surficial sediment PCB concentrations in the Twelve-Mile Creek Arm compared to historical data; concentrations ranged from 1–5 mg/kg (USEPA, 2004a). However, no clear trend of decreasing PCB concentrations has been shown in fish tissues, and PCB concentrations in all fish species remain above the 2.0 mg/kg FDA limit (URS, 2008). The discrepancy between sediment and pelagic fish tissue PCB trends might be the result of a continuing surface water source of PCB contamination, either from the original source (the former Sangamo plant site) or from low-level PCB exports from Twelve-Mile Creek (USEPA, 2004a), or may be due to other incompletely characterized and controlled exposure pathways.

The 2004 review recommended modifications to the annual monitoring program, including the addition of congener specific analyses, increasing replication to better support statistical evaluations, adding lipid analysis for *Corbicula* samples, and reducing gender bias in game fish samples (USEPA, 2004a). Additional source control efforts have been undertaken in response to monitoring results.



HIGHLIGHT 7-2. Monitoring PCBs in surface sediment and biota, Lake Hartwell, SC.

## 7.5 Adaptive Site Management for MNR

Ideally, the CSM, baseline monitoring, and long-term monitoring are integrated to provide feedback during operation of the remedy to demonstrate that recovery processes are functioning within acceptable time frames to achieve remedial goals and cleanup levels (USDOE, 1999). Monitoring plans and data are evaluated within an adaptive site management framework (Figure 7-4) (NRC, 2003a). Adaptive site management encourages routine data analysis and review and involvement of stakeholders in the monitoring process.

Adaptive site management should foster frequent interactions between site managers, regulators, and stakeholders that will improve communication, build trust and credibility, improve flexibility, and lead to greater efficiency in site remediation. Adaptive site management encourages regular review periods, such as the 5-year review schedule outlined in the CERCLA regulatory process.

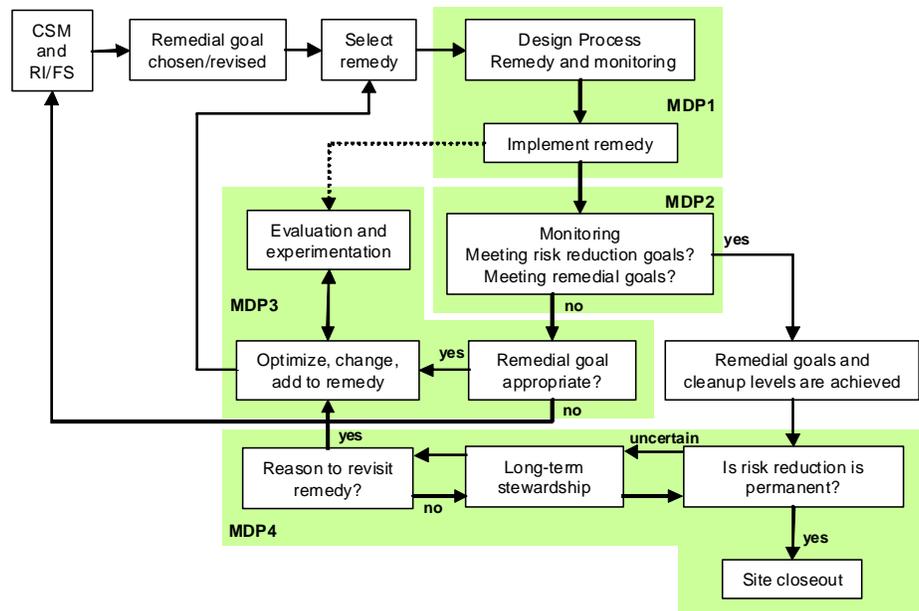


FIGURE 7-4. Adaptive site management process: post-remedy selection. The shaded areas show the activities related to the management decision periods (MDP) described in the text. Adapted from NRC (2003a).

The adaptive site management framework utilizes management decision periods (MDP) to make decisions based on pilot-scale work, on changes in land use or stakeholder needs, and on monitoring data and other information that may require a management decision to be revised. MDPs represent formal opportunities for project managers, regulators,

and interested stakeholders to evaluate data and reach agreement on management strategy.

The purpose of the first element of the framework, MDP1 (Figure 7-4), is to ensure that the selected remedy is practicable and implementable under current site conditions and that an appropriate monitoring plan is developed. This period is important because there is often a lag time between remedy selection and implementation. In the case of MNR, it is important to review baseline conditions at this point to select appropriate monitoring elements that will provide data to verify and refine the CSM. Monitoring plan elements must also focus on the effectiveness of the remedy at achieving remedial goals and cleanup levels. Decision rules that will guide adaptive site management after monitoring begins are established by stakeholders in MDP1.

Long-term monitoring data collected during MDP2 is used to determine whether the MNR remedy is effective, as well as to refine the CSM. Updating the CSM will reduce uncertainty in the remedy's performance, but it should also stimulate stakeholders to review the RI/FS and risk assumptions to verify the appropriateness of the remedial goals. Monitoring should continue to evaluate the remedy for effectiveness while natural processes continue to reduce risk at the site. However, if natural processes are found to be insufficient in reducing risk, MDP3 is entered. It is important to allow sufficient time to pass before deciding whether a system is meeting remedial goals and cleanup levels, but the time frame should be finite so an ineffective remedy is not left in place indefinitely.

If the remedy is not sufficient to meet remedial goals and cleanup levels within an acceptable time period, the project manager, regulators, and stakeholders should address in MDP3 whether remedial goals remain appropriate for site conditions and how the remedy can be modified or optimized to meet remedial goals (NRC, 2003a). New goals may be established that are better aligned with the natural processes and that can guide the project towards an equally beneficial endpoint (Thom and Wellman, 1997). Alternate remedies or remedy modifications can be evaluated as on- or off-site pilot-scale activities, by expert panels, or through literature reviews or case studies (NRC, 2003a). Modifications to the MNR remedy might include extending the time period for the MNR remedy to take effect, augmenting the monitoring program to better quantify recovery processes, employing EMNR in depositional areas, or introducing sequestering agents to reduce bioavailability. Alternatively, MNR may be replaced by other remedies entirely.

That additional remediation may be required in the event of failure to meet remedial goals is sometimes perceived as a drawback of the MNR approach. However, the possibility of remedy failure is in no way unique to MNR (NRC, 2007a). In the event that remedial goals are not being met, adaptive management promotes a re-planning process that takes into account all of the information available at the time that the need to re-plan is recognized. As such, adaptive management is preferable to a less flexible “contingency remedy” approach, in which a predefined contingency plan is determined at the time of remedy selection (USEPA, 1999b). Clearly defining the adaptive management framework as part of the remedy selection process may help to promote remedy acceptance without predetermining future remedy modifications.

When the MNR remedy achieves remedial goals and cleanup levels, MDP4 produces a road map for site closure. Site closeout can only occur after risk reduction is determined to be sufficiently permanent and protective to enable unrestricted site use. Deliberations in MDP4 include planning for long-term stewardship and monitoring. In the case of MNR, components evaluated during MDP4 may include low-frequency monitoring after disturbance events, ongoing verification of source control, and/or institutional controls. Factors that contribute to remedy permanence are both site-specific and process-specific. Stewardship monitoring elements should address the following natural process characteristics.

**Chemical Transformation.** Remedy permanence hinges on the completeness and geochemical stability of the transformation process, along with the toxicity characteristics of the transformation products. If the contaminant is largely degraded to nontoxic products, the transformation is irreversible, or the kinetics of reversible reactions do not adversely increase risks, then long-term monitoring may not be necessary after remedial goals are achieved.

**Reduced Bioavailability and Mobility.** Remedy permanence is dependent on the stability of the binding, precipitation, or sequestration processes that contribute to reduced exposure and risk. If binding processes have been demonstrated to be stable, long-term monitoring may not be needed after remedial goals have been achieved. However, if binding processes are reversible or depend on site-specific geochemical conditions, additional monitoring may be required to establish remedy permanence.

**Physical Isolation.** Where natural recovery is achieved through isolation, long-term sediment stability and the potential effects of changes in biological communities should be considered. Physical disturbances that

can impact isolation process may include storms, propeller wash, ice scour, river channel migration, and off-site construction or diversion projects that might influence deposition and erosion patterns at the site. Sediment disturbance does not necessarily imply remedy failure, unless risks are increased unacceptably, or unless the event prevents continued natural recovery and risk reduction. Sediment instability may be localized and may have little net impact on risk. Once isolation has been demonstrated to be stable over the course of several years, and over the course of predictable high-energy events, then additional monitoring may not be needed.

Dispersion. For natural recovery through dispersion, the contamination will either have been transported off site or mixed vertically through the sediment column to the extent that exposures and risks are no longer significant at the site. From a long-term monitoring perspective, the key issue will be whether or not the off-site transport will create off-site risks.

## 7.6 MNR Performance Checklist

The following checklist summarizes considerations for developing a monitoring program and interpreting monitoring results.

CHECKLIST 7-1. Implementation considerations.

**1. Has the practical relationship between remedial action objectives and monitoring goals been established for the site? Consider the following components:**

- Monitoring elements needed to determine progress toward remedial goals.
- Utility of monitoring natural processes (e.g., sediment deposition rates) in addition to elements more directly related to risk reduction (e.g., chemical concentrations in fish tissue).
- Time frame(s) for monitoring elements with different potential recovery rates.
- Consistency of monitoring targets with the time frame defined for successful system recovery.

**2. Has the USEPA's Data Quality Objectives (DQO) process been used in developing the monitoring plan? Consider the following components, specifically (as defined by the USEPA):**

- The purpose of the monitoring.
- Whether detection limits are adequate to meet the purpose of the monitoring.
- How factors such as local conditions or habitats influence the natural recovery process and the applicability of monitoring data.
- Whether potentially confounding factors are well understood.
- Frequency (how often) and duration (how long) of monitoring required to achieve the stated purpose of the data collection program.

- Whether monitoring data can be readily placed into electronic databases and shared with others.
- Who is responsible for reviewing the monitoring data.
- Methods and triggers used to identify trends or thresholds in the data.
- The most appropriate methods, such as statistical tests or qualitative analyses, for analyzing the monitoring data.
- If statistical analysis is planned, that there will be sufficient data to support it.
- An agreement on actions to be taken as the result of evaluating monitoring data.
- How results will be effectively communicated to the public, and who will be responsible for this communication.

**3. Do the selected monitoring elements provide feedback on system progress toward achieving remedial goals? Consider the following components:**

- Interim remedial targets for the site.
- In progress toward achievement of interim remedial targets, identify whether risk assumptions have changed in a manner that could influence system progress toward long-term recovery.
- Whether the time frame for achieving interim remedial targets is consistent with site remedial objectives.
- Whether progress toward achieving interim remedial targets supports recovery rates predicted in the site CSM.
- If progress toward achieving interim remedial targets supports predicted recovery rates, consider development of a plan to reduce the frequency or intensity of monitoring events.
- If progress toward achieving remedial targets does not support predicted recovery rates, assess the extent to which the CSM requires updating and/or source control is an ongoing concern for the site.

**4. Will demonstration of remedy success be statistical in nature for the site? Consider the following components:**

- Whether additional data will be required beyond what was collected during the RI/FS process to define baseline conditions for the site.
- Develop monitoring plan hypotheses.
- Define the power of planned statistical tests.

**5. Have decision rules been developed for interpretation of site monitoring data? Consider the following components:**

- Whether a hierarchy of significance will be required for interpreting potentially conflicting lines of evidence.
- If a hierarchy of significance is required, confirm that it is consistent with stated remedial goals.
- If a hierarchy of significance is not required, confirm that there are sufficient lines of evidence under consideration to parameterize remedy success.
- Whether sufficient data have been collected to statistically resolve underlying recovery trends.

**6. How is “permanence of remedy” defined for the site? Consider the following components:**

- Decision rule(s) that define when site monitoring can stop.
- System variables such as disturbance events that might impact remedy permanence.
- An agreement regarding the extent to which such events should be planned for.
- If permanence of remedy cannot be achieved, develop a long-term stewardship plan for the site.

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# TECHNICAL GUIDE

Monitored Natural Recovery at Contaminated Sediment Sites

## APPENDIX A

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### MNR Case Studies

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## Acronyms and Abbreviations

ASB	Aerated Stabilization Basin
BNC	Bremerton Naval Complex
CB/NT	Commencement Bay Nearshore/Tideflats
<sup>137</sup> Cs	cesium-137
cm/yr	centimeters per year
COCs	chemicals of concern
Cr(VI)	hexavalent chromium
Cr(III)	trivalent chromium
CSM	conceptual site model
DNAPL	dense nonaqueous phase liquid
EMNR	enhanced monitored natural recovery
FRFood	Fox River Food model
FS	feasibility study
GBFood	Green Bay Food
GBTOXe	Enhanced Green Bay Toxics
GFP	Gateway Forest Products
KPC	Ketchikan Pulp Company
LSP	Life Science Products
LTR	long-term residual (risk)
MCUL	minimum cleanup level
mg/kg	milligrams per kilogram
MNR	monitored natural recovery
MRP 15	Mississippi River Pool 15
MTCA	Model Toxics Control Act
NPL	National Priorities List
OC	organic carbon
OMMP	Operations, Maintenance, and Monitoring Plan
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
RAO	remedial action objective
RI	remedial investigation
RI/FS	remedial investigation and feasibility study
ROD	Record of Decision
SEDCAM	Sediment Contamination Assessment Model

APPENDIX A: MNR CASE STUDIES

USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound
VSWCB	Virginia State Water Control Board
WASP	Water Quality Analysis Simulation Program
WBOR	west branch of the Ompompanoosuc River
WDNR	Wisconsin Department of Natural Resources
wLFRM	Whole Lower Fox River Model

# 1 Overview

*Descriptions of real-world projects where monitored natural recovery (MNR) is ongoing*

This case study review discusses real world applications of MNR to contaminated sediment sites. MNR has been evaluated and implemented at large and small sites, with a variety of hydrological conditions, contaminants, ongoing and historical sources, risk drivers, natural recovery processes, and complementary remedial strategies. The number of sites at which MNR has been employed attests to its versatility and applicability to a wide range of conditions.

Selection of MNR as a remedial alternative has been based on a variety of lines of evidence, focusing most commonly on physical isolation. Lines of evidence used to inform remedy selection range from qualitative assessments of natural recovery processes to empirical data collection and modeling quantifying rates of reduction in sediment concentrations and ecological receptors. At some sites, MNR has been selected to preserve sensitive habitat, or because other remedies are infeasible or the cost-effectiveness of MNR is paramount. The time required for MNR to achieve sediment remedial goals typically ranges from 5–30 years after MNR is selected as a remedy.

MNR monitoring programs have focused primarily on documenting the achievement of remedial goals by monitoring sediment chemistry and chemical concentrations in biota. Fewer than half of the sites continue to quantify natural recovery processes (such as sediment deposition rates) during the monitoring period.

The most effective MNR applications engage in the following practices: constructing and continually refining a fate/transport-focused conceptual site model (CSM); characterizing and controlling sources; quantifying natural recovery processes via measurement and modeling that enables spatially and temporally explicit predictions of risk reduction; and quantitatively documenting natural recovery processes and progress toward achieving remedial action objectives.

**T**his appendix reviews the implementation or investigation of MNR at 13 sites (Table A-1). The case studies selected for this review offer a sampling of lessons learned and offer insights into the investigation of and use of MNR as a sediment remedy.

## Where Is MNR Being Used?

The case studies reviewed include sites from across the United States (Figure A-1) that exhibit a variety of hydrological conditions, contaminants, sources, risk drivers, natural recovery processes, remedial strategies, and sizes (Table A-2).

Many of the discussed sites fall under the Superfund program because the implementation of MNR as a remedy is well-documented in these cases. However, MNR has also been employed in a variety of other legal and regulatory contexts, such as judicial enforcement actions and state-led programs (e.g., Red Bank Creek, SC [Highlight 4-1]; Belews Lake, NC [Highlight 4-5]).

Hydrological conditions. MNR has historically been associated with large embayments, where low-energy flows facilitate physical isolation via sedimentation. However, several case study sites are located in higher energy systems. Mississippi River Pool 15, the Elizabeth Mine site, the James River, and the Fox River are examples of river sites with remedies that rely on physical isolation in low-energy, net depositional areas, and dispersion in areas of high energy.

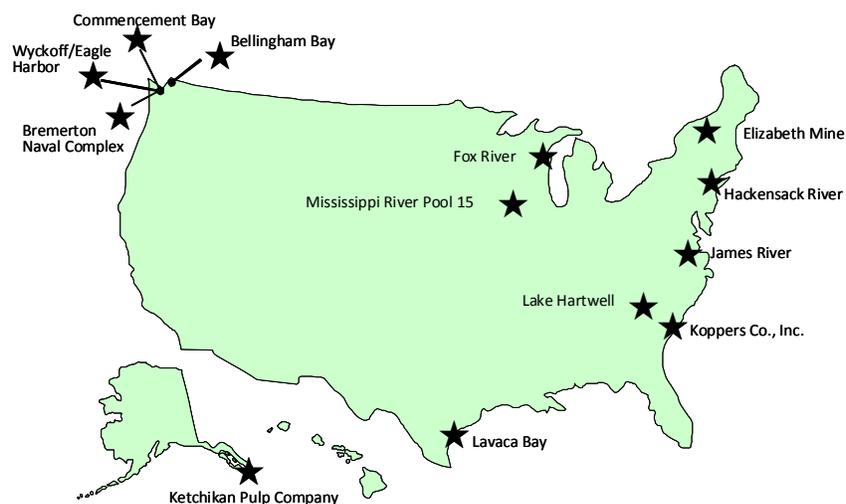


FIGURE A-1. Location of sites reviewed in Appendix A.

Chemicals of concern (COCs). MNR has been employed to address a variety of sediment contaminants, including recalcitrant organic compounds such as polychlorinated biphenyls (PCBs), degradable organic compounds such as polycyclic aromatic hydrocarbons (PAHs), and metals. Notably, there is a paucity of MNR case studies for relatively biodegradable compounds, such as nitrotoluenes or tributyltin. This appears to be due to the virtual disappearance of these compounds via transformation and degradation processes, once their respective sources are controlled. Thus, their degradation leads to no further action instead of an MNR remedy. That is, although natural recovery processes contributed to their removal from the environment, monitoring is not required.

Contaminant sources and source control. Although many of the sources of sediment contamination at the case study sites were associated with past direct and indirect discharges, several sites had not achieved complete source control before implementing an MNR remedy. Most ongoing sources were related to runoff from upland sources such as contaminated soils or groundwater. In some cases, such as Eagle/Wyckoff Harbor and Elizabeth Mine, upland source removal continued during the course of the sediment MNR remedy. In the case of Lake Hartwell, it is hypothesized that source control may have been insufficient, as fish tissue PCB concentrations have not declined in tandem with surface sediment concentrations.

Any sediment remedy will be ineffective if continued contaminant releases to the site result in unacceptable risk. However, the lack of complete source control does not necessarily preclude evaluation of MNR processes and even the selection of an MNR remedy, although persistent sources typically slow recovery. For sites where source control remains an obstacle to recovery, modeling may be conducted to compare the rates of ongoing contaminant deposition versus the rate of risk reduction afforded by natural recovery processes. Additionally, upstream and internal sediment sources can be addressed effectively through a “hybrid” MNR remedy that includes focused capping or dredging.

**Risk Drivers.** MNR has been employed to reduce risks to human and environmental receptors to levels consistent with ecological and human health risk-based goals. It is important for stakeholders to understand that risks are present during the natural recovery period as well as during alternative remedy design and implementation time frames. For example, in Commencement Bay, an acceptable natural recovery time period was defined under the Record of Decision (ROD) as 10 years following completion of active remedial measures. If natural recovery was not predicted to meet cleanup levels within 10 years at a given subarea or operable unit (OU), another remedy (e.g., capping or dredging) was required.

In Lake Hartwell, institutional controls, such as restricted access for anglers and posting of fish consumption advisories, ameliorate risks during recovery. For sites at which human exposure is low or can be reasonably controlled by institutional controls, implementation of MNR can produce fewer adverse impacts to habitat and the environment than those commonly caused by capping and dredging.

**Natural recovery processes.** Physical isolation of contaminated sediments by sedimentation was the most common natural recovery process identified for the sites reviewed. Sediment burial and physical isolation occurs in net depositional environments, where the rate of sediment deposition exceeds the rate of sediment resuspension and export (Magar, 2001). Ironically, these depositional environments are likely repositories for contaminated sediment particles; in other words, the same natural sediment transport mechanisms that remediate contaminated sediment environments through natural burial were probably the cause of the initial deposition and accumulation of contaminated particles. It is therefore unsurprising that physical isolation is the dominant natural recovery process reported.

**Chemical natural recovery processes** (chemical transformation and reductions in contaminant mobility and bioavailability) were often cited as being complementary to physical isolation processes and were important in supporting the permanence of risk reduction at sites in which the stability of freshly deposited sediment was in question. However, over the time periods important to stakeholders, physical isolation typically achieved more immediate risk reduction, particularly for persistent chemicals with slow transformation rates. Dispersion was identified as a natural recovery process at several sites, particularly in high-energy areas of stream and river systems.

**Spatial Scale of MNR.** MNR has been implemented at sites and subareas of sites ranging from a small 5-acre application in an intertidal area of the Wyckoff/Eagle Harbor site to a 2,600-square mile application in Green Bay. There is no optimal spatial scale for MNR implementation, as the lines of evidence that evaluate natural recovery and predict risk reduction rates over time are largely independent of site size. However, site size may influence the cost of developing MNR lines of evidence during the feasibility study (FS) and monitoring phases.

**Stand-Alone or Complementary Application of MNR.** The case studies demonstrate that MNR is not an all-or-nothing remedy. While MNR may be implemented as a stand-alone remedy, it is often combined with capping or dredging (Table A-2). In some areas, natural recovery may appear to be the most appropriate remedy, yet the rate of sedimentation or other natural processes is insufficient to

reduce risks within an acceptable time frame. Where this was the case, enhanced MNR (EMNR) via thin-layer placement of clean material was used (e.g., Ketchikan Pulp Company, Bellingham Bay).

## How and Why Was MNR Selected?

Development of the lines of evidence to support MNR is a critical element for investigating the feasibility of natural recovery to address site risks. The sites reviewed varied in the level of effort involved to develop lines of evidence, in the projected times to achieve remedial goals, and in monitoring costs (Table A-3).

**Lines of Evidence.** At most sites at which MNR was evaluated, lines of evidence included empirical investigation of site conditions, followed by modeling to interpret the data and predict achievement of remedial goals and cleanup levels. Empirical lines of evidence usually included measurements to identify sedimentation rates at the site, particularly when physical isolation was a key recovery process. Tools including bathymetry, radioisotope monitoring, and sediment traps often were employed to measure current or historical deposition rates. Measurements of deposition rates served as input variables for various mechanistic deposition models that then predicted future surface sediment concentrations (e.g., Commencement Bay, Koppers Barge Canal, Lower Fox River and Green Bay). In some cases, model predictions were supported by empirical time trends depicting decreasing surface sediment concentrations over time, or sediment coring data that showed decreasing sediment concentrations in surface sediments (e.g., Lower Fox River and Green Bay, Lake Hartwell). Modeling also supported the permanence of risk reduction. For example, at Lavaca Bay, a model was used to investigate the stability of freshly deposited sediments during a hurricane.

Where chemical transformation was expected to play a role in risk reduction, chemical fingerprinting was often combined with sediment coring. Chemical fingerprinting qualitatively documented the transformation of PAHs (Wyckoff/Eagle Harbor) and PCBs (Lake Hartwell) over time. At Lake Hartwell, PCB dechlorination rates were derived from sediment core data; results indicated that  $16.4 \pm 11.6$  yr was required per *meta* plus *para* chlorine removal (ranging from 4.3–43.5 yr per chlorine removal) (Magar et al. 2005b). Since the original release, this has led to the progressive dechlorination of PCBs and to the accumulation of less toxic, lower chlorinated congeners dominated by *ortho* chlorines.

For the natural recovery processes of dispersion or reduction in contaminant mobility and bioavailability, formal lines of evidence (modeling, data, literature reviews) were usually a secondary consideration. In many cases, dispersion is considered the opposite of physical isolation, and the same lines of evidence (hydrodynamic modeling, sediment profile imagery) address both. However, given the depositional nature of most contaminated sediment sites, these lines of evidence are not typically used to establish dispersion processes. For large and/or hydrodynamically complex sites including both depositional and erosional areas (e.g., Fox River), dispersion modeling was explicitly developed as a line of evidence. However, in many cases, dispersion processes were simply assumed to occur based on general knowledge of hydrodynamic, sediment transport, and contaminant behaviors.

At some sites, MNR was selected because alternative remedies were impracticable, or because alternative remedies would cause more harm than good. In the case of Elizabeth Mine, MNR was selected primarily because dredging and capping risked unacceptable levels of ecological damage. Similarly, at Wyckoff/Eagle Harbor, MNR was selected because preservation of eelgrass habitats in intertidal areas outweighed the benefits associated with addressing sediment contamination via capping or dredging. Dredging and capping remedies were characterized as infeasible or were associated with disproportionately high costs relative to environmental benefits in portions of the Ketchikan Pulp Company site and Lower Fox River and Green Bay, leaving EMNR or MNR as the most viable remedial alternatives.

**Recovery Timelines.** Expected attainment of remedial goals ranged from 5 years for the Koppers Barge Canal and Lavaca Bay to 40 to greater than 100 years for Lower Fox River and Green Bay (not taking into account upstream sediment remediation projects that should control sources to the MNR areas). For Commencement Bay, Ketchikan Pulp Company, Koppers Barge Canal, and Lower Fox River and Green Bay, recovery times were predicted through mechanistic models that relied on empirical site data incorporating natural recovery processes (such as physical isolation rates), statistical models that used time trends in historical sediment concentration data to project future sediment concentrations, or a combination of both. For other sites, recovery time periods were not predicted, or were assumed to occur within a typical time frame for regulatory remedial success (e.g., 30 years).

**Projected Monitoring Costs.** Costs associated with MNR usually were orders of magnitude lower than those associated with dredging and capping. Costs generally were in the range of several hundreds of thousands of dollars (as estimated at the time of the feasibility study). The highest projected cost was for the Lower Fox River and Green Bay MNR implementation; current estimated costs for the long-term monitoring plan range between \$7 and \$13 million (2008 net present value basis) over an estimated 50-year monitoring period. For the sites at which a cost could be normalized to area and time, estimated costs were \$6 per acre per year (Lake Hartwell), \$80 per acre per year (Lower Fox River), \$300 per acre per year (Bellingham Bay), \$500 per acre per year (Commencement Bay), and \$900 per acre per year (Wyckoff/Eagle Harbor).

## Has MNR Been Successful?

MNR has been successful at most of the sites reviewed (Table A-4). In almost every case where long-term monitoring is sufficient to evaluate remedy success, remedial goals are being achieved or have been achieved. Although none of the sites have achieved closure, the Koppers Barge Canal site may be nearing cessation of monitoring in the subarea at which MNR has been implemented. Only one example, Lake Hartwell, suggests mixed results for MNR. At Lake Hartwell, surface sediment concentrations have continued to decrease due to physical isolation and are generally meeting cleanup levels. However, PCB concentrations in fish tissue remain above fish consumption standards. Natural recovery continues to be monitored at Lake Hartwell through sediment and fish tissue analyses, and fish consumption restrictions remain in effect at this site.

MNR success has been documented mainly via a comparison of measured concentrations in sediment to a sediment cleanup level. Biological monitoring, such as concentrations in fish tissue, sediment toxicity, and benthic invertebrate community analysis, also is a component of long-term monitoring at nearly all the sites.

## Implementing Effective MNR Programs

The following practices were common to the most effective MNR programs reviewed:

- Documentation of past and present sources.
- Characterization of site hydrological conditions.
- Early identification of primary natural recovery processes (usually physical isolation).
- Development of quantitative lines of evidence via the collection of empirical data and parameterization of mechanistic models capable of predicting the effect of natural recovery on surface sediment concentrations.
- Support of modeling exercises with historical surface sediment concentration data or coring studies to confirm decreases in surface concentrations over time.
- Use of modeling lines of evidence to inform a quantitative prediction of remedial goal and cleanup level attainment.
- Monitoring of natural recovery processes (e.g., sedimentation rates and sediment stability) and remedial goal and cleanup level attainment (e.g., decreasing concentrations in sediment and biota).

TABLE A-1. Overview of case study sites (page 1 of 2).

Site Name, Operable Unit/Subarea	Location	Regulatory Agencies	Summary
Bellingham Bay, Whatcom Waterway	Bellingham, WA	Washington Ecology	Quantitative lines of evidence supported the selection of MNR to address physical isolation of mercury-containing sediments.
Bremerton Naval Complex, OU B	Bremerton, WA	U.S. Navy, USEPA, Washington Ecology	Lines of evidence documented natural recovery via physical isolation, which facilitated the selection of MNR in a combination remedy. MNR augments risk reduction from dredging and thin layer capping in PCB- and mercury-contaminated sediment. The monitoring program focuses on natural sedimentation.
Commencement Bay, Nearshore/ Tide Flats	Tacoma, WA	USEPA	Documented natural recovery processes include physical isolation, chemical transformation, and dispersion of sediments containing numerous contaminants. At the Sitcum Waterway subarea, MNR addressed post-dredging residuals.
Elizabeth Mine	Strafford and Thetford, VT	USEPA	Qualitative evidence indicates physical isolation and dispersion processes are occurring. MNR was selected as the most cost-effective and least damaging option for wetland and stream resources. However, recovery is not expected until acid mine drainage can be controlled.
Hackensack River, Study Area 7	Jersey City, New Jersey	U.S. District Court of New Jersey	Baseline risks are low due to past transformation of hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) and associated reduction of bioavailability and toxicity. The demonstrated physical stability of site sediments and chemical stability of Cr(III) justified leaving buried chromium-containing sediments in place.
James River	Hopewell, Virginia	Virginia Department of Environmental Quality	One of the earliest examples of MNR; pioneered the use of radioisotope analysis and sediment age dating to demonstrate physical isolation through sediment deposition. Fish tissue concentrations fell below the action level by the late 1980s.
Ketchikan Pulp Company, Ward Cove	Ketchikan, AK	USEPA	MNR was selected for portions of the site where capping and dredging were infeasible due to physical conditions. Physical isolation of sediments is the primary process reducing benthic toxicity from ammonia, sulfide, and 4-methylphenol.
Koppers Co., Inc., Barge Canal	Charleston, SC	USEPA	Investigations during the design phase for a capping remedy demonstrated significant natural recovery of PAH-contaminated sediments through sedimentation, and the remedy was changed to MNR. The monitoring program confirms predicted sedimentation rates with long-term monitoring data.

Table A-1. Overview of case study sites (page 2 of 2).

Site Name, Operable Unit/Subarea	Location	Regulatory Agencies	Summary
Lavaca Bay	Point Comfort, TX	USEPA	Measurements of sedimentation rates supported physical isolation as the dominant natural recovery process. Hurricane scour modeling evaluated the potential for sediment erosion and mercury redistribution during future hurricane events and concluded that a category 5 hurricane (Saffir-Simpson scale) would not create unreasonable risk.
Lower Fox River/Green Bay: OUs 2 and 5	Fox River Valley, WI	Washington Department of Natural Resources	MNR was selected for OUs where capping and dredging are not implementable. Constraints include shallow bedrock and high dispersion potential in OU2 and an excessive volume of low-level contaminated sediment in Green Bay. Physical isolation and dispersion are predicted to reduce PCB risks over a period of decades.
Mississippi River Pool 15	Scott County, IA	USEPA	MNR was selected for a freshwater riverine environment, relying on several natural recovery processes to address PCB-contaminated sediments. Temporal trends of decreasing PCB concentrations in sediment and fish and low human and ecological risks supported the selection of source control and MNR to address localized shoreline contamination.
Sangamo Weston/ Twelve-Mile Creek/ Lake Hartwell, OU2	Pickens County, SC	USEPA, South Carolina Department of Health and Environmental Control	Lines of evidence supporting MNR focused on physical isolation to address PCB-contaminated sediments. Results show that while objectives are being attained in sediments, concentrations of PCBs in fish tissue remain at levels of concern, likely due to incomplete source control.
Wyckoff/Eagle Harbor, West Harbor Intertidal	Puget Sound, WA	USEPA	MNR was selected for a portion of the site where habitat preservation (i.e., preservation of eel grass beds) outweighed the potential benefits of sediment removal or capping. Physical isolation processes are expected to effectively address PAH-contaminated sediment in this area.

TABLE A-2. Site conditions and remedial objectives for MNR sites (page 1 of 3).

Site Name, Operable Unit/Subarea	Hydrologic Conditions	Primary COCs	Primary Contaminant Source(s)	Source Control Achieved Prior to Remedy Selection	Risk Driver	Primary Natural Recovery Processes	Remedies Applied	
Bellingham Bay, Whatcom Waterway	Marine embayment	Mercury	Past direct discharges and releases from a chlor-alkali plant	Yes	Ecology Human health	Physical isolation	MNR	110 acres
							Capping and dredging	90 acres
Bremerton Naval Complex, OU B	Marine embayment	PCBs Mercury	Past direct discharges and releases, including from miscellaneous waste material used as fill during expansion of the Naval Complex; ongoing minor releases from upland soils via storm water discharge	No	Human health	Physical isolation Chemical transformation	MNR	230 acres
							Dredging, isolation capping, and thin-layer capping	61 acres
Commencement Bay, Nearshore/Tideflats	Marine embayment	Metals PCBs PAHs	Past and present wastewater discharges from numerous and varied industrial operations; past and present non-point contributions to watershed	No	Ecology Human health	Physical isolation Chemical transformation Dispersion	MNR	60 acres
							Capping and dredging	240 acres
Elizabeth Mine	Freshwater stream	Numerous metals, including copper and selenium	Past and present leachate from abandoned metal mines	No	Ecology	Physical isolation Dispersion	MNR	5-10 river miles

TABLE A-2. Site conditions and remedial objectives for MNR sites (page 2 of 3).

Site Name, Operable Unit/Subarea	Hydrologic Conditions	Primary COCs	Primary Contaminant Source(s)	Source Control Achieved Prior to Remedy Selection	Risk Driver	Primary Natural Recovery Processes	Remedies Applied	
Hackensack River, Study Area 7	Estuary	Chromium	Chromium ore processing residue used as fill in the Study Area 7 waterfront	Yes	Ecology	Chemical transformation Reduction of bioavailability and mobility Physical isolation	Dredging	0.5 acres
							Capping	30 acres
							MNR	53 acres
James River	Freshwater river	Kepone	Past direct discharges and releases from manufacturing operation	Yes	Ecology Human health	Physical isolation Dispersion	MNR	98 river miles
Ketchikan Pulp Company, Ward Cove	Marine embayment	Ammonia Sulfide 4-methyl-phenol	Past pulp mill effluent discharges	Yes	Ecology	Physical isolation	MNR	52 acres
							EMNR	28 acres
							Dredging	10,000 CY
Koppers Co., Inc., Barge Canal	Marine embayment	PAHs	Past direct discharges and releases from wood treating operations; past and present releases from upland soils and groundwater	No	Ecology Human health	Physical isolation	MNR	3.2 acres
							Capping and Dredging	5.3 acres
Lavaca Bay	Estuarine embayment	Mercury PAHs	Past direct discharges and releases from metal refining and chlor-alkali processes.	Yes	Ecology Human health	Physical isolation	MNR	1700 acres
							Dredging	280,000 CY

TABLE A-2. Site conditions and remedial objectives for MNR sites (page 3 of 3).

Site Name, Operable Unit/Subarea	Hydrologic Conditions	Primary COCs	Primary Contaminant Source(s)	Source Control Achieved Prior to Remedy Selection	Risk Driver	Primary Natural Recovery Processes	Remedies Applied	
Lower Fox River/Green Bay: OU2 and OU5	Freshwater river and embayment	PCBs	Past discharges from production and recycling of carbonless copy paper in the Fox River Valley; ongoing releases from upstream sediments	No	Ecology Human health	Dispersion Physical isolation	MNR	20 river miles (Fox River), 2650 acres (Green Bay)
							Capping and dredging	19 river miles (Fox River); 50 acres (Green Bay)
Mississippi River Pool 15	Freshwater river	PCBs	Past direct discharges and releases from aluminum sheet and plate rolling mill; past releases from upland soils and groundwater	Yes	Human health	Physical isolation Dispersion Reduction in contaminant bioavailability and mobility	MNR	1 river mile
Sangamo Weston/ Twelve-Mile Creek/Lake Hartwell, OU2	Freshwater stream and lake	PCBs	Past direct discharges and releases from capacitor manufacturer; ongoing minor releases from upland soils and groundwater	No	Human health	Physical isolation	MNR	730 acres
Wyckoff/Eagle Harbor, West Harbor Intertidal	Marine embayment	PAHs Mercury	Past direct and indirect discharges from a wood-treating plant using creosote; ongoing releases from upland sources	No	Ecology Human health	Physical isolation Chemical transformation	MNR	5 acres
							Capping, dredging, EMNR	495 acres

TABLE A-3. Lines of evidence used to investigate natural recovery at MNR sites (page 1 of 3).

Site Name, Operable Unit/Subarea	Primary Lines of Evidence		Expected Recovery Period (years)	Projected Monitoring Costs
Bellingham Bay, Whatcom Waterway	Physical isolation	Sediment core sampling and radioisotope analysis Bathymetric data and sediment traps Modeling Temporal trends in sediment toxicity test results	30	\$1,000,000
Bremerton Naval Complex, OU B	Physical isolation	Bathymetric data Sediment profile imagery	10-30	\$2,500,000
Commencement Bay, Nearshore/Tideflats	Physical isolation	Modeling takes into account additional mass deposition from ongoing sources, sediment deposition, and bioturbation	10	\$310,000
	Chemical transformation			
	Dispersion			
Elizabeth Mine	Physical isolation	Sediment sampling along the Ompompanoosuc River, a high-gradient stream with abundant boulders and limited sediment, indicated sediment deposition is occurring	Not available	\$110,000
	Dispersion	Flow measurements and streambed geology suggested sediment erosion and off-site transport during high-energy events		

TABLE A-3. Lines of evidence used to investigate natural recovery at MNR sites (page 2 of 3).

Site Name, Operable Unit/Subarea	Primary Lines of Evidence		Expected Recovery Period (years)	Projected Monitoring Costs
Hackensack River, Study Area 7	Chemical transformation, reduction in bioavailability and mobility	Indicators of redox conditions Pore water analyses Sediment resuspension and oxidation tests Biota tissue analyses Toxicity tests	Recovery achieved; monitoring focuses on verifying permanence	Not available
	Physical isolation	Sediment trap analysis Radio-isotope analysis Hydrodynamic modeling Sedflume shear strength studies Sediment coring and vertical chromium profiling		
James River	Physical isolation	Radioisotope analysis and sediment age dating to document sedimentation rates Temporal trends of Kepone in fish tissue	10-15	Not available
Ketchikan Pulp Company, Ward Cove	Physical isolation	Modeling Assessment of MNR success in sites with similar organically rich conditions	8-20	Not available
Koppers Co., Inc., Barge Canal	Physical isolation	Two-dimensional hydrodynamic and sediment transport modeling study Bathymetric surveying to document sedimentation rates Aerial photography to document vegetation encroachment suggestive of sedimentation	5	Not available
Lavaca Bay	Physical isolation	Radioisotope analysis and sediment age dating to document sedimentation rates Modeling to predict sediment stability during a hurricane	10-15	\$1,660,000

TABLE A-3. Lines of evidence used to investigate natural recovery at MNR sites (page 3 of 3).

Site Name, Operable Unit/Subarea	Primary Lines of Evidence		Expected Recovery Period (years)	Projected Monitoring Costs
Lower Fox River/Green Bay, OU2 and OU5	Physical isolation	Historical bathymetric surveys Sediment coring and vertical PCB profiling Sediment bed stability studies Time-trend analysis comparing direct discharges of PCBs from paper mills with steady-state releases from sediments Modeling	40 to >100 (not considering sediment remediation in upstream source areas)	\$7,000,000 to \$13,000,000
	Dispersion			
Mississippi River Pool 15	Physical isolation	Aerial photography to document physical changes of shoreline due to sedimentation and development of vegetation	Not available	\$360,000
	Dispersion	Assumed to occur in riverine environment during flood events		
	Overall recovery	PCB concentrations in fish tissue samples have decreased over time		
Sangamo Weston/ Twelve-Mile Creek/Lake Hartwell, OU2	Physical isolation	Sediment coring and vertical PCB profiling Radioisotope analysis and sediment age dating	30	\$132,000
	Chemical transformation	PCB congener analysis and PCB compositional analysis		
Wyckoff/Eagle Harbor, West Harbor Intertidal	Physical isolation	Radioisotope analysis and sediment age dating to document sedimentation rates Watershed modeling to predict sediment deposition rates	30	\$137,000
	Chemical transformation	PAH fingerprinting to document chemical transformation		

TABLE A-4. Monitoring design, current (2008) status, and current view of MNR success at MNR sites (page 1 of 3).

Site Name, Operable Unit/Subarea	Monitoring Objective	Monitoring Element	Current (2008) Status	MNR Viewed as Success?
Bellingham Bay, Whatcom Waterway	Physical isolation	Bathymetric surveys Sediment cores Visual inspections of intertidal and shoreline areas	An engineering design report describing long-term monitoring plan details is expected in 2009 or 2010.  Monitoring data since the early 1970s show that natural sedimentation has occurred at significant rates and that mercury levels in surface sediments have decreased.	Yes
	Risk reduction	Surface sediment chemistry Mercury bioaccumulation in Dungeness crabs		
Bremerton Naval Complex, OU B	Physical isolation	Bathymetric surveys and modeling	Results of 2005 monitoring event indicate PCB concentrations continue to exceed cleanup levels. Monitoring is expected to extend until 2017, with at least four more sampling events planned.	Not yet determined
	Risk reduction	Surface sediment chemistry		
Commencement Bay, Nearshore/ Tideflats	Physical isolation	Sediment coring and vertical profiling Radioisotope analysis and sediment age dating Surface sediment chemistry and grain size	Area B of Sitcum Waterway: cleanup levels have been achieved with natural recovery, and the long-term monitoring therefore was deemed complete in 2004.  Information regarding MNR in Hylebos Waterway is not available. Baseline monitoring has been performed in Thea Foss and Wheeler-Osgood Waterways, with long-term monitoring planned to begin in 2008.	Yes, where sufficient monitoring data have been collected (Sitcum Waterway)
	Chemical transformation	PAH fingerprint analysis to assess vertical/lateral profiles and trends in chemical transformation		
	Risk reduction	Visual inspection of exposed tideflats to document benthic burrowing activity Biota tissue analysis		
Elizabeth Mine	Risk reduction	Surface sediment chemistry Sediment toxicity analysis	No long-term monitoring program has been developed as of January 2008. Monitoring is expected to occur after upland remediation has been completed.	Not yet determined

TABLE A-4. Monitoring design, current (2008) status, and current view of MNR success at MNR sites (page 2 of 3).

Site Name, Operable Unit/Subarea	Monitoring Objective	Monitoring Element	Current (2008) Status	MNR Viewed as Success?
Hackensack River, Study Area 7	Physical isolation	Tide gauge monitoring to model shear forces Bathymetric surveys Sediment profile imagery to assess erosion	Baseline monitoring scheduled	Not yet determined
	Risk reduction	Pore water chemistry		
James River	Risk reduction	Monitoring of Kepone in fish tissue	Continued low-level contamination in fish tissue, below action level. Fish consumption advisory remains in effect but is less stringent than for PCBs in the same area (from other sources).	Yes
Ketchikan Pulp Company, Ward Cove	Risk reduction	Surface sediment chemistry Sediment toxicity analysis Characterization of benthic communities	MNR is functioning as intended. Recovery is sufficient to suggest cessation of monitoring in some areas.	Yes
Koppers Co., Inc., Barge Canal	Physical isolation	Bathymetric surveys Aerial photography to document sedimentation and vegetation encroachment	PAH concentrations have been decreasing. Lateral encroachment of shoreline vegetation has been observed in analysis of aerial photographs, confirming sedimentation. Bathymetric surveys show net sediment accumulation within the Barge Canal (0.5-2 feet accumulation from 2000–2004). Second Five-Year Review Report (2008) recommends discontinuing further monitoring in the Barge Canal.	Yes
	Risk reduction	Surface sediment chemistry		
Lavaca Bay	Risk reduction	Monitoring of mercury in fish tissue Surface sediment chemistry	Concentrations of mercury in surface sediments are achieving cleanup levels. Tissue concentrations of mercury in fish and crab have exhibited annual fluctuations but remain elevated compared to concentrations in the reference area.	Not yet determined

TABLE A-4. Monitoring design, current (2008) status, and current view of MNR success at MNR sites (page 3 of 3).

Site Name, Operable Unit/Subarea	Monitoring Objective	Monitoring Element	Current (2008) Status	MNR Viewed as Success?
Lower Fox River/Green Bay, OU2 and OU5	Risk reduction	Surface water quality Fish and waterfowl tissue sampling for human receptor risks Fish, bird, and zebra mussel tissue sampling for ecological receptor risks Surface sediment chemistry Population studies of bald eagles and double-crested cormorants for reproductive viability	Baseline monitoring of PCB concentrations in MNR-designated areas was completed in August 2007. The MNR program will be finalized in June 2009.	Not yet determined
Mississippi River Pool 15	Physical isolation	Not yet developed	As of October 2008, the MNR program that will be implemented during the Remedial Action phase has not yet been developed. Fish studies conducted prior to remedy selection demonstrated a decreasing trend in PCB levels in fish collected along the Alcoa-Davenport Works facility shoreline.	Not yet determined
	Risk reduction	Monitoring of PCBs in fish tissue		
Sangamo Weston/ Twelve-Mile Creek/ Lake Hartwell, OU2	Risk reduction	Deployment and tissue analysis of caged clams Monitoring of PCBs in fish tissue Surface water and surface sediment chemistry	General trends indicate significant reductions of PCB concentrations in surface sediment. The majority of surficial sediments in the Twelve-Mile Creek Arm of Lake Hartwell will achieve the 1 milligram per kilogram (mg/kg) cleanup level between 2007 and 2011. However, edible fish from Lake Hartwell continue to exceed the FDA tolerance limit for PCBs (2 mg/kg). It is suspected that groundwater contaminated with PCBs is a continuing source.	Mixed results due to incomplete source control
Wyckoff/Eagle Harbor, West Harbor Intertidal	Risk reduction	Biota collection and body burden analysis Surface and deep sediment chemistry	The implemented MNR remedy is achieving remedial goals.	Yes

## 2 Bellingham Bay, Whatcom Waterway

### Bellingham, Washington

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#### WHATCOM WATERWAY

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- ☆ **Key concerns:** Ecological risks associated with mercury.

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- ☆ **MNR application:** Natural recovery occurred over most of the site prior to 2007, and contaminant concentrations over most of the site currently comply with site-specific cleanup goals.

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- ☆ **Cleanup goals:** Achieving compliance with cleanup standards in the bioactive zone.

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- ☆ **Natural recovery processes:** Natural recovery relies on isolation via natural sedimentation.

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- ☆ **Monitoring:** Monitoring includes measurement of chemical concentrations in sediments and crabs, sediment bioassays, bathymetry, sediment cores, and visual inspections of intertidal and shoreline areas.

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- ☆ **Current status:** The long-term MNR program is yet to be developed; an engineering design report is expected in 2009 or 2010.

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The Whatcom Waterway site is located in Bellingham Bay, near downtown Bellingham, Washington. Industrial activities began on and around this site in the late 1800s. These activities included log handling and rafting, pulp and paper mill operations, chemical manufacturing, cargo terminal operations, grain shipping, fish processing and cannery operations, coal shipping, bulk petroleum operations, boatyard operations, and sand and gravel handling. Resulting industrial discharges to Whatcom Waterway primarily included mercury from a chlor-alkali plant, wood pulping, wood waste and degradation products from log rafting, and phenols from pulp mill wastewater.

Georgia-Pacific Corporation used mercury in its chlor-alkali plant and discharged wastewater containing mercury to Whatcom Waterway between 1965 and 1971. From 1971–1979, pretreatment methods reduced mercury levels in effluent; in 1979 direct wastewater discharge to Whatcom Waterway was discontinued and use of an aerated stabilization basin was begun. In 1999, the chlor-alkali plant was closed and mercury was no longer used (Washington State, 2008).

Monitoring data collected under wastewater discharge permits, supplemented with additional research data, provide an accurate reconstruction of annual mercury loadings to the bay, relative to background inputs (Figure A-2) (Bothner et al., 1980; Officer and Lynch, 1989; Anchor 2000). These data document that significant reduction in mercury loadings to the bay were achieved at the site by the early 1970s.

The Starr Rock sediment disposal area was used for management of sediments dredged from the Whatcom Waterway and adjacent areas during the 1960s. Georgia-Pacific initiated a remedial investigation and feasibility study (RI/FS) of the Starr Rock site in 1996. The RI/FS was completed in 2000, and interim sediment cleanup and habitat restoration actions were performed in 2000/2001 near the original source area, which had the potential to act as an internal source of mercury to the adjoining waterway through sediment resuspension. In 2007, a Consent Decree for Whatcom Waterway cleanup was signed

by the Washington State Department of Ecology, the Port of Bellingham, the City of Bellingham, the Washington State Department of Natural Resources, and Meridian-Pacific, LLC. The consent decree included a cleanup action plan.

## Contaminants of Interest

Based on investigations of surface and subsurface sediments in 1996, 1998, and 2002, the primary COCs for site sediments are mercury, 4-methylphenol, and phenol. Because mercury is the only bioaccumulative COC, it was the only compound evaluated for ecological and human health risks in the RI/FS. Unacceptable risks to tribal fishermen and ecological receptors were identified in the assessment.

## Remedial Action

### Objectives

The sediment cleanup action objectives defined in the 2007 Cleanup Action Plan focus on achieving compliance with cleanup standards in surface sediments of the bioactive zone. Washington State Department of Ecology's sediment quality standard for mercury to protect ecological receptors is 0.41 mg/kg, while the minimum cleanup level (MCUL) for mercury is 0.59 mg/kg.

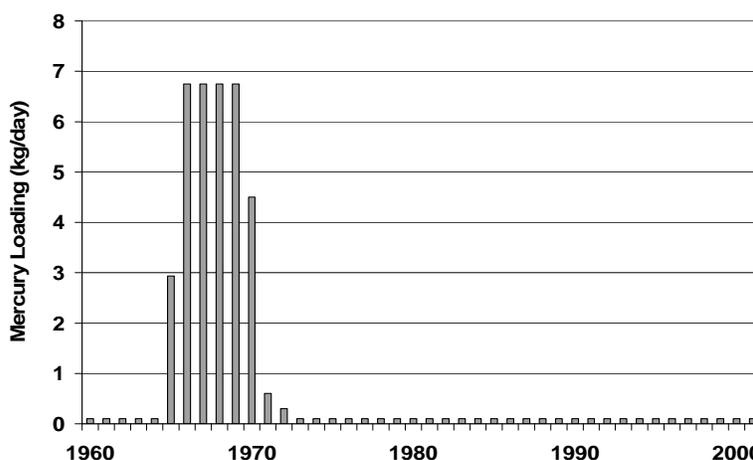


FIGURE A-2. Historical changes in mercury loading to Bellingham Bay.

## Ongoing Natural Recovery Processes

The primary natural recovery process ongoing at Whatcom Waterway is physical isolation. Lines of evidence compiled to support physical isolation include:

- Sediment traps. Sediment traps were deployed over a one-year period in 1996 to determine sedimentation rates. Sediment trap data verified sedimentation rates and confirmed that relatively low concentrations of COCs were being deposited, directly measuring the effectiveness of prior source control measures.
- Bathymetry. Current bathymetry data (i.e., depths at present) and data from prior navigational dredging events including dredge cut depths (i.e., depths in the past) were analyzed to further corroborate sedimentation rates.
- Sediment coring. Subsurface sediment coring data with supporting radioisotope geochronology and chemical analyses of total mercury and total solids were collected at several time intervals following source control (Figure A-3). Results demonstrated historical

recovery between 1996 and 2007. The data indicate sedimentation occurs at a rate of approximately 1.6 centimeters per year (cm/yr), and bioturbation of the surface 16 cm of sediments occurs at an average measured rate of 34 cm<sup>2</sup>/yr (Bothner et al., 1980; Officer and Lynch, 1989; Anchor, 2000).

- Sediment bioassays. Although the RI/FS did not identify bioaccumulation-related risks in Bellingham Bay, whole-sediment acute and chronic bioassays performed on surface sediment samples (0–15 cm) collected from the site indicated that certain areas of the site posed ecological risks to benthos, particularly during the early stages of the recovery period (PTI, 1989). Whole sediment bioassays included amphipod acute toxicity bioassays, bivalve larval toxicity/abnormality bioassays, and juvenile polychaete growth tests. Consistent with the chemical monitoring record, the area of sediment toxicity in Bellingham Bay had been reduced by nearly 10-fold by 1996 (Figure A-4) and had nearly fully recovered to below ecological risk-based criteria by 2002 (Anchor, 2000; 2003). Thus, the biological endpoint monitoring record available for inner Bellingham Bay supplied important corroborating evidence that environmental exposure at this site had recovered to below risk targets.

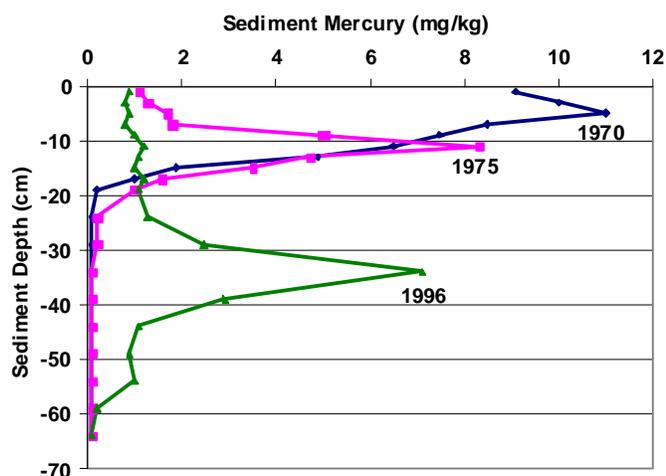


FIGURE A-3. Historical changes in sediment core profiles, Inner Bellingham Bay.



FIGURE A-4. Aerial extent of sediment toxicity in 1984 and 1996, Bellingham Bay.

## Recovery Modeling

A one-dimensional natural recovery model (Officer and Lynch, 1989) was developed to predict mercury concentrations in sediment, based on past and current sedimentation rates. The model accounts for physical isolation and dispersion (via bioturbation), exchanges between bottom sediments and the water column, and non-advective exchanges. For a conservatively chosen average bioturbation zone depth of 16 cm, a bioturbation rate of 34 cm<sup>2</sup>/yr was input into the model.

Based on the modeling, surface sediment in most areas of the site were expected to naturally recover to below sediment quality standards by 2005; Figure A-5 shows observed sediment concentrations (1996) versus model predictions (2005). Verification sampling is currently underway.

## Exponential Decay Modeling

Abundant sediment chemistry data collected since the early 1970s demonstrated continuously decreasing surface-sediment mercury concentrations in most areas of the site after the peak discharge period (1965–1970). Future reductions in mercury concentrations were projected over a 10-year period by fitting an exponential decay curve to core profiles during the recovery period (Figure A-6).

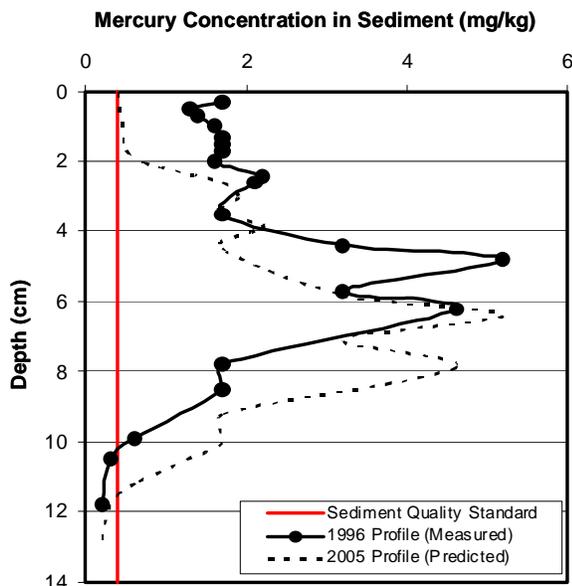


FIGURE A-5. Observed concentration profile for mercury in sediment in 1996 (a) versus concentration profile in 2005 (b) predicted using the Officer and Lynch (1989) model. Sediment Quality Standard (cleanup target) of 0.41 mg/kg is shown as the red line. Figure adapted from Anchor Environmental, L.L.C., and Hart Crowser (2000).

## Remedy Selection

The 2000 RI/FS demonstrated that physical isolation processes were generally consistent throughout most of the site, especially deep-water areas where wind/wave erosional forces are minimal. The 2007 Cleanup Action Plan initially identified eight alternative remedies for Bellingham Bay. Alternatives 1 through 4 were not implementable for various reasons; Alternatives 5 through 8 are described in Table A-5.

Exponential decay modeling indicated that mercury concentrations in inner Bellingham Bay would decrease by 30–40% between 1995 and 2005. This was considered a conservative estimate because the model was based on then-current conditions and did not account for remedial capping at other areas of the site. These activities would have reduced mercury concentrations in resuspended sediments, augmenting the rate of reduction.

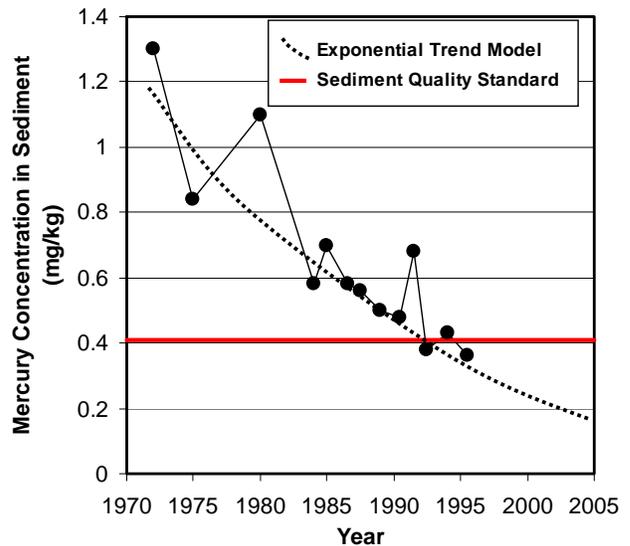


FIGURE A-6. Projected trends in concentrations of mercury in sediment. Sediment Quality Standard (cleanup target) of 0.41 mg/kg is shown as the red line. Adapted from Anchor Environmental, L.L.C., and Hart Crowser (2000).

TABLE A-5. Potential remedial alternatives for Bellingham Bay.

	Alt. 5	Alt. 6	Alt. 7	Alt. 8
Aerated Stabilization Basin (ASB)	dredge	dredge	dredge	dredge
Outer Waterway	cap/dredge <sup>1</sup>	dredge	dredge	dredge
Inner Waterway Multipurpose Channel	dredge, cap <sup>2</sup>	dredge, cap	dredge, cap	dredge, cap
Inner Waterway Industrial Channel	-	-	-	-
Areas in Bay	cap, MNR	cap, MNR	cap, MNR	dredge

1. "Cap/dredge" indicates some contaminated areas will be capped, while others are dredged.

2. "Dredge, cap" indicates the area will be dredged and then capped.

- Indicates the area will not be remediated

TABLE A-6. Remedial alternative analysis for Bellingham Bay.

Basis for Ranking under Washington State Department of Ecology's Model Toxics Control Cleanup Act and Sediment Management Standards				
Evaluation Criteria	Alt. 5	Alt. 6	Alt. 7	Alt. 8
<b>Overall Protectiveness</b> increases with volume of sediment removed	5	6	7	8
<b>Permanence</b> increases with volume of sediment removed	5	6	7	8
<b>Long-Term Effectiveness</b> increases with use of high-preference remediation technologies	7	8	9	9
<b>Short-Term Risk Management</b> decreases with increased dredging	8	7	6	4
<b>Implementability</b> decreases with increasing complexity, time-frame, shoreline stabilization requirements, and conflicts with planned land uses	8	8	4	3
<b>Consideration of Public Concerns</b> addresses volume of contamination	7	8	5	4
<b>Restoration Time-Frame (years)</b>	5-6	5-6	5-8	8-13
<b>Probable Cost (\$Million)</b>	\$42	\$44	\$75	\$146
<b>Benefit Score</b>	6.2	6.9	6.8	6.9

In Table A-6, Alternative 6 is identified as the preferred alternative, based on an analysis of disproportionate costs utilizing the Washington State Department of Ecology’s Model Toxics Control Act (MTCA) and Sediment Management Standards. Because the incremental costs of implementing Alternatives 7 and 8 were disproportionate to the benefits attained by the remedies, MTCA specifies that these alternatives are impracticable and that a lower cost alternative should be selected. The incremental costs of Alternatives 5 and 6 are proportionate to increases in remedy benefits, so these alternatives are considered practicable. Because Alternative 6 will attain a greater overall benefit than Alternative 5, it is considered “permanent to the maximum extent practicable” under MTCA. The

dredging and removal actions performed under Alternative 6 target the sediments with the highest contaminant levels that conflict with navigation and are likely to be disturbed in the future due to planned land use and that can be removed safely without an excessive level of short-term risk. MNR was selected for Starr Rock and offshore low-energy areas of the Whatcom Waterway.

## Monitoring

An engineering design report describing long-term monitoring plan details is expected in 2009 or 2010. Long-term monitoring of natural recovery performance will include measurement of physical isolation rates via bathymetric surveys, sediment cores, and visual inspections of intertidal and shoreline areas. Remedial goal monitoring will consist of surface sediment chemistry surveys in years 0, 1, 3, 5, 10, 20, and 30 and mercury bioaccumulation monitoring in adult male Dungeness crab muscle during years 3, 5, and 10.

## Current Status

Based on the documented historical natural recovery, as indicated by decreasing mercury concentrations and measured toxicity reductions in sediment, MNR has been a successful remedy at Bellingham Bay. Bellingham Bay is a compelling example of an integrated program consisting of effective and early implementation of source controls, focused cleanup of higher risk areas to accelerate recovery, and monitoring over time to document recovery of chemical and biological conditions. The current site status can be found at the Whatcom Waterway website: (<http://www.ecy.wa.gov/programs/TCP/sites/whatcom/ww.htm>).

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Washington State. 2008. Whatcom Waterway Site Information. Department of Ecology. Available at: <http://www.ecy.wa.gov/programs/TCP/sites/whatcom/ww.htm>.

## 3 Bremerton Naval Complex, Operable Unit B

### Sinclair Inlet, Puget Sound, Bremerton, WA

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#### BREMERTON NAVAL COMPLEX

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- ☆ **Key concerns:** Human health risks from PCBs and mercury.

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- ☆ **MNR application:** Natural recovery augments dredging and thin layer capping and serves as the primary remedy in areas of lower initial PCB concentrations.

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- ☆ **Cleanup goals:** Reduction of human health risks due to PCBs in sediments and fish.

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- ☆ **Natural recovery processes:** Natural recovery relies on isolation via natural sedimentation and chemical transformation via PCB dechlorination.

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- ☆ **Monitoring:** Long-term monitoring evaluates surface sediment PCB concentrations and sediment stability.

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- ☆ **Current status:** PCB concentrations are trending toward the MCUL. Monitoring is expected to continue until 2017.

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**B**remerton Naval Complex (BNC) is located on Sinclair Inlet in the southwest region of Puget Sound in Bremerton, Washington. In operation since the 1890s, the BNC is bordered by the City of Bremerton, a Washington State ferry terminal, and Sinclair Inlet (USEPA, 2000; 2002). Early naval operations at the BNC consisted of ship construction, drydocking, repair, and overhaul. Since the 1890s, land use has expanded to include heavy and light industry (e.g., shipbuilding and vehicle maintenance), berthing for naval vessels, commercial activities, and housing. Currently, the BNC consists of the Bremerton Naval Station—a deep-draft port for aircraft carriers and supply ships—and the Puget Sound Naval Shipyard, which provides maintenance and repair services to the naval fleet.

The site comprises approximately 380 acres of upland and 270 acres of sediment. Approximately 1000 acres of railroad areas are contiguous with the site, but are not part of any operable units. The upland areas consist of relatively low-lying marsh that slopes gradually along the waterfront; the waterfront was created via filling of marshes and tidelands. The submerged area extends from the mooring and drydock areas outward approximately 1500 feet into Sinclair Inlet.

As part of remedial action investigations, the BNC has been divided into six areas of interest, including OU A, OU B (marine), OU B (terrestrial), OU C (Site 11), OU D, and OU NSC. This case study focuses on OU B (marine), which consists of approximately 230 acres of limited intertidal area lying primarily in the subtidal zone of Sinclair Inlet, extending approximately 1500 feet offshore, with depths near 40 feet mean lower low water.

### Contaminants of Interest

The site is situated above various fill substrates believed to contain hazardous materials. Fleet support activities such as shipbuilding, maintenance, and mooring have contributed to hazardous materials at

the site. Specifically, waste disposal, spills, and leaks of industrial materials (e.g., metal plating, metal filings, electrical transformers [containing PCBs], batteries, paint and paint chips [containing heavy metals], acids, and other caustic substances) have led to significantly elevated levels of numerous contaminants in BNC surface and subsurface substrates (USEPA, 2000).

The primary COC is PCBs in fish tissue, which would pose an unacceptable risk to the subsistence tribal fishermen who currently consume seafood from the Bremerton Naval Complex site or nearby locations in Sinclair Inlet, or who may consume seafood from the site under future land use scenarios that include open access to all areas of the site. At the time of the remedial investigation (RI), mercury was not identified as a risk driver for human health; however, additional data became available after the RI that indicated that mercury may be a concern for human health. Therefore, mercury was included in the Record of Decision (ROD) but no cleanup level was identified. There were no ecological risks identified at this site.

## Remedial Action Objectives

Remedial action objectives (RAO) for the BNC aim to minimize human health risk by:

- Reducing the concentration of PCBs in the biologically active zone (0–10 cm of surficial sediments) in order to reduce the concentrations of PCBs in edible tissues of fish and seafood
- Controlling erosion of contaminated fill material
- Removing sediment with high concentrations of mercury collocated with PCBs.

Site-specific cleanup levels for sediments and remedial goals for fish include:

- A remedial action level for total PCBs in sediment of 6 mg/kg organic carbon (OC) for the biologically active zone (0–10 cm) throughout OU B (marine)
- A long-term cleanup goal for total PCBs in Sinclair Inlet sediments equivalent to the reference area concentration of 1.2 mg/kg OC
- A PCB remedial goal for fish tissue of 0.023 mg/kg wet weight.

## Ongoing Natural Recovery Processes

Physical isolation was demonstrated by documenting continuing sedimentation (0.5–0.75 cm/yr) and concurrent absence of erosional areas. Ongoing sedimentation processes were established by:

- Bathymetry. Current and historical bathymetry data were analyzed to determine sedimentation rates.
- Sediment profile imaging. Sediments were mapped to provide information about substrate and recently deposited layers.

## Remedy Selection

The area-weighted average concentration of PCBs in sediments within OU B (marine) was 7.8 mg/kg OC at the time the ROD was written. The selected remedy included dredging, thin-layer capping, MNR, and shoreline stabilization to reduce erosion of contaminated sediments. A dredging action level of 12 mg/kg OC was selected to delineate areas for sediment removal (approximately 200,000 cubic yards of sediment). Following dredging, the area-weighted average was expected to be 4.1 mg/kg OC, and MNR was expected to augment the risk reduction from dredging by natural deposition of additional material over time (USEPA, 2000).

Thin-layer placement of clean sediment augmented by natural recovery processes (EMNR) was selected in areas exceeding the remedial action level of 6 mg/kg OC, approximately 16 acres adjacent to OU A outside the navigation channel. The thin-layer cap consists of a 10–20 cm layer of clean sediment in which existing organisms establish themselves, while reducing contaminant concentrations and minimizing short-term disruption of the benthic community relative to measures such as isolation capping and dredging (USEPA, 2000). An additional 13 acres of OU B (marine) were managed through isolation capping.

Following implementation of dredging and thin-layer capping, MNR was expected to reduce OU B (marine) weighted average PCB concentrations to below 3 mg/kg OC within 10 years (by 2014) and to below the 1.2 mg/kg OC reference area goal within approximately 30 years throughout Sinclair Inlet (USEPA, 2000).

## Monitoring

The objectives of the monitoring program are summarized below:

- To verify attainment of the remedial goals
- To confirm predicted natural recovery of sediments in OU B (marine)
- To evaluate the success of the remediation in reducing COC concentrations in fish tissue.

The following monitoring activities and study results were published in the Final 2005 Marine Monitoring Report (URS Group, 2006):

- Bathymetric surveys. Sediment elevation measured in the post-construction survey (2001) and the 2003 and 2005 surveys track within one to two feet of each other. Differences of this magnitude were considered to be within the range of expected intersurvey variability.
- Surface sediment sampling. The PCB concentrations within OU B (marine) exceeded the 3 mg/kg short-term goal.
- Ongoing natural recovery modeling. Modeling of the 2005 findings predicts that the natural recovery goals identified in the ROD will likely not be met in a 10-year time frame.

## Current Status

Long-term monitoring began with a baseline evaluation in 2003. The monitoring plan called for additional assessments in 2005, 2007, 2012, and 2017 (URS Group, 2003). Fish tissue was not sampled in 2005 because reductions in tissue PCB levels are expected to occur relatively slowly. It is expected that at least four subsequent monitoring events will be required to assess remedy performance and confirm remedy permanence within OU B (marine). The results of three monitoring events (through 2007) indicate a trend of decreasing sediment PCB concentrations, consistent with attainment of the cleanup goal before the target date of 2014 (Leisle and Ginn, 2009).

## References

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## 4 Commencement Bay, Nearshore/Tideflats

### Puget Sound, Tacoma Washington

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#### COMMENCEMENT BAY

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- ☆ **Key concerns:** Human health and ecological risks from PCBs, PAHs, 4-methylphenol, and VOCs.

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- ☆ **MNR application:** MNR was selected for “marginally contaminated” areas that were predicted (by fate and transport models) to achieve sediment quality objectives via natural recovery within 10 years after completion of sediment remedial actions in more contaminated areas of the site.

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- ☆ **Cleanup goals:** Goals focused on the reduction of human health and ecological risks. Remedy success was defined as sediment quality objectives met by surface sediments.

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- ☆ **Natural recovery processes:** Dispersion, physical isolation, and chemical transformation are ongoing.

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- ☆ **Monitoring:** Sediment physical and chemical analysis (e.g., chemical fingerprinting) and radioisotope geochronology.

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- ☆ **Current status:** MNR is considered successful in Area B of the Sitcum Waterway. EMNR is successful in the Middle Waterway.

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The Commencement Bay Nearshore/Tideflats (CB/NT) site is located in the City of Tacoma and the Town of Ruston, Washington, and the southern end of the main basin of Puget Sound. The site includes an active commercial seaport and 10–12 square miles of shallow water, shoreline, and adjacent land, owned by numerous parties including the State of Washington, the Port of Tacoma, the City of Tacoma, Pierce County, the Puyallup Tribe, and private entities (USEPA, 2007).

Industrial and commercial operations located in the vicinity of CB/NT have included shipbuilding, transportation, chemical manufacturing, ore smelting, scrap metal recycling, oil refining, lumber milling, food preserving, cargo handling, and storage. Surveys conducted by the Tacoma-Pierce County Health Department and the Port of Tacoma indicate that more than 281 industrial facilities are active in the CB/NT vicinity. Approximately 34 of these have National Pollutant Discharge Elimination System permits for storm drain, seep, and open-channel discharges; groundwater seepage; atmospheric deposition; and spills. The Tacoma-Pierce County Health Department has identified several hundred non-point sources that discharge to Commencement Bay and 70 facilities that are ongoing contaminant sources (USEPA, 1999).

CB/NT was added to the National Priorities List (NPL) in 1983. An RI/FS was conducted by the Washington State Department of Ecology in 1988. The RI/FS concluded that sediment contamination involved numerous hazardous substances. Selected actions include site restrictions, source control, natural recovery, removal, capping, and source and sediment monitoring.

### Contaminants of Interest

Contaminants found in CB/NT waters and sediments include metals (arsenic, lead, zinc, cadmium, copper, mercury), volatile organic compounds (VOCs), PCBs, PAHs, and phthalates. Twenty-eight

chemicals or chemical groups were detected at concentrations 100–1000 times greater than in reference areas.

## Remedial Action Objectives

The RAO is “to achieve acceptable sediment quality in a reasonable time frame,” where “acceptable sediment quality” is defined as “the absence of acute or chronic adverse effects on biological resources or significant human health risks.” The “reasonable time frame” was generally defined as within a period of 10 years following the completion of dredging and/or capping in individual operable units. Remedial goals for sediments, sources, and biota adhere to guidelines established by the Puget Sound Estuary Program. The developed remedial goals were based on apparent effects thresholds generated from data from various areas in Puget Sound, including a relatively large data set collected at the CB/NT Site.

## Ongoing Natural Recovery Processes

Primary ongoing natural recovery processes at CB/NT include physical isolation, dispersion, and chemical transformation. The RI/FS included deployment of sediment traps to characterize the status of source controls and sediment inputs, and sediment core profiling and radioisotope analysis to characterize key fate and transport processes and document historical recovery rates. Models used to interpret these lines of evidence and predict sediment concentrations over a 10-year period include:

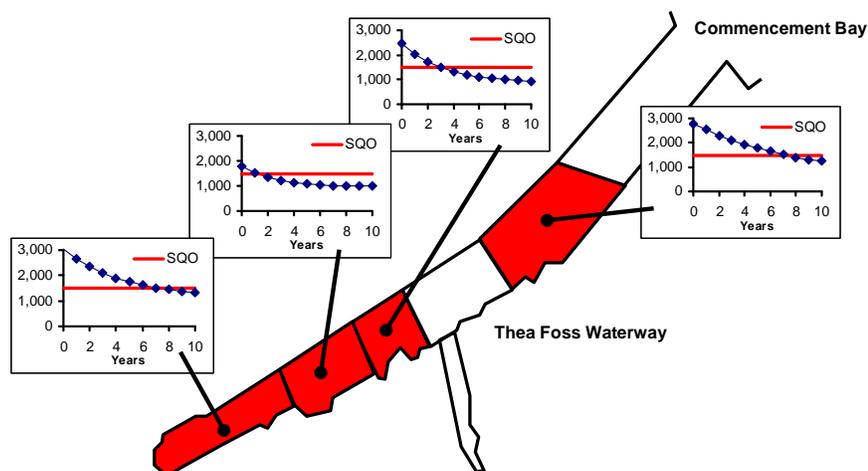


FIGURE A-7. WASP-model predicted declines in surface sediment phenanthrene concentrations ( $\mu\text{g}/\text{kg}$ ; blue diamond symbols) for segments of Thea Foss Waterway with concentrations greater than the cleanup level (red-shaded segments; red line in graphs). (Adapted from USEPA 1998).

- Sediment Contamination Assessment Model (SEDCAM). SEDCAM is a mass balance equation that predicts sediment concentrations given source loading and rates of sedimentation, sediment mixing, chemical transformation, and dispersion and diffusion.
- Sedimentation/bioturbation modeling. A one-dimensional natural recovery model (Officer and Lynch, 1989) was developed to predict concentrations in sediment, based on past and current sedimentation rates.

- Water Quality Analysis Simulation Program (WASP). WASP two-dimensional contaminant transport modeling predicted a decline in sediment concentrations of phenanthrene to below the cleanup level within 10 years (Figure A-7) (Ambrose et al., 1993).

## Remedy Selection

Model predictions were generated for a 10-year natural recovery period. The 10-year period was selected based on “precedents in environmental legislation” (USEPA, 1989). If model predictions did not achieve cleanup levels within the 10-year period, alternate remedies were selected for the area. Additionally, empirical trend analysis depicting decreasing surface sediment concentrations was used to support MNR in areas where historical data were available.

MNR was selected for several CB/NT areas: Hylebos Waterway, Area B of Sitcum Waterway, Middle Waterway, Thea Foss, and Wheeler-Osgood Waterways. The RI/FS suggested that recovery rates in these areas would likely be substantially accelerated by dredging of more contaminated sediments elsewhere in CB/NT. The selected remedies consisted of:

- Evaluation and control of upland sources of contamination
- Removal of sediments with chemical concentrations high enough to be internal sources of recontamination (e.g., greater than 5 mg/kg mercury—roughly 10 times higher than the cleanup level)
- Cap placement over areas of high concern for adverse biological effects and potential contaminant resuspension and bioaccumulation
- MNR or EMNR using thin-layer caps in areas of moderate concern
- Institutional controls (limits on consumption of fish and shellfish, anchorage restrictions).

Selection of MNR for Sitcum Waterway. Following dredging of a portion of under-pier side slope areas of Area B of the Sitcum Waterway, some areas had remaining sediments that exceeded USEPA cleanup levels. Based on the post-dredging conditions of the waterway, it was determined that under-pier sediments in the Sitcum Waterway would be appropriate for MNR. The natural recovery determination was made as part of an established evaluation process that had commenced during pre-remedial design and continued through the remedial action phase. The effectiveness of natural recovery processes at the Sitcum Waterway site had initially been indicated through a focused RI/FS and pre-design evaluation program. Following collection and review of the post-dredging sediment quality data, the natural recovery processes were evaluated based on current waterway conditions.

## Monitoring

Monitoring activities to assess the performance of natural recovery processes and RAO attainment include:

- Sediment accumulation rates using radioisotope analysis to assess sedimentation and erosion rates
- Detailed PAH fingerprint compositional analysis to assess vertical/lateral profiles and trends of PAHs and document further chemical transformation of PAHs
- Analysis of the chemistry, grain size, and water content of surface sediment and thin-layer capping material (for EMNR) to evaluate potential erosion and sediment deposition
- Surface and deep sediment core sampling to assess sediment concentrations and document anticipated declines in surficial concentrations over time
- Visual inspection of exposed tideflats during low tide to document presence of benthic burrowing activity, indicating ecological recovery
- Biota collection and body burden analysis to address chemical exposure and risk.

## Current Status

Sitcum Waterway. Consistent with USEPA-approved plans, the Port of Tacoma performed focused MNR surface sediment quality monitoring in 1998 and 2003, following completion of the remedial action (USEPA, 2004). Monitoring verified that sediment concentrations of lead and high-molecular-weight PAHs in the under-pier area recovered to below cleanup standards, consistent with model predictions.

Recovery was confirmed to have been accelerated by the Port of Tacoma's remedial dredging action. Dredging exposed clean sediment within the channel and berth areas, which are the primary sources of material to the under-pier area. The resuspension of these clean source materials and their deposition under the pier has reduced sediment concentrations to cleanup levels within the MNR area. Long-term monitoring was deemed complete in the Second Five-Year Review Report (USEPA, 2004).

Storm water source controls are ongoing to prevent recontamination and to ensure the continued success of the remedial action in localized under-pier outfall areas.

Middle Waterway. Monitoring has confirmed that the backfill function and thickness of the thin-layer cap are not compromised in areas of minor residual contamination. The 2006 Monitoring Report for Middle Waterway indicates that remedial goals have been achieved in sediment management unit 51b (Hart Crowser, Inc., 2007).

Other areas. Information regarding MNR in the Hylebos Waterway is not available. Baseline monitoring has been performed in Thea Foss and Wheeler-Osgood Waterways, with long-term monitoring planned to begin in 2008 (Pers. comm., S. Haas, 2008; N. Saunders, 2008; City of Tacoma et al., 2006).

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## 5 Elizabeth Mine

### Ompompanoosuc River and Tributaries, Strafford and Thetford, Vermont

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#### ELIZABETH MINE

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- ☆ **Key concerns:** Ecological risks from metals, including copper and selenium. Acid rock drainage is of particular concern.

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- ☆ **MNR application:** MNR was selected for sediments in the Copperas Brook, Lord Brook, and west branch of the Ompompanoosuc River.

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- ☆ **Cleanup goals:** Reduction of ecological risks.

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- ☆ **Natural recovery processes:** Physical isolation and dispersion.

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- ☆ **Monitoring:** Anticipated long-term monitoring will confirm ongoing natural recovery and will measure chemical concentrations in sediment, water and biota. However, to date no monitoring program has been developed.

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- ☆ **Current status:** Monitoring has not yet begun.

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The Elizabeth Mine site is an abandoned mine located in east-central Vermont in the towns of Strafford and Thetford. Discovered in 1793, the mine contained large deposits of sulfide ore, from which pyrrhotite was obtained to produce copperas, or iron (II) sulfate. Major production of copperas began in about 1809, and copper mining and refining began in the 1820s or 1830s. During the 1880s, site operations transitioned completely to copper mining and processing.

The mine operated intermittently throughout the 1920s and 1930s until it was reopened and expanded in 1942 as part of World War II operations. After the war, operations and expansions continued until the mine was shut down in 1958. By this time, the site covered approximately 1,400 acres.

The mine property has since been sold but has not been redeveloped. A building and a trailer on the site are rented as residences, and a garage is used for equipment storage (USEPA, 2007).

Acid rock drainage has resulted in accumulation of metals in stream sediments in three small watersheds—Copperas Brook, Lord Brook, and Sargent Brook. These watersheds all drain into the west branch of the Ompompanoosuc River (WBOR), which—approximately 10 miles downstream of the site—flows into the Connecticut River.

Soils, groundwater, and sediments at the site are heavily contaminated with numerous metals. In addition, iron precipitation and waste ore are present in the stream channel of Copperas Brook. The Elizabeth Mine site was added to the NPL in 2001; a ROD was issued by USEPA in September 2006. Five OUs at the site have been defined to facilitate remedial action. This case study focuses on the sediment-related OU.

## Contaminants of Interest

USEPA has identified numerous metals as contaminants of potential concern in site sediments. Revised USEPA Region V ecological screening levels were the main screening criteria for contaminants of potential concern. If ecological screening levels were not available, other sediment quality criteria were used (USEPA, 2006a).

Metals detected in on-site sediments at levels exceeding USEPA screening levels include:

- Copperas Brook: copper and selenium
- Lord Brook: copper, selenium, zinc, cadmium, chromium, manganese, and nickel
- WBOR: copper, selenium, and zinc.

The high concentrations of metals in these waterways have severely affected fish and benthic communities. Water and sediment toxicity tests demonstrate severe toxicity, and benthic and fish communities are impaired downstream of source areas. For example, the fish population in Lord Brook drops by 90% downstream of source areas and recovers with increasing distance downstream (Arthur D. Little, 2001; USEPA, 2006a).

The sediments and surface water of Sargent Brook are not considered to present ecological or human health risks.

## Remedial Action Objectives

The RAO and cleanup level for sediments are specified in the ROD (USEPA, 2006a):

- Reduce sediment concentrations to levels that are no longer acutely toxic and allow the surface water to achieve federal Clean Water Act and Vermont Water Quality Standards for Class B surface water in Copperas Brook, the WBOR, the unnamed tributaries to Lord Brook, and Lord Brook.
- The cleanup level for sediments in Copperas Brook, the WBOR Mixing Zone, and the unnamed tributaries to Lord Brook shall be based upon toxicity testing. The cleanup level shall be met when toxicity testing demonstrates that the sediments are no longer acutely toxic to benthic organisms.

## Ongoing Natural Recovery Processes

The primary natural recovery processes identified include dispersion and physical isolation, as supported by the following lines of evidence:

- Flow measurements and streambed geology. Data suggests that contaminated sediments in some portions of the impacted streams may be dispersed during high-energy events.

- Sediment sampling. The WBOR is a high-gradient stream with abundant boulders and limited sediment. Areas of sedimentation were observed during sampling along the WBOR, indicating physical isolation is a primary natural recovery process (Pers. comm., E. Hathaway, November 7, 2008).

## Sediment Remedy Selection

Mine drainage to these streams is an ongoing source of chemical contamination to stream sediments, and MNR is not expected to reduce sediment risk until sources are controlled by terrestrial remediation. MNR was determined to be the least damaging option for wetland and aquatic resources along the waterway and the least expensive remedial alternative that could achieve threshold criteria (USEPA, 2006b).

## Monitoring

Monitoring of the chemistry and biology of Copperas Brook, Lord Brook, and WBOR, and additional toxicity testing are expected to track long-term progress. A 5-year review of the cleanup action will ensure that the cleanup is protective of human health and the environment (USEPA, 2006b). An MNR monitoring program is yet to be developed.

## Current Status

Monitoring or related activities have not yet been performed. Source control activities are ongoing (Pers. comm., E. Hathaway, November 7, 2008).

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## 6 Lower Fox River/Green Bay Wisconsin

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### LOWER FOX RIVER

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- ☆ **Key concerns:** Human health and ecological risks from PCBs, dioxins and furans, arsenic, lead, and mercury.

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- ☆ **MNR application:** MNR was selected for most of OU2 and OU5, where PCB concentrations in sediments generally do not exceed 1.0 mg/kg.

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- ☆ **Cleanup goals:** Goals focused on the reduction of human health and ecological risks. Remedy success is measured by determining PCB concentrations in sediment and monitoring environmental receptor.

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- ☆ **Natural recovery processes:** Physical isolation and dispersion (via diffusion of contaminants into the water column and sediment erosion) are the primary natural recovery processes.

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- ☆ **Monitoring:** Monitoring has not been scheduled.

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- ☆ **Current status:** The MNR program has not yet been developed.

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The Fox River empties into Green Bay, an extension of Lake Michigan in eastern Wisconsin. The Lower Fox River/Green Bay site is defined as the lower 39 miles of the river as well as the bay. The Fox River Valley is a heavily urbanized and industrialized area, with one of the largest concentrations of paper mills in the world.

The paper industry has been active here since the mid-1800s. Other regional industries include printing; metalworking; and the manufacture of food and beverages, textiles, leather products, wood products, and chemicals. Other regional uses include agricultural, light industrial, residential, recreational, and wetland.

Water quality problems (i.e., ecological, chemical, aesthetic) have been observed and measured on the Lower Fox River since the early 1900s. These problems have been attributed to a variety of sources, including effluent from pulp and paper mills and municipal sewage treatment plants.

The presence of PCBs in water and sediments is attributed to the manufacture and recycling of carbonless copy paper in the Fox River Valley. The manufacturer stopped using PCBs in the production of copy paper in 1971, and as a result PCB levels in fish have decreased significantly over time, particularly during the 1970s. However, since the 1980s, the rate of PCB reduction in fish may be slowing in some areas. Predictive models created using pre-remedy data are unclear whether PCB concentrations in fish may plateau or continue to decrease over time (Polissar et al., 2002; RETEC, 2002a).

Since the termination of industrial PCB production, it has been determined that more than 95% of the PCBs found in the water of the Lower Fox River originate in its sediments.

To facilitate remediation, five OUs have been defined at the site. This case study focuses on OU2 (the Lower Fox River from Appleton to Little Rapids) and OU5 (Green Bay). Remediation of sediments at these OUs relies primarily on natural processes.

## Contaminants of Interest

PCBs are the primary COC at the Lower Fox River/Green Bay site. Other COCs include dioxins and furans, pesticides, arsenic, lead, and mercury.

Cancer and non-cancer risks were determined to be unacceptable for recreational anglers and high-intake fish consumers who ingest local fish containing PCBs. Risks for local residents, recreational water users, and marine construction workers were not found to be significant.

PCB concentrations in sediments from all areas of OU2 and OU5 present significant risks to ecological receptors. Notably, reproductive impairment and physical deformities have been documented in terns, cormorants, and bald eagles and appear to be due at least in part to PCB exposures (Stratus Consulting Inc., 1999).

## Remedial Action Objectives

The RAOs for sediments at the Lower Fox River/Green Bay site, as stated in the 2002 and 2003 RODs, are as follows for OUs 2 and 5:

- Protect humans who consume fish from exposure to COCs that exceed protective levels. This RAO is intended to protect human health by targeting removal of fish consumption advisories. The Wisconsin Department of Natural Resources (WDNR) and USEPA defined the expectation for the protection of human health as the likelihood for recreational anglers and high-intake fish consumers to consume fish within 10 years and 30 years, respectively, at an acceptable level of risk or without restrictions following completion of a remedy.
- Minimize the downstream movement of PCBs during implementation of the remedy.

A remedial action level of 1.0 mg/kg for PCBs in site sediments was established by USEPA and WDNR. Sediments exceeding the remedial action level will be dredged or capped in order to achieve surface-weighted average concentration goals developed by USEPA and WDNR (0.25–0.28 mg/kg, depending on the area).

According to Mr. Greg Hill, project coordinator at WDNR, surface-weighted average concentration goals were not developed for the areas in which MNR is to be implemented (Pers. Comm., January 2008). Remedial goals for these areas are not based on PCB concentrations in sediments but rather on PCB concentrations in surface water and biota, as indicated in the RAOs.

## Modeling Natural Recovery Processes

The primary natural recovery processes identified for OU2 and OU5 are physical isolation and dispersion, as supported by modeling that took advantage of various empirical measurements, including stream flow velocity analysis, bathymetric survey, geochemical analyses of water and sediments, analysis of biological monitoring data, time-trend (i.e., statistical) analyses of PCB concentrations in sediments and fish (RETEC and Natural Resource Technology, 2002). Two fate and

transport models predicted PCB concentrations in water and sediments: the Whole Lower Fox River Model (wLFRM) and the Enhanced Green Bay Toxics (GBTOXe) model. Additionally, two bioaccumulation models predicted contaminant transfer within the food webs of the River and Bay: the Fox River Food (FRFood) model and the Green Bay Food (GBFood) model (Figure A-8). The fate and transport models served to generate inputs for the food web models used to predict sediment concentrations and ecological and human health risks for different remedial scenarios.

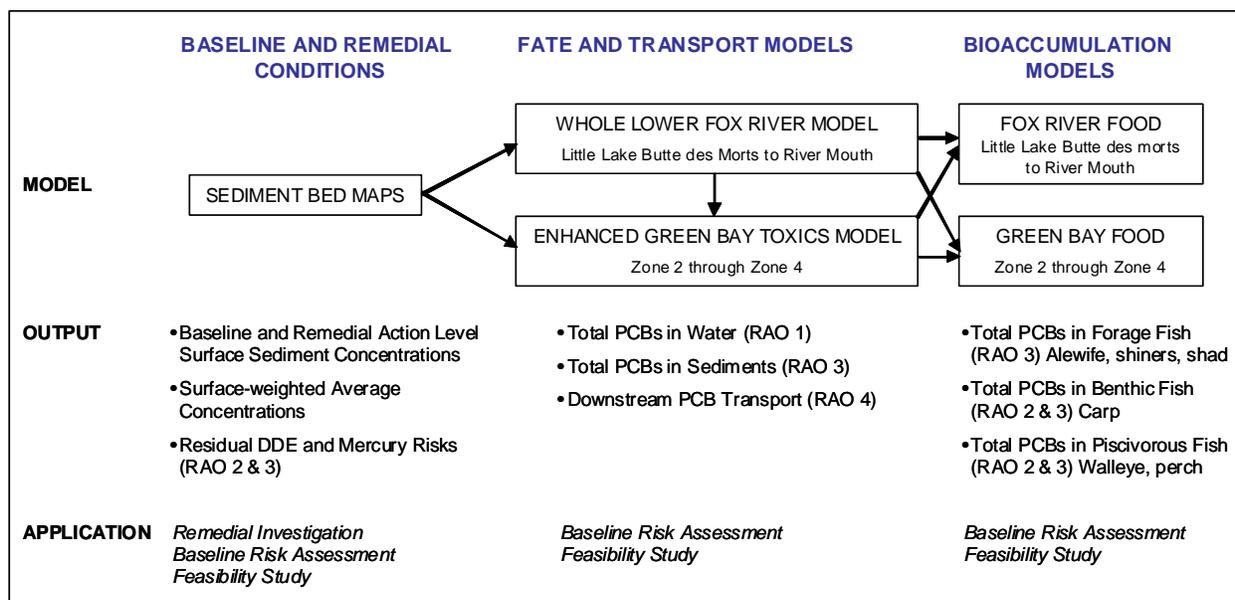


FIGURE A-8. Relationship of models used for risk projections in the Lower Fox River and Green Bay (adapted from RETEC 2002).

The wLFRM model predicted the movement of solids and PCBs and the concentration of organic carbon in the water column. This model incorporated data collected between 1989 and 1995 for total suspended solids, dissolved/particulate PCBs in water, sediment bed elevation, and net sediment burial rate. Transport mechanisms considered in the wLFRM included dispersion and physical isolation. The outputs of the wLFRM served as inputs to the GBTOXe, FRFood, and GBFood models.

The GBTOXe model predicted total PCBs and three phases of carbon in the water column and sediments. This model incorporated empirical PCB and carbon data from 1989–1990. Transport mechanisms considered in the GBTOXe model included dispersion and physical isolation. The outputs of the GBTOXe model served as inputs to the FRFood and GBFood models.

The FRFood model predicted PCB transfer within the food webs of the Lower Fox River and Zones 1 and 2 of Green Bay. The GBFood model predicted PCB transfer within the food webs of all of Green Bay (zones 1–4). The webs of specific interest were those leading to forage fish, benthic fish, and game fish. The models incorporated data from the Fox River Database, scientific literature-derived values, peer-reviewed studies, and/or site-specific data. The FRFood model was also used to estimate sediment quality thresholds in the baseline human health and ecological risk assessments of the RI/FS

(WDNR and USEPA, 2002; 2003). Refer to Highlight 5-1 for additional discussion of the role of models in the Lower Fox River/Green Bay site.

## Sediment Remedy Selection

MNR was selected for OU2 and OU5, where capping and dredging are not implementable. Constraints include shallow bedrock and high dispersion potential in OU2 and an excessive volume of low-level contaminated sediment in Green Bay. Active remediation in these areas would not produce results significantly better than those predicted for MNR. An evaluation of sediment volumes within OU2 found only one deposit greater than 10,000 cubic yards that had a PCB concentration above the 1.0 mg/kg action level. Thus, it was inferred that relatively few areas of OU2 require remediation, and the risk of exposure from these areas is low. RI/FS analysis indicated no significant differences between the results of the alternatives considered for OU5. Minor dredging will be conducted in OU5 at the river mouth (50 acres) and OU2 in a downstream depositional area (8 acres).

Under all the alternatives (including dredging and capping), risks would continue for decades. At OU2, MNR was predicted to require 40–70 years to reach acceptable fish tissue concentrations for human health risks and may take more than 80 years to reach safe ecological levels for carp. Water quality standards are not expected to be reached for surface water within 100 years. At OU5, it would take more than 100 years to achieve human health risk thresholds for walleye and ecological risk thresholds for sediment (WDNR and USEPA, 2002; 2003; 2007). Recovery times may be overestimated, however, as these predictions do not consider removal of upstream contaminated sediments.

## Monitoring

The remedial design plan for MNR in OU2 and OU5 will be finalized in late 2008 or early 2009 (Pers. comm., G. Hill, January 2008). Baseline monitoring was conducted between September 2006 and August 2007. The Lower Fox River/Green Bay site is subject to statutory 5-year review.

According to the RODs, MNR in OU2 and OU5 will employ a 40-year monitoring program to measure the progress and achievement of the RAOs. Monitoring elements will include:

- Surface water quality sampling to determine the downstream transport of PCB mass into Green Bay
- Fish tissue sampling to determine the residual risk of PCB and mercury consumption to human and environmental receptors
- Possible surface sediment sampling in MNR areas to assess potential recontamination from upstream sources and the status of natural recovery.

## Current Status

Monitoring data are not yet available.

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- WDNR and USEPA. 2007. Record of Decision Amendment: Operable Unit 2 (Deposit DD), Operable Unit 3, Operable Unit 4, and Operable Unit 5 (River Mouth), Lower Fox River and Green Bay Superfund Site. Wisconsin Department of Natural Resources and U.S. Environmental Protection Agency, Region 5.

# 7 Hackensack River, Study Area 7

## Hudson County, New Jersey

HACKENSACK RIVER	
☆	<b>Key concerns:</b> Ecological risks from chromium in sediment.
☆	<b>MNR application:</b> MNR was selected for areas where Cr in sediments deeper than 30 cm exceeds 370 mg/kg.
☆	<b>Cleanup goals:</b> Goals focused meeting a court-mandated charge to remediate sediment in accordance with the NJDEP effects-range-median sediment quality goal of 370 mg/kg.
☆	<b>Natural recovery processes:</b> Chemical transformation of Cr(VI) to Cr(III) reduced Cr bioavailability and risks. Physical isolation is ongoing and contributes to reduced exposures.
☆	<b>Monitoring:</b> Monitoring will focus on physical stability of buried sediments and geochemical stability of Cr(III).
☆	<b>Current status:</b> Baseline monitoring is scheduled.

Study Area 7 is a 34-acre parcel in Jersey City, New Jersey, adjacent to the Hackensack River, near the confluence with Newark Bay. The site is located in an area that has been used for industrial and commercial purposes for over 100 years. Chromium contamination is related to a former sodium dichromium manufacturing facility operated by Mutual Chemical Company of America from 1905–1954.

With local and state government approval, chromium ore process residue was widely used as fill material. The material was deposited mechanically and hydraulically on top of an organic-rich layer referred to as “meadow mat.” Approximately 1 million cubic yards of chromium ore processing residue were used as fill in Study Area 7. Historical groundwater seepage and surface runoff from Study Area 7 led to elevated chromium concentrations in Hackensack River sediment (ENVIRON, 2006).

## Contaminants of Interest

Contaminants found in sediment include a wide variety of chemicals associated with urban and industrial development of the Newark Bay watershed. However, the only chemical of interest related to Study Area 7 is chromium. Relevant species include hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)), of which Cr(VI) is much more soluble and toxic. Cr(VI) transforms rapidly to Cr(III) under reducing or mildly oxidizing conditions. Although thermodynamically favored under aerobic conditions, Cr(VI) is rarely formed in nature due to kinetic constraints, and Cr(III) is much less bioavailable and much less toxic than Cr(VI) (Sorensen et al., 2007; Martello et al., 2007).

## Remedial Action Objectives

A consent decree governing the site required that a remedy be applied to all sediments, regardless of depth, exceeding the New Jersey Department of Environmental Protection’s effects range-median sediment quality goal of 370 mg/kg (U.S. District Court, 2003). This

cleanup goal is not based on site-specific risks but rather resulted from litigation that took place before investigations of possible chromium toxicity and natural recovery processes.

## Ongoing Natural Recovery Processes

Chemical transformation of Cr(VI) to Cr(III) and the associated reduction in both bioavailability and toxicity occurred almost immediately upon contact with site sediments, which were characterized as reducing. These processes resulted in minimal baseline risks related to chromium. Additionally, physical isolation of buried sediments contributed to compliance with the Court requirement to remedy sediments containing greater than 370 mg/kg total chromium.

Multiple lines of evidence demonstrated very low bioavailability of chromium in sediments in the Hackensack River (Martello et al., 2007; Magar et al., 2008; Sorensen et al., 2007):

- Indicators of redox conditions in surface sediment included analyses of acid volatile sulfide, sediment profile imaging, and direct redox and dissolved oxygen measurements. Reducing conditions that are incompatible with Cr(VI) were shown to predominate surface sediment.
- Cr(VI) was not detected in sediment pore water in approximately 100 pore water samples. Cr(III) was found only at low concentrations in pore water. Pore water sampling included targeted sampling of oxic surface sediment from intertidal areas to maximize the probability of encountering potentially bioavailable Cr(VI) had Cr(VI) been present.
- A sediment resuspension and oxidation test simulated conditions during a severe storm or anthropogenic scouring event or dredging. No Cr(VI) was detected in sediment elutriate following extended exposure to oxygen via aeration and mixing with site water.
- Cr(VI) was found in subsurface groundwater only in an area directly affected by a groundwater plume underlying the river. This finding is consistent with the conceptual model, where Cr(VI) originating from a subsurface source is reduced to Cr(III) well before it reaches biologically active surface sediments. The detection of Cr(VI) in a subsurface groundwater plume beneath the river demonstrates that the site investigation methods can identify the presence of Cr(VI) in pore water if and where it exists. The chromium-containing groundwater is being addressed through source control and a separate groundwater remediation effort.
- Biota tissue analyses showed no relationship between chromium concentrations in sediment and in tissue of laboratory-exposed and indigenous invertebrates. Concentrations were within the range of those found in laboratory control organisms.
- Toxicity tests showed adverse effects of site sediments on amphipods but not polychaetes, although the polychaete test species was known to be particularly sensitive to Cr(VI). Effects on amphipods were attributed to PAH concentrations in sediments. Tests at a similar, upriver site affected by chromium ore process residue demonstrated no toxicity to amphipods at total chromium concentrations up to 1,490 mg/kg (Becker et al., 2006).

Lines of evidence documenting physical isolation processes and sediment stability include (ENVIRON, 2006):

- Sediment trap analysis indicated net deposition of coarse sediments, resulting in sediment-bed armoring over time. Study Area 7 accumulates sediments originating from the Passaic River and Newark Bay.
- Radiological tracer measurements in sediment cores provided evidence of historically high deposition rates.
- Sediment shear strength studies demonstrated that sediments are well consolidated and physically stable even under extreme disturbances.
- Hydrodynamic modeling predicted sediment erosion depths will not exceed 4 cm, even under extreme conditions.
- Analysis of vertical chromium profiles in sediment cores suggested historical contaminant releases from Study Area 7 have remained in place.

## Remedy Selection

Remedy selection was informed by a detailed comparative risk evaluation, which considered the following components (ENVIRON, 2006):

- Worker risks associated with construction and transportation, including quantitative estimation of transportation injury and fatality risks and qualitative evaluation of risks to site remediation workers.
- Community quality of life impairments, such as noise, odor, diesel emissions, and traffic congestion.
- Short-term benthic habitat loss and recovery times, as well as the potential for long-term changes in habitat quality.
- Water quality impacts related to sediment resuspension and redistribution due to dredging.
- Risk reduction associated with changes in surface sediment concentrations of chromium and other, non-site-related chemicals, and also considering the very low baseline risk conditions associated with reduced chromium (i.e., Cr(III)) in surface sediment.
- Long-term recontamination potential from contaminated sediments nearby and uncontrolled sources within the watershed.

Risk-of-remedy analysis for Study Area 7 quantified the short term risks associated with the implementation of each remedy alternative as well as the expected long-term risk reduction. MNR was compared to six other alternatives: no action, three capping remedies, and two dredging remedies.

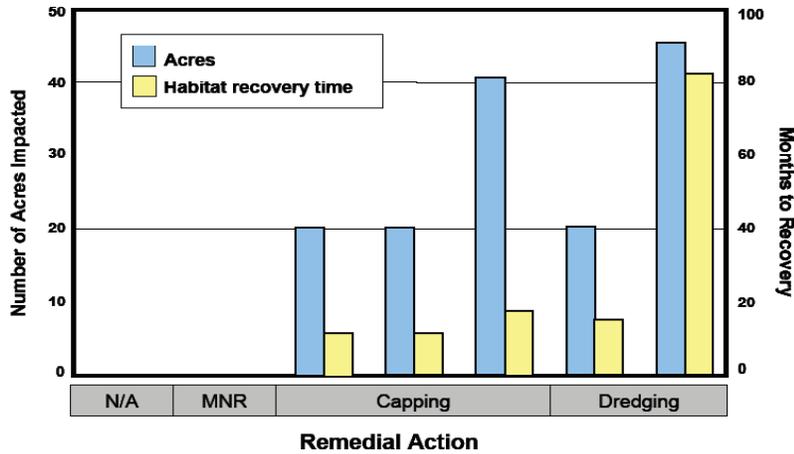


FIGURE A-9. Comparative analysis of habitat recovery time for different sediment management options (Study Area 7, Hackensack River, New Jersey).

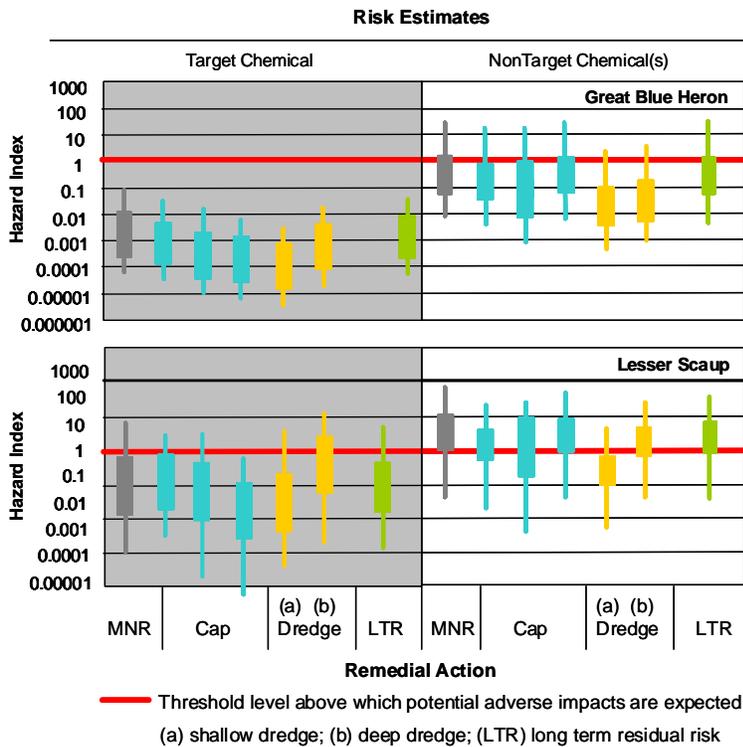


FIGURE A-10. Post-remedy comparative risk analysis and long-term residual risks of chemical exposure for two species of water birds.

Fig A-10 also shows that deep dredging may increase risk estimates when buried contaminants are resuspended. MNR provides comparable risk reduction to the other remedies and more risk reduction than the deep dredge option.

Risk reduction also can be compared with remedy cost. Figure A-11 shows a cost-benefit analysis conducted to evaluate the amount of risk reduction contributed by different remedies and the relative costs of those remedies. Increasing costs associated with capping and dredging did not provide commensurate reductions in risk at Study Area 7.

The graphical presentation of quantitative results comparing risks of remedy and risk reduction achieved by alternative remedies was a compelling tool to communicate the viability and effectiveness of MNR compared to other remedial alternatives. Figure A-9 shows the spatial and temporal scales of impacts to the benthic macro-invertebrate community.

Temporal impacts include the duration of remedy implementation and post-disturbance recovery rates. Changes relative to baseline, pre-remedy conditions show that dredging impacts may alter ecological conditions for a longer period of time relative to other remedies, including MNR; however, the impacts may be perceived as short-term in comparison to the long-term benefits of a removal action.

Figure A-10 shows a comparative risk assessment using the Trophic Trace® model (USACE, 2005) to evaluate the effects of six different sediment management options on chemical exposures for two species of water birds. The analysis also considered anticipated long-term residual risks. The figure shows that MNR provides risk reduction comparable to the other remedies.

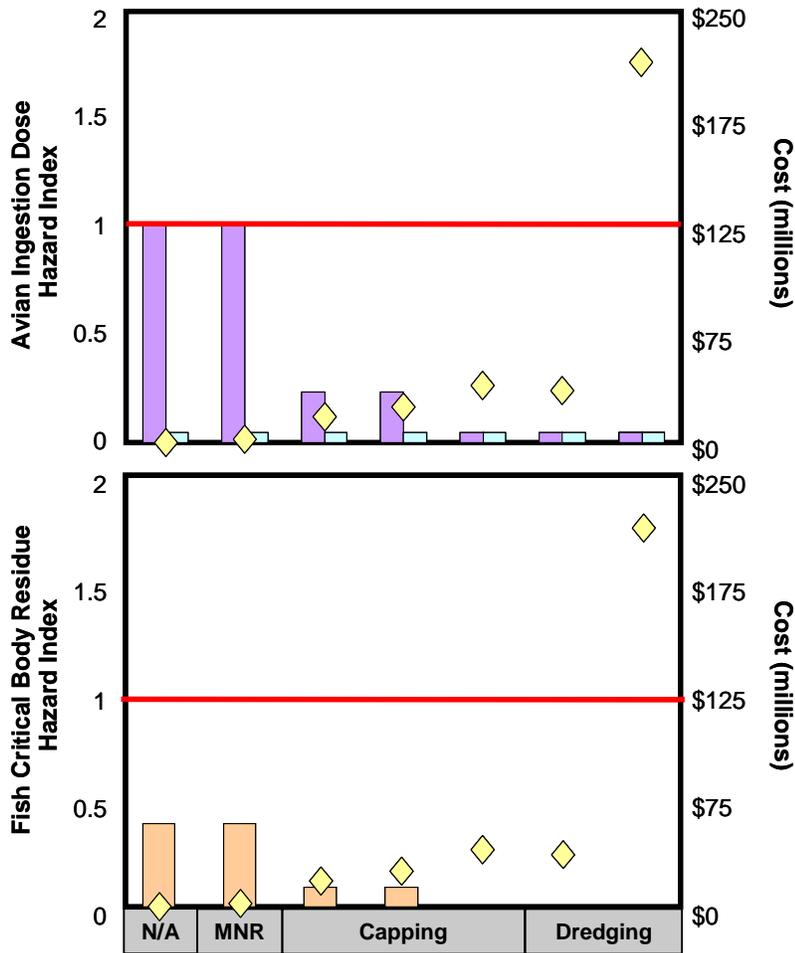


FIGURE A-11. Cost-benefit analysis of risk reduction contributed by MNR, capping, and dredging at the SA7, Hackensack River site.

The risk-of-remedy analysis was instrumental in achieving an outcome that limited risks to nearby residential communities, workers, and ecological receptors (Magar et al., 2008). Comparison of short-term implementation risks and long-term potential risk reduction with associated costs made it possible to evaluate the relative cost-benefit of the remedies, pointing toward a relatively low-impact MNR remedy that achieved comparable or greater risk reduction than other remedies while minimizing the impact and costs of removing sediment that posed no unacceptable risk to human health or the environment.

Based on findings that chromium was present in a geochemically stable, non-bioavailable form in a net-depositional area with only moderate resuspension expected during high-energy events, the recommended remedy alternative involved source control, capping of sediments with total chromium values greater than 2,000 mg/kg,

and MNR of remaining areas. This remedy provided risk reduction while limiting remedy-imposed risks. Ultimately, and despite the low baseline risks at the site, the negotiated remedy included dredging 2,000 cubic yards over 0.5 acres; a 14-acre, 12-inch cap; a 15-acre, 6-inch cap; and MNR over 20 acres where subsurface concentrations exceeded 370 mg/kg. The capping remedy targeted areas where surface sediment total chromium concentrations were greater than the effects range-median sediment quality goal of 370 mg/kg, consistent with the consent decree governing the site. MNR was employed in areas where surface sediment concentrations were less than 370 mg/kg, but buried concentrations were greater than 370 mg/kg.

## Monitoring

At Study Area 7, MNR will include monitoring sediment stability and the physical isolation of elevated chromium concentrations, geochemical stability of Cr(III), and sediment cap integrity. Monitoring elements and decision rules are described in Table A-7.

Monitoring will continue until objectives have been achieved and maintained for 15 years, or through at least two high-energy events. If bathymetric surveys show acceptable sediment bed elevations after 5 years of routine monitoring and 15 years of severe event monitoring, the MNR remedy will be considered successful.

TABLE A-7. Decision rules to guide long-term monitoring of Study Area 7.

Monitoring Element	Decision Rule
Tide gauges gather data for modeling velocities, shear forces, and hydrodynamic conditions for diurnal conditions and wet weather events, used to determine the maximum velocities under which MNR performs acceptably.	If analysis after a high-energy event indicates conditions were capable of generating shear forces exceeding the maximum for sediment stability, bathymetry should be performed by side-scan sonar.
Bathymetric and SPI camera data readings determine the extent of erosion. Bathymetry analysis indicates changes in sediment bed elevations.	If bathymetry indicates scour greater than 1 foot, risks should be evaluated for the scoured area. Chromium chemistry monitoring should be performed.
Pore water is sampled for Cr(VI) in the top 12 inches of sediment.	If the area-weighted average concentration of Cr(VI) is greater than the ambient water quality criterion, source identification and CSM revision should proceed.

## Current Status

Baseline monitoring is expected to occur in 2009.

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## 8 James River

### Hopewell, Virginia

JAMES RIVER	
☆	<b>Key concerns:</b> Human health and ecological risks from Kepone.
☆	<b>MNR application:</b> MNR was selected for all areas of the site.
☆	<b>Cleanup goals:</b> Goals focused on the reduction of human health risks.
☆	<b>Natural recovery processes:</b> Dispersion from high-energy areas and physical isolation in low-energy areas.
☆	<b>Monitoring:</b> Monitoring of fish tissue continues. Previous monitoring included sediment and surface water.
☆	<b>Current status:</b> MNR is considered to be a successful remedy. However, low levels have persisted in fish tissue since the late 1980s, suggesting some degree of continued resuspension.

The James River, located in Virginia, flows into the Chesapeake Bay. The city of Hopewell is located on the southern bank of the river, approximately 80 miles northwest of the mouth of the river.

In 1966, Allied Chemical Corporation began manufacturing an insecticide known as Kepone (chlordecone) in Hopewell. In 1974, the production of Kepone was contracted out to Life Science Products (LSP), at another facility in Hopewell. Production peaked during this year, at an estimated 457,630 kg. In 1975, the manufacture and use of Kepone was banned after LSP employees developed serious health problems linked to the chemical (Luellen et al., 2006).

During the production of Kepone, both Allied and LSP disposed of Kepone and Kepone-containing wastewater directly into the James River. It is estimated that approximately 90,720 kg was released to the environment through wastewater, disposal of bad batches, and atmospheric emissions (Luellen et al., 2006).

The water-insoluble Kepone sorbed to suspended particulates and bottom sediments in the river. According to USEPA, approximately 9,070–18,140 kg were deposited to the top 30 cm of sediments in the James River. Some researchers have estimated that up to 30,000 kg of Kepone could have deposited into sediments (Luellen et al., 2006).

In 1975, a ban was placed on both commercial and recreational fishing in the James River and its tributaries. The ban on recreational fishing was lifted in 1980, when Kepone levels in fish began to fall below the established action level. All fishing restrictions related to Kepone contamination were lifted in 1989. While fishing is permitted, a fish consumption advisory remains in place (Luellen et al., 2006).

The lead agency has been the Virginia Department of Environmental Quality, formerly the Virginia State Water Control Board (VSWCB).

### Contaminants of Interest

The contaminant of interest is Kepone, a carcinogenic chlorinated hydrocarbon.

## Remedial Action Objectives

An action level for Kepone levels in fish tissue was established at 0.3 mg/kg wet weight (Luellen et al., 2006).

## Ongoing Natural Recovery Processes

Dispersion from high-energy areas and physical isolation in low-energy areas were the primary natural recovery processes.

- Evidence of rapid natural sedimentation rates within the estuary was established through sediment core sampling of radionuclides and Kepone, in a pioneering use of radioisotope analysis and sediment age dating. In 1978, box core samples were collected from 21 locations within the estuary to test for Kepone and  $^{137}\text{Cs}$ . Based on the coring results, it was estimated that sedimentation rates ranged from less than 1 cm/yr to greater than 19 cm/yr. The rates were estimated to be at least 8 cm/yr at eight of the sampling locations (Cutshall et al., 1981).

The highest levels of Kepone occurred at the sampling locations with the greatest estimated sedimentation rates (Cutshall et al., 1981).

## Sediment Remedy Selection

Recovery of sediments in the James River has relied on physical isolation (Cutshall et al., 1981; Luellen et al., 2006). Modeling of the fate and bioaccumulation of Kepone in white perch and striped bass was performed by consultants in the evaluation of sediment remedies. The modeling predicted that natural sedimentation would cause Kepone concentrations in fish tissue to fall below the action level by the late 1980s (Quantitative Environmental Analysis, 2002 and undated).

## Monitoring

In 1976, the VSWCB began overseeing fish tissue, river water, and sediment sampling (Luellen et al., 2006). Figure A-8 shows declining Kepone concentrations in fish tissue. VSWCB continues to monitor Kepone levels in fish tissue and sediment to address concerns about contaminated sediment resuspension after high-energy events (Alliance for the Chesapeake Bay, 2003).

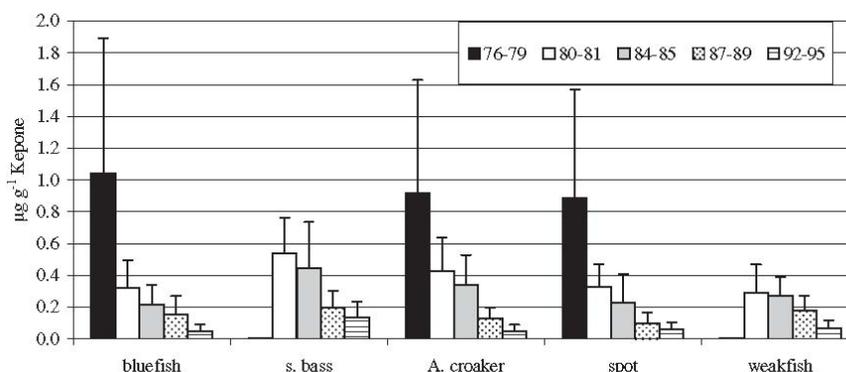


FIGURE A-12. Reduction of average Kepone concentrations over time in five fish species. Error bars show the standard deviation for each time period. Reprinted from Luellen et al. (2006), with permission from Elsevier.

From 1976–1978, Kepone was not detected in 45–67% of the collected water samples, and no significant difference was found between levels in the surface water and the bottom of the water column. By 1981, the average Kepone concentration in the water was sufficiently low that the VSWCB decided to end water sampling (Luellen et al., 2006).

## Current Status

Natural recovery is generally considered to have been a successful in reducing Kepone contamination in the James River. The average Kepone concentration in fish fell below the action level by 1986, 11 years after the contaminant source was controlled. Kepone has persisted in fish tissue samples at low levels that have remained consistent since the late 1980s. Since 1987, 94% of samples have continued to contain Kepone concentrations above detection limits (Luellen et al. 2006). The sustained low-level concentrations suggest continued resuspension of Kepone during high-energy events (Luellen et al., 2006; Duxbury, 2008). A fish consumption advisory is still in effect but is less stringent than the advisory for PCBs in fish from the same area (Virginia Department of Health, 2008).

## References

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## 9 Ketchikan Pulp Company, Ward Cove

### Ketchikan, Alaska

KETCHIKAN PULP COMPANY	
☆	<b>Key concerns:</b> Ecological risks from ammonia, sulfide, and 4-methylphenol.
☆	<b>MNR application:</b> MNR has been applied to approximately 52 acres.
☆	<b>Cleanup goals:</b> Goals focused on the reduction of risks to benthic organisms.
☆	<b>Natural recovery processes:</b> Natural recovery relies primarily on physical isolation.
☆	<b>Monitoring:</b> Remedy success is measured by determining chemical concentrations in sediment, sediment toxicity, and benthic community census.
☆	<b>Current status:</b> Based on monitoring results, MNR is viewed as successful.

The former Ketchikan Pulp Company (KPC) facility is located on the northern shoreline of Ward Cove, approximately 5 miles north of Ketchikan, Alaska. The KPC facility conducted sulfite pulp dissolving operations between 1954 and 1997. During that time, pulp mill effluent was discharged to Ward Cove. The processes and conditions thought to have been potential contaminant sources include wastewater discharges, wood waste and ash disposal in the onsite landfill, storm water discharges, airborne contaminants from boilers, and spills and accidental releases.

The upland KPC property was sold to Gateway Forest Products, Inc. (GFP) in 1999, and most of the KPC equipment has been dismantled and removed from the site. GFP produced lumber, veneer, pulp chills, and hog fuel at the site until 2001 or 2002. Due to bankruptcy, GFP no longer owns or operates on the KPC site. Currently, no operations are conducted at the site.

The site is not on the NPL; however, investigation and alternatives analysis for the site has followed the Superfund process. The site has been divided into two OUs to facilitate remediation: OU1 (Uplands) and OU2 (Marine). This case study focuses on OU2, approximately 80 acres of contaminated sediments. A ROD for OU2 was issued in March 2000, a long-term monitoring and reporting plan was approved in September 2001, and a 5-year review report was completed in August 2005.

### Contaminants of Interest

COCs identified at the site include ammonia, sulfide, and 4-methylphenol. These contaminants are not considered bioaccumulative. Ecological risks to sediment-dwelling organisms from exposure to sediment are considered significant, but human health risks are considered minimal.

## Remedial Action Objectives

RAOs for sediments at the KPC site, as stated in the 2000 ROD, are to:

- Reduce toxicity of surface sediments
- Enhance recolonization of surface sediments to support a healthy marine benthic infauna community with multiple taxonomic groups.

## Ongoing Natural Recovery Processes

Physical isolation is the primary natural recovery process at this site. Lines of evidence to establish physical isolation and predict recovery included (Pers. Comm., K. Keeley, January 9, 2008; USEPA, 2000):

- Numerical modeling. Natural recovery modeling was used to predict recovery rates. Within the Cove, modeling predictions suggested that recovery processes could take 8–20 years to yield healthy benthic communities. The lower end of this range is based on the estimated natural recovery rate for sulfide (primary cause of sediment toxicity). USEPA expects that such areas will become suitable habitat for benthic communities through natural processes of decay of toxic materials and natural accumulation of clean sediments.
- Case study review. Evaluations of the results of case studies on benthic communities in sediments and empirical documentation of natural recovery in sediments suggest that benthic communities in organically rich environments such as Ward Cove may recover within 10 years.

## Sediment Remedy Selection

Concerns regarding the infeasibility of capping and dredging influenced the selection of MNR. Many of the areas selected for MNR were too steep (>40% slope) or deep (>120 ft) for capping to be feasible. Some areas contained organic-rich sediment that did not have the bearing capacity to support a sediment cap. High debris density at the site (>500 sunken logs/10,000 square meters) also made dredging impractical (USEPA, 2000).

## Monitoring

In consideration of the numerical modeling results and the case study evaluations, recovery of benthic communities in Ward Cove may occur within approximately 10 years. For this reason, estimates of long-term monitoring costs were based on 10 years of monitoring. However, monitoring will occur until RAOs are achieved, as determined by USEPA. The primary components of the long-term monitoring program include (Exponent, 2001):

- Sediment chemistry. Surface sediment samples are analyzed for ammonia and 4-methylphenol. They also are analyzed for grain size distribution, organic content, and total solids, as these variables can influence the composition of benthic communities.
- Sediment toxicity. The toxicity of surface sediment samples is evaluated with 10-day amphipod tests using *Rhepoxynius abronius*. This test characterized sediment toxicity during the RI/FS, and the results indicated a potential relationship with sediment concentrations of ammonia and/or 4-methylphenol.
- Benthic communities. Organisms found in surface sediment samples are identified and enumerated to determine benthic community structure relative to reference community.

Sediment sampling occurs every third year in July (e.g., 2004, 2007, and 2010), until RAOs are achieved, or as modified and agreed to by USEPA. Monitoring of sediment concentrations, benthic toxicity, and community health in 2004 indicate that MNR is reducing risk. Benthic recovery at some areas suggests further monitoring may be unnecessary (Exponent, 2005). Refer to Highlight 7-1 for additional discussion of monitoring in Ward Cove.

## Current Status

According to the Five-Year Review Report (USEPA 2005), MNR is expected to reduce risk and achieve remedial goals in the predicted time frames.

## References

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- USEPA. 2005. Five-Year Review Report for Ketchikan Pulp Company Site, Ketchikan, Alaska. U.S. Environmental Protection Agency, Region 10.

# 10 Koppers Co., Inc., Barge Canal Charleston, South Carolina

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## KOPPERS

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- ☆ **Key concerns:** Ecological and human health risks from PAHs, arsenic, lead, chromium, copper, dioxin, and pentachlorophenol.

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- ☆ **MNR application:** MNR was selected for Barge Canal.

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- ☆ **Cleanup goals:** Goals focused on long-term protection of ecological resources.

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- ☆ **Natural recovery processes:** Natural recovery relies primarily on physical isolation.

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- ☆ **Monitoring:** Bathymetry is monitored to quantify sedimentation rates, and aerial photography supplies additional confirmation. Remedy success is measured by assessing chemical concentrations in sediment.

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- ☆ **Current status:** MNR is considered successful.

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The Koppers Co., Inc. (Koppers) site consists of approximately 102 acres located in northern Charleston, South Carolina, on the western side of the peninsula formed by the Ashley and Cooper rivers. This area consists of land, drainage ditches, a barge canal, tidal marshes, and a portion of the Ashley River.

An approximately 45-acre portion of the site was used for wood treatment operations from the 1940s to 1977. Primary operations consisted of treating raw lumber and utility poles with creosote. Pentachlorophenol and copper chromium arsenate were also used as preservatives in the treatment processes for short periods of time. Water from creosote separation tanks was discharged to drainage ditches leading to the Ashley River.

Subsequent operations conducted by other businesses on the 45-acre property include military ship cleaning, repair, and refurbishing; waste oil storage; ship bilge and tank waste storage; and marine structure prefabrication.

From 1953–1968, Koppers leased approximately 4 acres to the south of its property for the disposal of sawdust, bark, and other wood waste materials from stripping operations. In 1984, an approximately 3.2-acre barge canal (the Barge Canal) was dredged eastward from the Ashley River to the Koppers property. The dredging resulted in the exposure of creosoted poles, highly turbid water, and an oily sheen on the Ashley River. Following dredging, a fish kill occurred in the Ashley River ¼-mile downstream of the canal. It is believed that the canal was dredged through the area formerly leased by Koppers. The approximately 57-acre area through which the Barge Canal was dredged was incorporated into the boundaries of the Koppers site by USEPA in order to determine the environmental impacts of the dredging on the Ashley River and neighboring tidal marshes (USEPA, 2002).

The Koppers site is now used for various commercial operations. Surrounding areas contain a mixture of industrial, commercial, and residential properties.

Soils, sediments, and surface water at the Koppers site were contaminated by PAHs and pentachlorophenol, with trace levels of dioxin and metals. The site was added to the NPL in 1994. An RI/FS was completed for the site in December 1996. USEPA issued an Interim Action ROD in March 1995 to reduce off-site contaminant migration and potential exposure pathways to sediments and surface waters of on-site drainage ditches. Interim action extraction wells began operating full-scale in January 1997. The final ROD was issued in April 1998. Explanations of Significant Differences to the ROD were issued in August 2001 and September 2003.

## Contaminants of Interest

Human health risks for industrial and offsite resident exposures were driven by PAHs, arsenic, dioxin, and pentachlorophenol. Ecological risks for benthic communities, fish, mammals, and birds were driven by dioxin, PAHs, arsenic, lead, chromium, and copper (USEPA, 1998).

## Remedial Action Objectives

RAOs are not defined in the 1998 ROD. However, it is stated that “the primary evaluation criteria for sediments in the Ashley River, Barge Canal, and tidal marshes is the long-term protection of ecological resources.”

## Ongoing Natural Recovery Processes

Investigations subsequent to issuance of the ROD revealed that physical isolation via natural sediment deposition was ongoing at the Barge Canal. The following lines of evidence were gathered (USEPA, 2003):

- Sediment deposition modeling. A two-dimensional hydrodynamic and sediment transport modeling study was conducted for the Ashley River and Barge Canal in 1999. Simulations of baseline sedimentation rates (i.e., without enhanced sedimentation structures) predicted 3–6 inches accumulation per year along the longitudinal cross section of the Barge Canal. Predicted sedimentation rates were verified using physical measurements of sediment depths obtained from bathymetric surveys conducted in 1995 and 1999.
- Bathymetry. Bathymetric and hydrographic surveys of the centerline depths of the canal were performed in 1995, 1998, and 2000. The data collected over this time period indicate that the elevation of the sediment interface along the channel bottom rose approximately 2 feet, or approximately 5 inches per year. Furthermore, a historical review of the 1988 permit to construct the Barge Canal revealed the original depth of the canal; the 1995 bathymetric survey provided evidence that between 7 and 9 feet of sediment (i.e., approximately 8–11 inches per year) accumulated in the Barge Canal since the original dredging.
- Aerial photography. Encroachment of vegetation indicated in aerial photographs from 1994 and 2000 indicates that sediment levels in the Barge Canal are increasing in accordance with predictions made by modeling, analytical calculations, and physical survey data. According to the photographs, the Barge Canal reportedly gained approximately 0.50 acres of vegetative

growth, or approximately 15% of its original 3.2-acre size. The width of the unvegetated area of the Barge Canal reportedly narrowed approximately 20 feet during the time period between the 1994 and 2000 photographs.

## Sediment Remedy Selection

Subaqueous capping was selected for sediments in the Barge Canal at the time of the ROD. However, lines of evidence collected during the Remedial Design phase determined that physical isolation was a significant natural recovery process, and the 2003 Explanation of Significant Differences changed the remedy for the Barge Canal from subaqueous capping to MNR.

## Monitoring

Monitoring for the Barge Canal includes bathymetric surveys, aerial photography, and analysis of chemicals in sediment. Bathymetry data collected in 1995, 1999, and 2000 demonstrate a net accumulation of 0.5–2 feet of sediment within the central portion of the Barge Canal. Between 1995 and 2000, the net accumulation in some areas was approximately 5 feet (AMEC Earth and Environmental, Inc., 2004).

Aerial photographic documentation of shoreline vegetation also demonstrates the sedimentation in Barge Canal. Aerial surveys conducted in 1994, 2000, 2004, and 2007 indicate visible encroachment of marsh grass at the edges of the Barge Canal, primarily at the mouth, adjacent to the Ashley River. A net accumulation of approximately 0.319 acres of vegetation was observed between 2000 and 2004, and that amount increased to approximately 0.80 acres between 2000 and 2007. Site photographs (AMEC Earth and Environmental, Inc., 2002; 2004; 2007) further illustrate the apparent encroachment of the shoreline (Figure A-13).

Analysis of total PAHs in sediment samples collected in 1994, 2003, 2004, and 2007 indicate that total PAH concentrations are decreasing over time. Concentrations have been within the reported background range for Ashley River sediment (4-28 mg/kg) over the past three sampling events (USEPA, 2008).



FIGURE A-13. Aerial photograph attests to the continual encroachment of shoreline vegetation into the Barge Canal from 1994–2006. The encroachment of vegetation qualitatively suggests significant sedimentation in these areas.

## Current Status

The Second Five-Year Review Report determined that the MNR remedy for the Barge Canal sediments is adequately protective. Because total PAH concentrations are at background levels and are unlikely to decrease further and marsh vegetation continues to develop due to the dominant depositional environment, the Second Five-Year Review Report recommended discontinuing further monitoring of sediment and vegetation encroachment in the Barge Canal (USEPA 2008).

## References

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AMEC Earth and Environmental, Inc. 2004. Barge Canal Sediment Monitoring Plan: Final Report for Y2004.

AMEC Earth and Environmental, Inc. 2007. 2007 Barge Canal Sediment Sampling Report.

USEPA. 1998. EPA Superfund Record of Decision: Koppers Co., Inc (Charleston Plant), EPA ID: SCD980310239, OU 01, Charleston, SC. U.S. Environmental Protection Agency, Region 4. EPA/ROD/R04-98/102.

USEPA. 2001. EPA Superfund Explanation of Significant Differences: Koppers Co., Inc (Charleston Plant), EPA ID: SCD980310239, OU 01, Charleston, SC. U.S. Environmental Protection Agency, Region 4.

USEPA. 2002. Five-Year Review Report for the Interim Remedial Action at the Koppers Co., Inc. (Charleston Plant) NPL Site, Charleston, Charleston County, South Carolina. U.S. Environmental Protection Agency, Region 4.

USEPA. 2003. EPA Superfund Explanation of Significant Differences: Koppers Co., Inc (Charleston Plant), EPA ID: SCD980310239, OU 01, Charleston, SC. U.S. Environmental Protection Agency, Region 4.

USEPA. 2008. Second Five-Year Review Report for the Koppers Co., Inc. (Charleston Plant) NPL Site, Charleston, Charleston County, South Carolina. U.S. Environmental Protection Agency, Region 4.

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# 11 Lavaca Bay

## Point Comfort, Texas

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### LAVACA BAY

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- ☆ **Key concerns:** Human health and ecological risks from PAHs and mercury.

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- ☆ **MNR application:** MNR was selected for most of the bay.

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- ☆ **Cleanup goals:** Goals focused on reduction of ecological and human health risks.

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- ☆ **Natural recovery processes:** Natural recovery relies primarily on physical isolation.

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- ☆ **Monitoring:** Remedy success is measured by assessing chemical concentrations in sediment, fish, and crabs.

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- ☆ **Current status:** Based on monitoring results, MNR is viewed as successful.

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Lavaca Bay is an estuary of Matagorda Bay, located in southeastern Texas, adjacent to the Gulf of Mexico. The surface area of Lavaca Bay is approximately 60 square miles. An approximately 420-acre area known as Dredge Island was built up within Lavaca Bay from dredge materials. The area of the Bay surrounding Dredge Island is known as the Closed Area.

The Aluminum Company of America (Alcoa) Point Comfort Operations Plant is located on the eastern shore of Lavaca Bay, near the City of Point Comfort in Calhoun County. Aluminum smelting operations began at the facility in 1948 and were shut down in 1980. Bauxite refining operations at the facility began in 1958 and are ongoing. Other operations that were conducted at the site in the past include cryolite processing, chlor-alkali production of sodium hydroxide and chlorine (1966–1979), and coal tar processing (by Witco Chemical Corporation, 1964–1985).

Mercury-containing wastewater from the chlor-alkali process was transported to an offshore gypsum lagoon on Dredge Island. Overflow from the lagoon was subsequently discharged to Lavaca Bay after a settling period. The Texas Department of Health found elevated levels of mercury in crabs during the early 1970s. The Texas Water Quality Board subsequently ordered Alcoa to limit the mercury levels in its wastewater discharges (USEPA, 2008a). In 1980, the Texas Department of Health prohibited fishing in the Closed Area. The Department of Health reduced the size of the Closed Area in 2000, based on reduction of mercury concentrations in fish tissue (USEPA, 2008b).

The site was proposed for listing on the NPL in 1993 and was finalized in 1994. A non-time-critical removal action under the oversight of the USEPA was begun in 1998 and was completed in 2001. As part of a treatability study, Alcoa installed a groundwater extraction system at the former chlor-alkali process area in order to limit the discharge of mercury-contaminated groundwater to Lavaca Bay. USEPA issued a ROD for the site in December 2001. According to Mr. Gary Baumgarten, remedial project manager for the site, most source controls at the site had been completed by the time of the ROD. Alcoa signed a Consent Decree with USEPA in March 2005.

## Contaminants of Interest

The COCs identified for Lavaca Bay sediments are inorganic mercury, methylmercury, and PAHs. Risk assessments have demonstrated unacceptable risks to both human and ecological receptors.

## Remedial Action Objectives

The RAOs are designed to achieve a reduction of mercury levels in fish tissue such that overall risks throughout Lavaca Bay approach the level that would prevail but for the Point Comfort Operations Plant. The RAOs established in the ROD are listed below:

- Eliminate or reduce mercury and PAH loading from ongoing unpermitted sources to Lavaca Bay to the maximum extent practical.
- Reduce mercury concentrations in surface sediments of sensitive habitats to an appropriate level.
- Reduce mercury concentrations in open-water surface sediments that serve as a pathway for introducing mercury into the food web to an appropriate level.
- Reduce PAH concentrations in sediments to below 44.8 mg/kg total PAHs, the effects range-median benchmark established by the National Oceanic and Atmospheric Administration.

Two cleanup levels have been established for mercury in Lavaca Bay sediments, based on the location of the sediments:

- 0.5 mg/kg mercury for sediments in open-water habitats
- 0.25 mg/kg mercury for sediments in marsh habitats.

The 2:1 ratio of the cleanup targets for mercury in open-water habitats versus marsh habitats is based on a bioaccumulation study, which demonstrated that the rate of methylmercury uptake that occurs in marsh habitats of the Bay is approximately twice that of the open-water habitats (USEPA, 2001).

## Ongoing Natural Recovery Processes

Lines of evidence demonstrate that physical isolation is the primary recovery process in Lavaca Bay (USEPA, 2001):

- A radiochemistry study was conducted to determine the vertical extent of mercury contamination in site sediments and to evaluate sedimentation rates within the Bay. Sedimentation rates were found to range between approximately 0.3 and 2.0 cm/yr.
- Hurricane scour modeling evaluated the potential sediment movement and mercury redistribution during future hurricane events. Using conservative parameters, it was

determined that high-energy events would have negligible effects on mercury concentrations in surface sediments.

## Sediment Remedy Selection

The most highly contaminated sediments at the site had been dredged by 2003, according to an Operations, Maintenance, and Monitoring Plan (OMMP) (Alcoa Environmental, 2003). The initially selected remedy, described in the ROD and OMMP, included:

- Dredging of the most highly contaminated sediments and installation of a dense, nonaqueous phase liquid (DNAPL) collection or containment system (Witco Area).
- Extraction and treatment of chlor-alkali process area groundwater and monitoring of surface water to evaluate the effectiveness of the hydraulic containment system.
- EMNR of sediments north of Dredge Island (through thin-layer capping), to eliminate an ongoing source of PAHs to the rest of the Bay.
- MNR of remaining affected areas (aerial extent not available).
- Institutional controls to manage human exposure to fish and shellfish.
- Long-term annual monitoring of mercury in surface sediments, fish, and shellfish of the Bay to confirm the natural recovery of sediment and fish tissue to acceptable levels.

In preparation for placement of the thin-layer cap, monitoring revealed that natural recovery processes alone were sufficient to achieve remedial goals. Thus, EMNR was not implemented at the site (Alcoa Environmental, 2006). Approximately 1700 acres in the Closed Area are undergoing MNR.

## Monitoring

By 2004, Alcoa had fully implemented annual sampling programs for surface sediments and fish tissue in the MNR-designated areas. In 2004 and 2005, the mean concentrations of mercury in sediments of the Closed Area were 0.293 mg/kg and 0.276 mg/kg, respectively (Alcoa Environmental, 2006). The OMMP called for monitoring to be discontinued in areas that have achieved their designated cleanup levels two years in a row. However, Alcoa has voluntarily continued to monitor the area to the north of Dredge Island in order to better understand fish tissue trends (Alcoa Environmental, 2006).

Additionally, the cleanup level of 0.25 mg/kg mercury in marsh habitats was met in one marsh area in 2004 and 2005. Consequently, monitoring at this marsh was discontinued in 2006 (Alcoa Environmental, 2007).

## Current Status

The completed and ongoing remedial activities and natural recovery have resulted in downward trends in open water sediment and marsh sediment mercury concentrations in parts of the Closed Area. Four additional marshes have met the cleanup level since 2006. Localized areas of open water sediment are not recovering as expected (e.g., north of Dredge Island), and locally elevated concentrations of mercury remain in some marshes. These trends are possibly due to residual effects of the Dredge Island Stabilization Project performed in the period 1998–2001.

Red drum mercury tissue concentrations measured in the Closed Area continue to exhibit positive and negative interannual fluctuations. These fluctuations appear to be related in part to physical and biologic conditions not influenced by remedial activities (e.g., salinity of upper Lavaca Bay). The average mercury concentration of red drum from the Closed Area increased in 2007, but the juvenile blue crab average did not. The mercury concentrations of red drum collected in the Closed Area remain statistically elevated relative to red drum collected in the Adjacent Open Area. Alcoa is currently performing evaluations of additional data collected voluntarily in 2007. These evaluations may support the identification of additional adaptive sediment management activities that will facilitate achieving cleanup levels (Alcoa Environmental, 2008).

## References

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Alcoa Environmental. 2006. 2005 Remedial Action Annual Effectiveness Report.

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USEPA. 2008a. NPL Site Narrative for Alcoa (Point Comfort)/Lavaca Bay. U.S. Environmental Protection Agency, Region 6.

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## 12 Mississippi River Pool 15

### Scott County, Iowa

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#### MISSISSIPPI RIVER POOL 15

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- ☆ **Key concerns:** Human health risks from PCBs.

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- ☆ **MNR application:** MNR was selected for the entire site in conjunction with source control for upland media.

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- ☆ **Cleanup goals:** Goals focused on reduction of non-cancer human health risks.

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- ☆ **Natural recovery processes:** Natural recovery relies primarily on physical isolation, reduced bioavailability, and dispersion.

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- ☆ **Monitoring:** An MNR program has not yet been established. Remedy success is likely to be measured by assessing PCB concentrations in fish tissue and monitoring sedimentation and sediment bed stability.

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- ☆ **Current status:** The MNR program has not yet been developed; fish consumption advisories have been lifted.

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The Mississippi River Pool 15 (MRP15) consists of approximately 10 miles of the Mississippi River on the eastern border of Iowa in Scott County. This portion of the river is located between Federal Lock and Dam 14 (on the upriver end) and Federal Lock and Dam 15 (on the downriver end). MRP15 is an important commercial and recreational waterway for the Iowa-Illinois Quad Cities metropolitan area, supporting commercial barge traffic, commercial fishing, and recreational boating and fishing.

An aluminum sheet and plate rolling mill (Alcoa-Davenport Works), operated by Alcoa Inc., is located on the Iowa side of the river, midway between Dam 14 and Dam 15 in Riverdale, Iowa. Operations at the Alcoa-Davenport Works facility began in 1948 and have resulted in contamination of:

- Soil and groundwater at the Alcoa site
- Sediments and fish in MRP15 in the immediate vicinity of the Alcoa site.

The MRP15 site encompasses portions of MRP15 where contamination from the Alcoa-Davenport Works facility came to be located (i.e., primarily along the 1-mile shoreline of the facility). The Alcoa site and the MRP15 site are separate but related cleanup areas; this case study focuses on the MRP15 site. USEPA and the Iowa Department of Natural Resources are the lead and support agencies, respectively, for both sites. Site investigation activities began in the early 1980s and continued through 2003, with multiple rounds of sediment and fish sampling.

### Contaminants of Interest

Elevated concentrations of PCBs (the primary COC) and PAHs were found in sediments at localized areas along the Alcoa-Davenport Works facility shoreline, but the environmental significance appears minimal, based on the small size of the area and the expectation of further reductions in contaminant concentrations (USEPA, 2004).

## Remedial Action Objectives

RAOs for the MRP15 site are incorporated in the 2004 ROD:

- Reduce PCB concentrations in fish to levels that are protective of human health and the environment.
- Monitor natural recovery processes, including sediment depositional processes, to evaluate the potential for future exposures to contaminated sediments.

## Ongoing Natural Recovery Processes

The primary natural recovery processes ongoing at the MRP15 site include physical isolation, reduction of contaminant bioavailability and mobility, and dispersion. Qualitative evidence supporting these processes was included in the 2004 ROD, which states that MRP15, the smallest pool in the upper Mississippi River, is characterized by relatively high velocities. Site managers characterized the high velocities as capable of both deposition and erosion of sediments. Mobility and bioavailability of low-level PCB contamination in MRP15 sediments were found to have decreased as a result of sedimentation processes occurring along the Alcoa-Davenport Works facility shoreline.

Other evidence of ongoing natural recovery processes, according to the 2004 ROD, includes the following:

- Improved management of on-site upland media at the Alcoa-Davenport Works facility has resulted in control of ongoing sources to MRP15.
- Contaminant concentrations in sediments along the Alcoa-Davenport Works facility shoreline in MRP15 have decreased.
- PCB levels in fish collected along the Alcoa-Davenport Works facility shoreline in MRP15 have decreased to levels similar to those collected in reference areas.
- Current PCB levels in fish are near risk-based remedial goals.
- Sediment bed stability is evident in areas along the Alcoa-Davenport Works facility shoreline adjacent to MRP15, suggesting remedy permanence.

## Sediment Remedy Selection

A human health risk assessment was completed for the MRP15 site in 2000. Non-cancer risks from total PCBs were found to exceed the target hazard index of 1 for both boat and shoreline recreational fishermen. Cancer risks to these receptors from total PCBs were within the target risk range. Non-cancer risk to shoreline trespassers from total PCBs and benzo(a)pyrene were below the target hazard index of 1. Cancer risks to shoreline trespassers were within the target risk range.

An ecological risk assessment was completed for the MRP15 site in 2002. The assessment evaluated total PCBs, PAHs, VOCs, and semivolatile organic compounds. Risks to carnivorous birds and mammals were considered to be insignificant, and risks to benthic invertebrates were considered minimal (USEPA, 2004).

MNR with management of on-site media at the Alcoa-Davenport Works facility was selected as the remedy for the MRP15 site.

## Monitoring

An MNR program has not yet been developed (Pers. Comm., J. Colbert, January 3, 2008). Monitoring and related activities will be conducted at the MRP15 site during the Remedial Action phase. Monitoring guidance is included in the 2004 ROD, and a summary of the likely long-term monitoring plan follows:

- Monitoring of sediments and fish (from the Alcoa-Davenport Works facility shoreline and reference areas) will demonstrate that contaminant reduction is occurring and achieving remedial goals and will include at least three fish tissue and sediment monitoring events, including a baseline event and subsequent events during the fourth years of two successive 5-year review periods.
- Natural recovery performance monitoring will include evaluation of sediment bed stability in the areas along the Alcoa-Davenport Works facility shoreline and in the wetland area adjacent to the shoreline. This will monitor the permanence of risk reduction afforded by physical isolation natural recovery processes by documenting that recently deposited clean sediment layers remain stable and continue to isolate underlying contaminated sediments.

## Current Status

The MNR program has not yet been developed. It should be noted, however, that the Iowa Department of Natural Resources (2008) lifted the fish consumption advisory, which is further evidence that natural recovery processes are reducing risk at the site.

## References

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## 13 Sangamo Weston, Inc./ Twelve-Mile Creek/Lake Hartwell Superfund Site, OU2 South Carolina

LAKE HARTWELL OU 2	
☆	<b>Key concerns:</b> Human health risks from ingestion of PCB-contaminated fish.
☆	<b>MNR application:</b> MNR was selected for Lake Hartwell.
☆	<b>Cleanup goals:</b> RAOs focus on reduction of human health risks.
☆	<b>Natural recovery processes:</b> Natural recovery relies on physical isolation and chemical transformation.
☆	<b>Monitoring:</b> Remedy success is determined by assessment of PCB concentrations in sediment as well as bioaccumulation monitoring.
☆	<b>Current status:</b> MNR has been partially successful, reducing sediment PCB concentrations while PCB concentrations in fish persist at elevated levels. Incomplete success is likely due to insufficient source control.

The Sangamo Weston, Inc./Twelve-Mile Creek/Lake Hartwell Superfund Site is located in Pickens, South Carolina. The Sangamo facility manufactured capacitors from 1955 until 1987. Some dielectric fluids used in manufacturing processes contained PCBs.

The impacted property occupied 220 acres, including six satellite locations where waste disposal occurred. Onsite disposal practices included burying off-specification capacitors and sludge from industrial wastewater treatment. PCBs were released to the on-site wastewater treatment plant and subsequently were discharged along with wastewater effluent into Town Creek, a tributary of Twelve-Mile Creek that drains into Lake Hartwell. Lake Hartwell, 56,000 acres in size, was created by the construction of a dam on the Savannah River by the U.S. Army Corps of Engineers between 1955 and 1963.

Release of an estimated 400,000 pounds of PCBs to Town Creek occurred between 1955 and 1977. Additional, unspecified amounts of PCBs were buried onsite and at satellite locations. PCB use at the Sangamo plant stopped in 1977; however, Lake Hartwell has been under various fish consumption advisories since 1976.

Two areas of interest or OUs were defined to facilitate remedial action: OU1, which addresses land-based source areas including the plant and six satellite areas, and OU2, which addresses sediment, surface water, and biological migration pathways downstream from source areas (USEPA, 1994). This case study focuses on OU2.

### Contaminants of Interest

PCBs are the primary COC for this site, posing unacceptable risks to human health through direct contact with contaminated soil and sediment, in addition to potential risks of eating contaminated fish. Other contaminants such as VOCs have been found at depth in on-site soil.

## Remedial Action Objectives

RAOs for OU2 include (USEPA, 1994):

- Achieving the cleanup level in surface sediments of 1 mg/kg between 2007 and 2011
- Reducing contaminants in fish to levels protective of human health and the environment (i.e., the FDA tolerance level of <2 mg/kg PCBs in fish).

## Ongoing Natural Recovery Processes

Ongoing physical isolation and chemical transformation (PCB dechlorination) processes are occurring at OU2 (USEPA, 1994). The following lines of evidence established these processes:

- Radioisotope geochronology. Demonstration of physical isolation processes via chemical geochronology measurements revealing sedimentation rates of 5–15 cm/yr (Brenner et al., 2004).
- PCB congener analysis. Demonstration of chemical transformation (PCB dechlorination) via PCB congener analysis of sediment cores (Magar et al., 2005a, b).

Physical isolation was found to be the dominant natural recovery process. Dechlorination of PCBs was found to be slow and limited to anaerobic subsurface sediment, thus contributing little to short-term risk reduction. However, PCB dechlorination reduces long-term risks associated with potential sediment resuspension. Refer to Highlight 4-3 for additional discussion of lines of evidence documenting physical isolation of PCBs at Lake Hartwell.

## Sediment Remedy Selection

Source control involved the excavation of 40,000 cubic yards of PCB- contaminated materials from OU1 and treatment using thermal desorption, which was completed in 1999. Groundwater continues to be treated for PCB and VOC recovery for OU1. Groundwater discharge to surface water may be a continuing source of contamination to Twelve-Mile Creek and subsequently Lake Hartwell, as site geology (e.g., fractured bedrock) presents significant challenges for source containment.

MNR, in combination with institutional controls (fish consumption advisories), was selected as the remedy for OU2. According to the 1994 ROD:

If more than 1 to 2 years elapse between the signing of the ROD and the initiation of the Remedial Design, the dredging alternatives will not achieve protectiveness appreciably faster than that obtained under baseline (no-action) conditions.

Accelerated sedimentation for the Twelve-Mile Creek arm of Lake Hartwell has been facilitated by release of accumulated sediment from three upstream dams. Additionally, two of the upstream dams will be removed, which should further enhance sedimentation rates.

## Monitoring

Annual monitoring of progress toward RAO attainment includes measuring chemicals in sediment and aquatic biota in OU2, including:

- Sediment sampling at 21 locations of the tributary and lake to verify predicted decreases in surface sediment PCB concentrations
- Fish tissue analysis at six lake stations for largemouth bass, catfish, and hybrid striped bass to track human health risk reduction over time
- Tissue sampling of forage fish at three lake locations for use in food web modeling
- Deployment and subsequent PCB analysis of caged *Corbicula* clams in Twelve-Mile Creek and Lake Hartwell to determine current PCB loading.

## Current Status

Concentrations of PCBs in caged *Corbicula* indicate a substantial reduction in source loading since the mid-1990s, but PCB releases appear to persist at lower levels (Figure A-14). Surface sediment PCB concentrations also show substantial decreases, especially for those locations that exhibited the highest PCB concentrations initially (Figure A-15). Declines in surficial PCB concentrations are less marked in areas that initially contained low to moderate contamination (URS 2008). As predicted from earlier investigations (USEPA, 2004), all surface sediment analyses in 2007 showed PCB concentrations below the 1 mg/kg cleanup level, and this result was replicated for most sample locations in 2008 (URS, 2008).

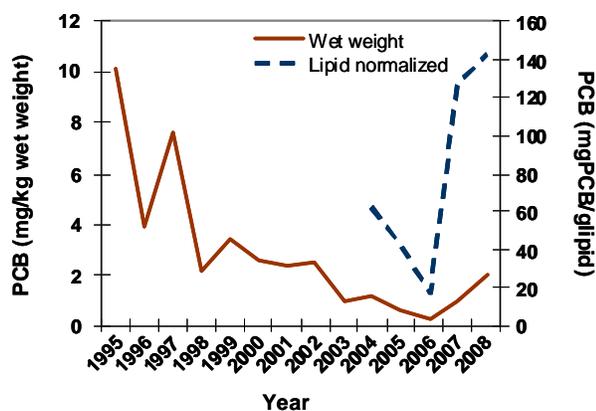


FIGURE A-14. Temporal trend of PCB concentrations in caged *Corbicula* downstream of the former Sangamo outfall. Concentrations are shown on both a wet-weight and a lipid-normalized basis.

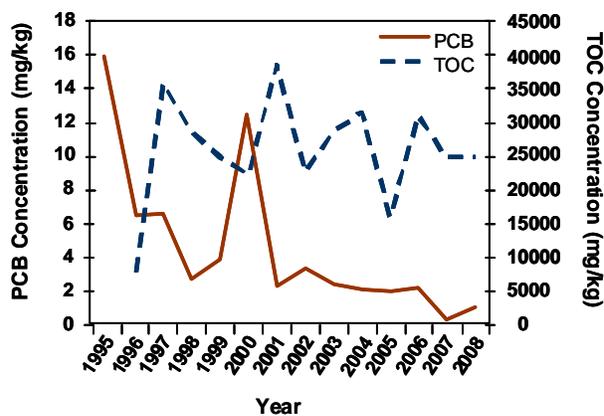


FIGURE A-15. Temporal trend in surface sediment PCB and TOC concentrations, Twelve-Mile Creek arm of Lake Hartwell (location SD011).

Concentrations of PCBs in fish tissue have not decreased in tandem with surface sediment concentrations. Concentrations in channel catfish fell below the FDA tolerance limit of 2 mg/kg for several years, but this trend has not been sustained since 2005. The other five fish species monitored show no clear trend of decreasing PCB concentrations (e.g., Figure A-16) (URS, 2008). It is suspected that groundwater contaminated with PCBs may be a continuing source to OU2, and additional source control efforts in OU1 are underway.

Fish consumption advisories remain in effect for Twelve-Mile Creek and Lake Hartwell. The South Carolina Department of Health and Environmental Control recommends that no fish be consumed from the Twelve-Mile Creek arm of Lake Hartwell and only one meal of largemouth bass or catfish per month be consumed from the remaining waters of Lake Hartwell (SCDHEC, 2007). Public education regarding fish consumption is also an institutional control element.

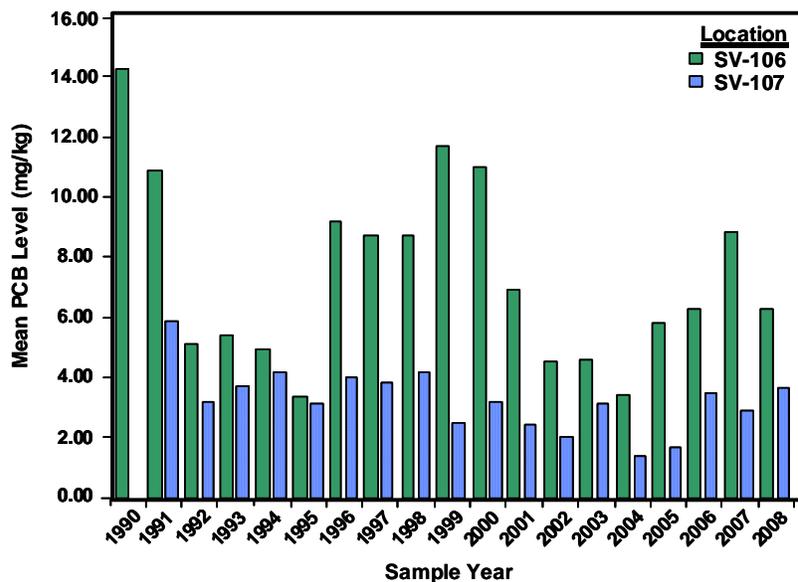


FIGURE A-16. Temporal trend of PCB concentrations in largemouth bass filets, Lake Hartwell.

Although sediment cleanup levels are being met, concentrations of PCBs in fish tissue remain high. These findings indicate natural recovery processes are continuing, though perhaps at a slower rate than expected, and additional source control measures are needed. Annual monitoring continues as directed by the ROD. The next 5-year review (expected by September 2009) will include updated observations and trend analysis.

## References

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## 14 Wyckoff/Eagle Harbor

### Intertidal Puget Sound, Bainbridge Island, Washington

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#### WYCKOFF/EAGLE HARBOR

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- ☆ **Key concerns:** Human health and ecological risks from PAHs and mercury.

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- ☆ **MNR application:** MNR was selected for intertidal areas of the West Harbor OU.

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- ☆ **Cleanup goals:** RAOs focus on reduction of human health and ecological risks.

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- ☆ **Natural recovery processes:** Natural recovery relies on physical isolation and chemical transformation of PAHs.

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- ☆ **Monitoring:** Remedy success is determined by measuring PAH and mercury concentrations in sediment and fish.

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- ☆ **Current status:** Institutional controls and fish advisories are in place. RAOs are met in the West Harbor.

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The Wyckoff/Eagle Harbor Superfund site is located in central Puget Sound, Washington, on the east side of Bainbridge Island. There are two separate areas associated with the site. West Harbor is the site of a former shipyard and is currently a Washington Department of Transportation ferry maintenance facility. The former Wyckoff wood-treating facility, located on the southwest edge of Eagle Harbor, operated from the early 1900s to 1988. The entire Wyckoff site was sold in portions to the City of Bainbridge Island between 2004 and 2006. Anticipated future land uses include public use of the West Beach, hillsides, and newly developed park areas.

In December of 1952, the Pollution Control Commission reported discharges of oily material from the Wyckoff wood-treating facility which began appearing on beaches adjacent to the facility. USEPA began investigating the site in 1971. The Wyckoff facility was added to the NPL in 1987. Numerous investigations and remedial actions took place in the following years. Construction for the West Harbor site was considered complete in September 2002. The containment remedy for the former Wyckoff processing area is now being implemented.

Eagle Harbor supports various wildlife resources. Coho and chum salmon are known to spawn in the area, and surf smelt and Pacific sand lance likely spawn in the area. Many fish and invertebrates are present in the harbor, and several species of shellfish are known to be present in the intertidal and subtidal areas. Species of special concern for the site are Puget Sound Chinook, bull trout, Stellar sea lion, bald eagle, and marbled murrelet.

Site contamination is related to the former Wyckoff wood-treating facility operations and sources of contamination in nearby upland areas and a former shipyard located in the West Harbor. Shipyard operations included the use and removal of antifouling agents and paint.

## Contaminants of Interest

The principal COCs are PAHs. Other chemicals of interest include pentachlorophenol, solvents, gasoline, antifreeze, fuel and waste oil, and lubricants. Elevated concentrations of metals (mercury, copper, lead, zinc, cadmium, and arsenic) in sediment were found near the former shipyard in the West Harbor (USEPA, 1992, 1994, 1996, 2002).

## Remedial Action Objectives

Four areas of interest or OUs have been defined to facilitate remedial action: West Harbor, East Harbor, Soil of Wyckoff Facility, and Groundwater of Wyckoff Facility. This case study focuses on West and East Harbor OUs.

RAOs for the East Harbor OU (USEPA, 1994) include:

- Achieving MCULs within 10 years after the completion of sediment remediation using natural recovery for the top 10 cm of intertidal areas of the East Harbor OU (i.e., by February 2011)
- Capping or dredging of the top 10 cm in the subtidal areas of the East Harbor OU for sediments containing concentrations greater than the MCUL at completion of upland source control
- Reduction of contaminants in fish and shellfish to levels protective of human health and the environment.

RAOs for the West Harbor OU (USEPA 1992) include:

- Achieving MCULs in the top 10 cm throughout the West Harbor OU within 10 years after the completion of capping or dredging
- Reduction of contaminants in fish and shellfish to levels protective of human health and the environment.

## Ongoing Natural Recovery Processes

Chemical transformation of PAHs and physical isolation were hypothesized to be the dominant natural recovery processes at this site. The following lines of evidence were used to evaluate the risk reduction potential of the physical isolation process (USEPA, 1992):

- Radioisotope geochronology. Sediment core samples were subject to radioisotope analysis to quantify sediment accumulation rates.
- Sediment deposition modeling. Mathematical modeling was conducted during the RI/FS to evaluate the potential for natural recovery of contaminated Eagle Harbor sediments via estimation of sedimentation rates. Eagle Harbor is not fed by a river or other major upland

sources of suspended sediment, so estimated sedimentation rates were predicted to be relatively low, lessening the chances of significant risk reduction by physical isolation.

- Sediment traps. Sediment traps were deployed over several periods in 1988 and 1989. Sediment trap data verified sedimentation rates and confirmed that relatively low concentrations of COCs were being deposited.

The following lines of evidence were used to investigate chemical transformation:

- Qualitative consideration of hydrological conditions. Intertidal areas have an active water regime and are exposed to light and air, which encourages microbial and chemical degradation of PAHs.
- PAH fingerprinting. Detailed fingerprinting of sediments (Brenner et al., 2002) suggested PAH transformation had occurred at the site (Figure A-17). The percentage of low-molecular-weight (two- and three-ring) PAHs relative to total PAHs decreased with transformation. This line of evidence provided qualitative evidence that mass reduction in the PAH derived from creosote was occurring.

## Remedy Selection

Lines of evidence suggested that natural recovery processes were sufficient to achieve RAOs in intertidal areas of the West Harbor within 10 years of the date of assessment (circa 2004). Although sedimentation rates were low, physical isolation was judged to be the major natural recovery process. In these areas, preservation of eel grass habitat outweighed the potential benefits of sediment removal or capping.

Only minor reductions in subtidal concentrations were predicted over the

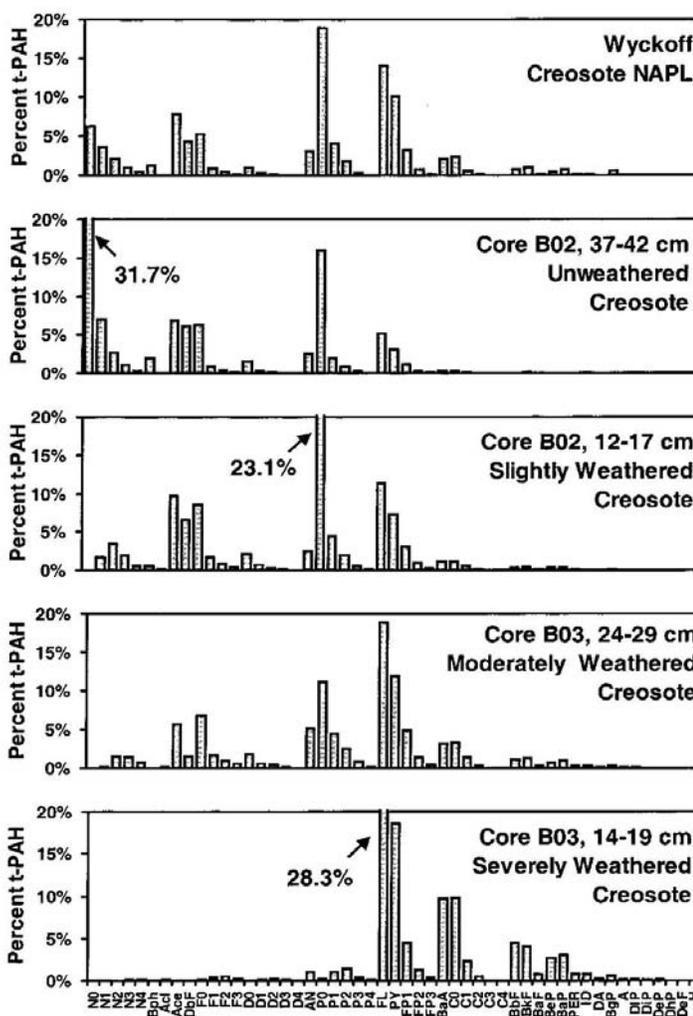


FIGURE A-17. PAH fingerprinting—a line of evidence for transformation in Eagle Harbor sediments. Reprinted with permission from Brenner et al. 2002. Copyright 2002 American Chemical Society.

10-year period for the remainder of Eagle Harbor. These areas were addressed through a combination of isolation capping, thin layer capping, and sediment removal.

## Monitoring

Monitoring includes surface and deep sediment sampling and biota collection and body burden analysis. The Second Five-Year Review (USEPA, 2007) suggested that MNR is achieving the cleanup levels in the West Harbor intertidal areas where it has been implemented.

## Current Status

Institutional controls are effective in controlling access to the upland areas, and fish advisories are in place. MNR is meeting RAOs in the West Harbor intertidal areas and is currently viewed as a success.

## References

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USEPA. 2007. Second Five-Year Review Report for the Wyckoff/Eagle Harbor Superfund Site, Bainbridge Island, Kitsap County, Washington. U.S. Environmental Protection Agency, Region 10.

# TECHNICAL GUIDE

Monitored Natural Recovery at Contaminated Sediment Sites

## APPENDIX B

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### Contaminant-Specific Factors

# Appendix B. Contaminant-Specific Factors

*Chemical-specific considerations relevant to MNR.*

Contaminant properties (e.g., solubility, hydrophobicity, redox and pH behavior, transformation and degradability, and toxicity) often govern fate and transport processes in aquatic environments and thus factor significantly in any monitored natural recovery (MNR) evaluation. Some key considerations are included in this section for the following contaminants and groups of contaminants:

- Arsenic (As)
- Chlorinated hydrocarbons (includes polychlorinated biphenyls (PCBs), polychlorinated dibenzo(p)dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs)).
- Chromium (Cr)
- Divalent metals
- Explosives
- Mercury (Hg)
- Organotins
- Pesticides
- Polycyclic aromatic hydrocarbons (PAHs) and petroleum hydrocarbons
- Radionuclides

These contaminants may be of concern at Department of Defense (DoD) sediment sites. Although some may be associated primarily with off-site sources, they are relevant to remedy selection and monitoring to the extent that they can contribute to unacceptable risks. Contaminants that are not persistent in sediment (such as volatile organic compounds) are not included here, as they are most appropriately addressed through source control rather than contaminated sediment management.

For each chemical or chemical group, Appendix B identifies common sources, typical risk drivers, and contaminant-specific considerations that primarily affect the two natural recovery processes of chemical transformation and reduction in mobility and bioavailability. A broad overview of these issues is presented to help guide conceptual site model (CSM) development and prioritization of

natural recovery processes. Other resources should be consulted for full details on contaminant-specific processes and their impact on contaminant fate and transport and MNR. Investigative tools to address key chemical-specific questions related to natural recovery process are described in Chapter 4.

Physical processes related to sediment deposition and resuspension, as they relate to the natural recovery processes of physical isolation and dispersion, are not chemical-specific and hence are not discussed in Appendix B.

## 1 Arsenic

**A**rsenic is a naturally occurring element and exhibits high natural background concentrations in some areas. Common anthropogenic sources include urban runoff, atmospheric release by smelters, wood treatments and preservatives, pesticides, and mining.

### Key risk considerations

- Risk drivers may include human or wildlife (e.g., avian) consumers of shellfish (Koch et al. 2007), or direct toxicity to invertebrates.
- Human and wildlife consumers of fish are typically at low risk because As in fish tissue is present in organic forms (primarily arsenobetaine), which is metabolically inert, and thus essentially nontoxic (Neff, 1997).

### Key issues

- Arsenic readily converts between As(III) and As(V) depending on ambient redox conditions. Specific factors that influence the dominant speciation of As between As(III) and As(V) include the redox potential of groundwater and sediment pore water, and the eutrophication state of surface waters. Because As mobility is affected by speciation, these conditions affect the extent to which advective or diffusive transport of As species becomes a site-specific concern.
- Arsenic speciation has less influence on As toxicity because no systematic difference is observed in the relative toxicity of As(III) and As(V) to aquatic organisms, and both species are toxic to humans under chronic exposure scenarios (Smedley and Kinniburgh, 2005).
- Arsenic is immobilized by sorption to iron oxides in aerobic sediments, and formation of frequently mixed-phase sulfide compounds in anaerobic sediments (i.e., As may sorb to other precipitating sulfide phases such as iron sulfides). The extent of As(III) and As(V) sorption to iron oxides or other precipitating phases is pH- and redox-dependent (Drever, 1997).
- Arsenic is mobilized at oxic-anoxic boundaries and in sulfide-poor reducing environments. As can exhibit vertical cycling within the sediment column; that is, dissolved As diffuses upward and sorbs to iron oxides in oxic surface sediment (e.g., Widerlund and Ingri 1995). This phenomenon can be influenced by sediment deposition rates (Toevs et al., 2008).
- The toxicity of dissolved arsenic in pore water can be limited by formation of soluble As-sulfide complexes (Rader et al., 2004).
- Volatilization of organoarsenic compounds has been noted in soils (Menzies, 2007) but is not currently recognized as a significant loss mechanism in sediments.

## Key questions

- What is the mobility and bioavailability of As, and is As mobility and bioavailability changing with time due to sedimentation processes or geochemical changes (such as pH or redox conditions) affecting the extent to which As is sorbed to sediment solid phases?
- How is As transformation affected by seasonal changes in redox conditions?
- What is the chemical stability of sequestered or nontoxic forms of As?
- Does vertical cycling significantly retard the effectiveness of MNR through As movement from buried sediments to surface sediments?

## 2 Chlorinated Hydrocarbons

This category of contaminants includes PCBs, PCDDs, and PCDFs. Among urban-associated chemicals, PCBs are less ubiquitous than PAHs and metals, but urban background levels in sediment are sustained by many sources including combined sewer outfalls, wastewater treatment plants, and deposition from atmospheric emission sources (USEPA, 2007).

PCDDs and PCDFs naturally occur at low levels and are widely distributed due to a variety of combustion-related and other industrial sources; thus, background concentrations may be significant relative to conservative risk benchmarks.

## Key risk considerations

- Bioaccumulation and adverse effects on fish-consuming wildlife are often risk drivers.
- Human health risk quantification is controversial, but unacceptable risks due to fish consumption are often predicted.
- The USEPA has issued a framework to assist scientists in using the toxicity equivalence methodology to assess ecological risks from chlorinated hydrocarbon mixtures (USEPA, 2008).

## Key issues

- Strongly hydrophobic characteristics limit contaminant mobility but also result in contaminant persistence in the environment.
- Sorption to black carbon can greatly decrease bioavailability compared to amorphous organic carbon, especially for planar congeners (Bucheli and Gustafsson 2003, Lohmann et al. 2005). Ongoing sorption and molecular diffusion processes over years or decades can increase sequestration; this may already be reflected in current conditions except in the case of recent releases.
- PCB, PCDD, and PCDF mobility is strongly influenced by the sorbent matrix, sediment age, and congener partitioning characteristics.
- Chemical transformations are not generally sufficient to provide significant risk reduction at a useful timescale for surface sediments. Thus, sedimentation processes (deposition and burial, or off-site dispersion) and geochemical processes (sorption and sequestration) typically dominate recovery processes at PCB, PCDD, and PCDF sites.
- Aerobic conditions favor microbial degradation of lower chlorinated congeners; reductive dechlorination of more highly chlorinated congeners occurs under anaerobic conditions, at a timescale of decades. Therefore, dechlorination occurs predominantly in subsurface sediments. The extent of PCB dechlorination is much higher for higher chlorinated congeners

**Key issues**

and tends to taper off for di- and trichlorobiphenyls, with *ortho*-PCBs typically remaining (Magar et al. 2005a,b). Dechlorination can provide long-term reduction of potential toxicity, but provides less risk reduction near the sediment-water interface than in more deeply buried sediments (Magar et al., 2005a,b).

- Dechlorination may also result in transformation to other congeners, including ones which may be equally or more bioavailable or toxic.

**Key questions**

- What is the mobility and bioavailability of chlorinated hydrocarbons, and do mobility and bioavailability change with time?
- Can fingerprinting (as with site-specific distributions of congeners) be used to characterize sources and/or transformation processes?
- For PCBs, do transformations in deeper sediments provide meaningful risk reduction with respect to future sediment resuspension events and long-term risk management?

### 3 Chromium

**C**hromium (Cr) is a naturally occurring element and is also associated with anthropogenic activities/processes including mining, combustion, plating, alloying, and the use of paints, toners, and drilling muds. Chromium exists in the environment primarily as Cr(III) or Cr(VI), valence states that exhibit very different properties. Due to its solubility, the presence of Cr(VI) in sediment likely indicates a persistent surface water or groundwater source.

**Key risk considerations**

- Appendix D of USEPA's (2005) "Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks" for divalent metals should guide the evaluation of chromium exposure and risk. Measurement of acid volatile sulfide (AVS) forms the basis for assessing Cr for the protection of benthic organisms.
- Cr(VI) is much more soluble, mobile, and toxic than Cr(III). To the extent that Cr poses significant risks, direct toxicity to aquatic organisms due to presence of Cr(VI) is the most likely risk driver.
- Cr(III) solubility is enhanced under low pH conditions, such as may be found with acid soils or as the result of acid mine drainage.
- Cr(VI) and Cr(III) do not bioaccumulate significantly, so ingestion pathways are of minor concern with respect to sediments (Sorensen et al., 2007).

## Key issues

- Rapid and spontaneous reduction of Cr(VI) to Cr(III) occurs under even mildly reducing conditions (e.g., redox conditions at which nitrate reduction dominates microbial respiration). Because Cr(III) exhibits minimal toxicity, this transformation serves as the primary MNR mechanism for Cr-contaminated sediment.
- Cr(III) is stable under aerobic conditions (Eary and Rai, 1987; Magar et al., 2008). Cr(III) oxidation to Cr(VI) involves surface reactions with Mn oxides. Insolubility and aging limit Cr(III) availability for such surface reactions.
- Cr(VI) is unstable in anoxic sediments (Martello et al., 2007; Eary and Rai, 1987) and is readily reduced to Cr(III). Thus, sediments containing measurable AVS (an indicator of anaerobic conditions, given the presence of sufficient sulfide to form metal precipitates) do not contain toxic Cr(VI).
- The solubility of Cr(VI), its instability under reducing conditions, and the relatively low solubility of Cr(III) in all but very low or very high pH conditions dictate that control of Cr(VI) sources will eliminate Cr(VI) persistence in sediment pore water. The low toxicity of aqueous Cr(III) and the geochemical stability of Cr(III) precipitates under both aerobic and anaerobic conditions (Masscheleyn et al., 1992; Magar et al., 2008) contribute to the long-term efficacy of MNR as a remedy for Cr contamination in reducing environments.

## Key questions

- Is Cr(VI) present at significant levels in sediment pore water? Note that solid-phase analyses may inaccurately indicate Cr(VI) presence due to method-related artifacts (Martello et al., 2007; Bery et al., 2004).
- Does the presence of Cr(VI) in sediment pore water indicate an ongoing source (e.g., an ongoing groundwater source)?
- Is Cr(III) geochemically stable in site sediments? (Note: the scientific literature on chromium indicates that Cr(III) is geochemically stable under ambient environmental conditions. In the absence of Cr(VI) measured in sediment pore water, this question is most likely answered in the affirmative.)

## 4 Divalent Metals

**D**ivalent metals include cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), and zinc (Zn). These metals are associated with a variety of urban and industrial sources; they also occur naturally in sediments. Metals may be relatively soluble and often are transported to sediments via surface or groundwater flow processes. Metals also may be transported to aquatic environments in particulate form via surface runoff and sedimentation processes.

## Key risk considerations

- Toxicity to benthic invertebrates is the typical risk driver.
- USEPA's (2005) "Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks" for divalent metals should guide the evaluation of metals exposure and risk. Measurement of AVS, simultaneously extracted metals (SEM), and organic carbon inform the assessment of metal bioavailability and toxicity.

## Key issues

- Once introduced to sediment, metals typically accumulate via adsorption or nonspecific binding to either inorganic (mineral) or organic phases. Metals also form precipitates of varying stabilities under either oxidizing or reducing conditions. Precipitation in oxic environments frequently takes the form of oxide ( $-O_x$ ) or oxyhydroxide ( $-OOH$ ) phases. Precipitation under reducing conditions requires the presence of dissolved sulfide, generally present as the result of microbial respiration of available sulfate. These mechanisms limit bioavailability and mobility (USEPA, 2005; Axe and Trivedi, 2002).
- Dissolved metal concentrations (e.g., in pore water or surface water) are more predictive of exposure than other measures. (The whole sediment metal concentration is not necessarily a good indicator of metal bioavailability and toxicity.)
- Sulfide, organic carbon, and pH are key factors controlling the bioavailability of divalent metals in sediment (Di Toro et al., 2005).
- The stability of sorbed and/or precipitated forms of divalent metals varies as a function of the specific metal and factors including organic matter input rates and system hydrodynamics that dictate ambient geochemical conditions (Kalnejais et al., 2007).
- Resuspension of anoxic sediments may cause oxidation and acidification (if sulfide were originally present), which may increase the mobility and bioavailability of previously sequestered divalent metals. However, dissolved metal concentrations associated with resuspension events are likely to be relatively low. Cantwell et al. (2008) found minimal release of dissolved metals upon resuspension of metal-contaminated estuarine field sediments or spiked sediments containing higher sulfide concentrations.
- Sequestration of metals in sediment is kinetically driven, with slow sorption processes enhancing the potential for metal sequestration for years following initial release into a sedimentary environment (Locat et al., 2003; Schnoor and Zehnder, 1996). If geochemical conditions are relatively stable, then—with the exception of recently released metals—current conditions may already reflect the long-term outcome of slow sorption processes.
- Long-term changes in sediment geochemistry (i.e., mineral diagenesis) can result in incorporation of metals into crystal lattices, a particularly stable form of sequestration. In some cases, metals sorbed to porous hydrous metal oxides can also be excluded during crystal formation, causing desorption (Ford 2007). This process of desorptive exclusion may also occur in reducing environments during the slow conversion of rapidly precipitating iron-sulfide phases ( $FeS$ ) to the more stable diagenetic form  $FeS_2$  (pyrite) (Roberts et al., 1969).

## Key questions

- What defines the mobility and bioavailability of divalent metals, and is either changing as a function of time?
- What is the likelihood that geochemical conditions will change diurnally, seasonally, or over longer time periods? Specifically, under what circumstances might reduction of metal oxides, oxidation of sulfides, or acidification occur, potentially releasing sequestered metals?
- What is the site-specific and chemical-specific stability of sequestered metals, given reasonably expected changes in geochemical conditions?

## 5 Explosives

The presence of relatively soluble explosive compounds in sediment may indicate a groundwater source rather than persistent sediment contamination.

### Key risk considerations

- Direct toxicity to invertebrates is the most likely risk driver for nitroaromatic compounds (Conder et al., 2004).
- Cyclic nitramine compounds (RDX, HMX) are minimally toxic to aquatic biota (Talmage et al., 1999; Lotufo et al., in press).

### Key issues

- Rapid transformation occurs via biotic and abiotic pathways. Transformation products are nontoxic or covalently bound and sequestered into the sediment organic matrix (not bioavailable) (Elovitz and Weber, 1999); complete mineralization can occur in some cases (Lenke et al., 2000).
- Sediment grain size may affect transformation rates (Lotufo et al., in press).
- Energetic compounds are often associated with hot spots, possibly unexploded ordnance, where high concentrations may be toxic to microorganisms, impeding their degradation (Lotufo et al., in press). Unexploded ordnance may physically break up with time due to ordnance casing deterioration, resulting in increasing bioavailability and mobility.
- Most energetic compounds are highly water soluble and maintain high concentrations in sediment pore water. A large proportion of sediment-associated compounds will readily dissolve into overlying water if sediment is disturbed, enabling dispersion.

### Key questions

- Is persistent sediment contamination of concern, or does the presence of soluble energetic compounds in sediment indicate an ongoing source?
- Is biodegradation occurring under site conditions, and at what rate?

## 6 Mercury

Atmospheric mercury (Hg) deposition is of major concern globally. In North America, the northeastern United States and eastern provinces of Canada are especially affected. Hg inputs to aquatic systems may result from direct atmospheric deposition, industrial discharges, or the erosion of watershed soils, also an indirect source of atmospheric inputs (Wang et al., 2004). Among the historical applications of mercury were antifouling coatings and fungicides.

## Key risk considerations

- Bioaccumulation and adverse effects on fish-consuming humans and wildlife are likely risk drivers.
- Effects on fish reproduction are predicted at environmentally relevant concentrations (Beckvar et al., 2005).

## Key issues

- Bacterially mediated methylation of inorganic Hg results in the formation of methylmercury, which is more bioaccumulative and toxic than inorganic mercury. Dissolved methylmercury concentrations (e.g., in pore water or surface water) are more predictive of bioaccumulation than other measures of mercury levels. (Whole sediment inorganic Hg concentration is not a good indicator of Hg methylation and bioavailability.)
- Site-specific net methylation and Hg bioaccumulation rates depend on many factors, including sulfide and sulfate concentration, pH, dissolved organic carbon concentration/composition, sediment organic carbon, iron, Hg aging, type and activity of bacteria, salinity, flow rate, temperature, redox potential, suspended solids, nutrient loading rates, fish age and size, prevalence of wetlands and forested land cover in watershed, and concentration-dependent (or independent) demethylation rates (Fitzgerald et al., 2007; Munthe et al., 2007; Ullrich et al., 2001). Certain types of sites particularly favor Hg biomagnification, as follows:
  - Newly flooded reservoirs (likely due to effects of flooding on the composition of the microbial community).
  - Acidic lakes (due to the role that pH may play in influencing the relative microbial availability of dissolved inorganic Hg species).
  - Coastal marshes, mudflats, and sites of nearshore organic enrichment (due to availability of organic matter and sulfate).
- Sediment-associated Hg may be much less bioavailable than aqueous-phase Hg (i.e., Hg in the form of soluble or degradable complexes) that may have originated from upstream sources (Orihel et al., 2007). As such, it may be important to distinguish the relative contribution of sediment-associated versus aqueous-source Hg in defining the potential for net methylmercury production and bioaccumulation (Southworth et al., 2002).
- Elemental mercury (Hg<sup>0</sup>) can be formed through methylmercury demethylation or Hg(II) reduction. The generation of Hg<sup>0</sup> causes a net transfer of mercury out of aquatic systems through Hg<sup>0</sup> volatilization (Wang et al., 2004).
- Hg can be sequestered by complexation with iron oxides (in aerobic sediments) or sulfide compounds (in anaerobic sediments). In either scenario, the long-term stability of the sequestered phase may be influenced by changes in the redox potential of the environment. Such changes may accompany re-suspension of sediments or may result from organic inputs (such as from algal blooms) that influence the depth-distribution of microbial processes.
- Hg can be mobilized at oxic-anoxic boundaries and can exhibit vertical cycling within the sediment column; aqueous Hg species diffuse upward and sorb to surface sediment iron oxides (Merritt and Amirbahman, 2007).

## Key questions

- Are conditions conducive to net methylmercury production and bioaccumulation?
- Are applicable, regional models available to predict methylmercury tissue concentrations in the absence of point sources (currently limited to lake ecosystems)?
- What is the stability of sequestered forms of Hg in site sediment?
- Are exposures decreasing due to source control, sedimentation, or changes in sediment

## Key questions

- geochemical conditions?
- Given the high complexity of mercury geochemistry, to what extent will a detailed investigation of methylation/demethylation and factors affecting these processes contribute to risk management objectives? For example, are mercury source control measures or changes in such variables as organic matter inputs anticipated that could affect net methylation potential over time?

## 7 Organotins

**T**hese chemical compounds are used in antifouling paints that protect marine equipment and structures (e.g., boats, buoys, pilings) from marine organisms such as barnacles. The use of tri-butyl tin (TBT) in antifouling paint is being phased out, but leaching from ship hulls continues to affect harbors and marinas.

## Key risk considerations

- Endocrine disruption and reproductive effects in sensitive invertebrate species are typical risk drivers.
- Higher levels of TBT in sediment may indirectly affect fish by diminishing the abundance of invertebrate prey species.
- Inorganic tin (Sn) tends to be much less toxic than organotin compounds.

## Key issues

- Biodegradation (i.e., debutylation) is often moderately rapid (months to years) (Maguire 2000). However, degradation on a timescale of decades has been observed in some cases (e.g., Viglino et al., 2004). Degradation may be inferred via measurement of inorganic tin species versus organotin compounds.
- Aerobic conditions favor more rapid degradation than anaerobic conditions.
- Bioavailability increases with decreasing sediment organic carbon content, increasing pH, and increasing salinity. Aging can increase sorption strength to sediment solid phases; sorption likely decreases bioavailability (including availability for microbial biodegradation).

## Key questions

- Is biodegradation occurring in site sediments, and at what rate?
- Are biodegradation rates sufficient to reduce exposure and risk?
- Can biodegradation and corresponding changes in exposure be inferred via measurement of ambient organic and inorganic Sn concentrations?

## 8 Pesticides

Pesticides are widespread in both agricultural and urban areas. The environmental prevalence of specific pesticides changes over time. For example, pyrethroids have recently been identified as a cause of sediment toxicity in suburban and agricultural areas (Amweg et al., 2006; Phillips et al., 2006). Because of continual product turnover, pesticides currently in use may not be included in routine sediment analyses, potentially confounding identification of toxicants.

### Key risk considerations

- Risk drivers may include direct toxicity to invertebrates or, for some pesticides (e.g. DDT, chlordane and the cyclodiene pesticides), bioaccumulation and toxicity to fish-consuming humans and wildlife.

### Key issues

- Degradation rates vary widely among different pesticides. Some current-use pesticides are highly degradable. Some historically used pesticides and their degradation products are highly persistent (e.g., DDT, chlordane and the cyclodiene pesticides).
- Sorption to sediment reduces mobility and bioavailability, while also slowing transformation by limiting bioavailability to microorganisms.
- Sorption to black carbon can decrease bioavailability compared to amorphous organic carbon. Slow sorption processes increase sequestration for several years after initial release to sediment; this process of sequestration may already be reflected in the current conditions at a given site.

### Key questions

- What is the mobility and bioavailability of pesticides, and are their mobility and bioavailability changing with time?
- Is significant biodegradation occurring in site sediments, and at what rate?
- Do degradation products exhibit significant persistence, and what is their relative toxicity compared to parent compounds?
- Do continuing primary or secondary sources contribute to persistent, low-level surface sediment concentrations and can additional source control contribute to natural recovery?

## 9 Polycyclic Aromatic and Petroleum Hydrocarbons

Urban background sources for polycyclic aromatic hydrocarbons (PAH) and petroleum hydrocarbons predominate. Point sources also can be significant, such as former wood treatment sites, manufactured gas plant (MGP) sites, refineries, and uncontrolled oil or fuel releases. Urban background PAHs can confound results of toxicity tests targeting other compounds.

### Key risk considerations

- Likely risk drivers include direct toxicity to invertebrates, and tumors and reproductive effects in bottom-dwelling fish.
- USEPA's (2003) "Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks" should guide the evaluation of PAH exposure and risk. Recent studies indicate that pore water measurements provide the most direct and accurate measure of risk for sites contaminated with coal tars (Hawthorne et al., 2007). However, ongoing USEPA research suggests that physical effects of the alkane component of oils may be more important than PAH concentrations in explaining toxicity to some invertebrate species, when PAH concentrations are lower relative to oil concentrations (Mount et al., 2009).
- Human health risks are possible if shellfish consumption is prevalent; consumption of vertebrate fish does not pose a risk because fish rapidly metabolize PAHs.

### Key issues

- Oil spill case studies indicate differing biodegradation rates for PAHs and petroleum hydrocarbons, from rapid (near-complete removal within a year) to very slow (Atlas, 1981). Lower-molecular-weight PAHs and hydrocarbons are more readily biodegraded compared to higher-molecular-weight PAHs and hydrocarbons.
- Aerobic conditions and nutrient availability promote degradation (Prince and Drake, 1999); rates are lower in anaerobic conditions (Durant et al., 1995; Milhelcic and Luthy, 1991).
- Degradation products are CO<sub>2</sub> and simple hydrocarbons; lower-molecular-weight PAHs are interim transformation products.
- Higher-molecular-weight PAHs and alkylated PAHs are more resistant to degradation but are less toxic to benthic organisms due to lower bioavailability (USEPA, 2003). Also, susceptibility to dissolution and volatilization decreases with increasing molecular weight. Thus PAH weathering should reduce toxicity over time.
- Sorption to soot, pitch, coke, and other black carbon forms can greatly decrease bioavailability of PAHs compared to amorphous organic carbon (Khaliland et al., 2006; Lohmann et al., 2005). Hence, whole sediment PAH concentrations are not necessarily good indicators of PAH bioavailability and toxicity.
- Slow sorption processes increase sequestration for several years after initial release to sediment; with the exception of recently released compounds, this process of sequestration may already be reflected in the current conditions at a given site.

### Key questions

- Is biodegradation occurring under site conditions, and at what rate?
- Do forensics analyses show evidence for transformation and weathering (see Brenner et al., 2001; Stout et al., 2001)?
- To what extent do degradation and weathering contribute to reduced hydrocarbon exposures and risk?
- What is the likelihood of dissolution and release?
- What is the mobility and bioavailability of PAHs and petroleum hydrocarbons in surface sediments, and are they changing with time?

## 10 Radionuclides

**B**ackground concentrations of elements that emit radiation may be due to natural sources as well as atmospheric fallout. For a dredging remedy, radionuclides pose unique ex situ sediment management and disposal challenges to protecting human health for workers and the public during construction.

### Key risk considerations

- Fish are more radiosensitive than aquatic invertebrates (Bechtel Jacobs, 1998), with the egg development stage of some teleost (bony) fish demonstrating the greatest sensitivity (Blaylock et al., 1993).
- Radionuclides may exert direct toxicity as metals, in addition to radioactive toxicity.
- Human health risks are generally limited by low bioaccumulation of radionuclides in fish and limited direct exposure to sediment. However, bioaccumulation and food-chain exposures increase for elements with biological function or biologically relevant analogs (e.g., radium and strontium, which substitute for calcium in bone) (Poston and Klopfer, 1988; Smith and Amonette, 2006).

### Key issues

- Radiological half-lives vary greatly among radionuclides (USEPA, 1989). For several key radionuclides (uranium, thorium, radium, plutonium), radioactive decay proceeds far too slowly to serve as a useful attenuation mechanism.
- Reductions in radionuclide mobility and bioavailability are due to sorption, co-precipitation, and/or ion-exchange reactions, plus complexation to sediment organic matter (IAEA, 2006). These mechanisms of reduced bioavailability all contribute to MNR.
- Slow sorption processes increase sequestration for several years after initial release to sediment; with the exception of recently released compounds, this process of sequestration may already be reflected in the current conditions at a given site.
- Redox conditions influence mobility for some radionuclides. For example, for uranium (U), technetium (Tc), and plutonium (Pu), the oxidized forms (U(VI), Tc(VII), and Pu(V,VI)) are either more soluble or less surface-reactive than the reduced forms (U(IV), Tc(IV), and Pu(III,IV)). Thus, for these elements, reducing conditions limit the potential for radionuclide migration by promoting sorption or precipitation reactions.
- Radon is formed from the radioactive decay of uranium, thorium, and radium, and it in turn decays to lead. Although radon gas has a short half life (3.8 days), it is more mobile than either its parent or its decay products. Radon may diffuse within the sediment column or disperse into water or air. Similar to the vertical cycling of arsenic within the sediment column, the high mobility of radon could potentially cause its decay product (lead) to accumulate in surface sediments.

### Key questions

- What is the timescale of radioactive decay at the site, for both the primary radionuclide and its decay products?
- What is the chemical stability of sequestered forms of radionuclides in site sediment?
- What is the rate of dispersion of radionuclides via diffusion (as with radon), and does this rate

## Key questions

- represent an acceptable level of off-site risk transfer?
- To what extent will radon diffusion retard the effectiveness of clean sediment deposition as a natural attenuation mechanism?

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# TECHNICAL GUIDE

Monitored Natural Recovery at Contaminated Sediment Sites

## APPENDIX C

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### Summary of Relevant Models

TABLE C-1. Hydrodynamic/Hydraulic/Sediment Transport Models.

Model	Description	Steady State/ Dynamic	Dimension	Supporting Agency/ Developer
ADCIRC / M2D / PTM	Hydrodynamic and Sediment Transport (Particle Tracking) Models for Coastal and Harbor Areas	Dynamic	2-D	USACE
CE-QUAL-RIV1	Hydrodynamic & Water Quality Model for Streams	Dynamic	1-D	USACE
CE-QUAL-W	2D Laterally-Averaged Water Quality Model	Dynamic	2-D vertical	USACE
CH3D-WES	Curvilinear Hydrodynamics in Three Dimensions - Waterways Experiment Station	Dynamic	3-D	USACE
CORMIX	Mixing-Zone Model	Steady-State	3-D	USEPA
DELFT3D	2D/3D Hydrodynamics and Sediment Transport	Dynamic	2-D and 3-D	Delft Hydraulics
DYNHYD5	Link-Node Tidal Hydrodynamic Model	Dynamic	1-D	USEPA/CEAM
ECOMSED	Hydrodynamic and Sediment Transport Model	Dynamic	3-D	HydroQual, Inc.
EFDC: Environmental Fluid Dynamics Code	Hydrodynamics and Transport Model	Dynamic	1-D to 3-D	TetraTech/Virginia Institute of Marine Sciences
HEC-2/HEC-RAS	River Analysis System	Steady-State	1-D (HEC2)	USACE/ HEC
HEM1D/HEM2D/HEM3D	Hydrodynamic Eutrophication Model	Dynamic	1-D to 3-D	Virginia Institute of Marine Science
HSCTM-2D	Hydrodynamic and Sediment and Contaminant Transport Model	Dynamic	2-D lateral	USEPA/CEAM
MIKE-11/ MIKE-21/ MIKE-3	Generalized Modeling Package-1D/ 2D/3D - Hydrodynamics	Dynamic	1-, 2-, and 3-D	Danish Hydraulic Institute
POM	Princeton Ocean Model	Dynamic	3-D	Princeton University
RIVMOD-H	River Hydrodynamic Model	Dynamic	1-D	USEPA/CEAM
RMA-2V	Hydrodynamic Analysis Model	Dynamic	2-D lateral	WES
UNET	1-D Unsteady Flow through a Full Network of Open Channels	Dynamic	1-D	USACE

Adapted from LimnoTech. 2002. Descriptive Inventory of Models with Prospective Relevance to Ecological Impacts of Water Withdrawals. Prepared for the Great Lakes Commission.

TABLE C-2. Hydrology/Watershed Models.

Model	Description	Supporting Agency/ Developer
AGNPS	Agricultural Non-Point Source Pollution Model	USDA
ALIS	Aquatic Landscape Inventory System	OMNR
ANSWERS	Event-Based Agricultural Area Runoff/ Erosion Model	University of Georgia
ATLSS	Across Trophic Levels System Simulation for the Freshwater Wetlands of the Everglades and Big Cypress Swamp	Coordinated through USGS
BASINS	Better Assessment Science Integrating Point and Non-Point Sources (NPSM – Dynamic, QUAL2E – Steady-state)	USEPA/CEAM
CREAMS/GLEAMS	Field-Scale Runoff/Erosion Model	USDA
ELM	Everglades Landscape Model	SFMD (H. Carl Fitz)
GAWSER	Object-Oriented Guelph All-Weather Storm Event Runoff Model	John A. Hinckley, Jr. (USACE)
GWLF	Generalized Watershed Loading Functions	EPA/CEAM
HSPF: Hydrological Simulation Program – FORTRAN	Simulation of Mixed Land-Use Watersheds (urban and rural) (1-D, Dynamic)	USEPA/CEAM
LBRM	GLERL Large Basin Runoff Model	GLERL/NOAA
OFAT	Ontario Flow Assessment Techniques Version 1.0	OMNR
SLAMM	Source Loading and Management Model	University of Alabama
SPARROW	Spatially Referenced Regression on Watershed Attributes	USGS
SWAT	Soil and Water Assessment Tool	USDA
SWMM	Storm Water Management Model	USEPA/CEAM
WAM	Watershed Assessment Model	SWET
WARMF	Watershed Analysis Risk Management Framework	System Engineering, Inc. under the sponsorship of EPRI
WATFLOOD	The WATFLOOD Hydrologic Model	Nick Kouwen (Univ. of Waterloo, Ontario, Canada)

Adapted from LimnoTech. 2002. Descriptive Inventory of Models with Prospective Relevance to Ecological Impacts of Water Withdrawals. Prepared for the Great Lakes Commission.

TABLE C-3. Surface Water Quality Models.

Model	Description	Steady State/ Dynamic	Dimension	Supporting Agency/ Developer
AQUATOX	Ecosystem Model	Dynamic	2-D	USEPA
CE-QUAL-ICM	3-D Time Variable Integrated Compartment Eutrophication Model	Dynamic	3-D	USACE
CE-QUAL-RIV1	Hydrodynamic and Water Quality Model for Streams	Dynamic	1-D	USACE
CE-QUAL-W2	2-D Laterally Averaged Hydrodynamic and Water Quality Model	Dynamic	1-D, 2-D	USACE
ECOFATE	Ecosystem Model	Dynamic	2-D	Simon Fraser University, Canada (Frank P. Gobas)
EUTROMOD	Receiving Water Model	Steady-State	1-D	NALMS
GBTOX/GBOCS	Green Bay Toxics Model	Dynamic	3-D	USEPA
HUDTOX	Contaminant Fate and Transport Model	Dynamic	3-D	USEPA
MIKE11-WQ MIKE21-WQ MIKE3WQ	Generalized Modeling Package- 1D(/2D/3D) Water Quality Module	Dynamic	1-D to 3-D	Danish Hydraulic Institute
QUAL2E	Steady-State, 1-D Stream Water Quality Model	Steady-State	1-D	USEPA/CEAM
QWASI	Quantitative Water-Air-Sediment Interaction Model	Steady-State	1-D	Trent University, Canada (Donald Mackay)
RATECON	Rate Constant Model for Chemical Dynamics	Dynamic	1-D	Trent University, Canada (Donald Mackay)
SAGEM	Saginaw Bay Ecosystem Model	Dynamic	3-D	USEPA
SMPTOX4	Simplified Method Program – Variable-Complexity Stream Toxics Model	Steady-State	1-D	USEPA/CEAM
WAQ-DELFTS3D	3-D Time Variable Water Quality Model	Dynamic	3-D	WL Delft Hydraulics
WARMF	Watershed Analysis Risk Management Framework	Dynamic	1-D	Systech Engineering, Inc. (w/EPRI)
WASP5	Water Quality Analysis Simulation Program	Dynamic	1-D to 3-D	USEPA
WASTOX	Water Quality Analysis Simulation of Toxics	Dynamic	1-D to 3-D	USEPA/CEAM

Adapted from LimnoTech. 2002. Descriptive Inventory of Models with Prospective Relevance to Ecological Impacts of Water Withdrawals. Prepared for the Great Lakes Commission.

TABLE C-4. Ecological Effects Models.

Model	Description	Supporting Agency/ Developer
ATLSS	Across Trophic Levels System Simulation for the Freshwater Wetlands of the Everglades and Big Cypress Swamp	Coordinated through USGS
ECOFATE	Model determines ecological or human health risk posed by chemical emissions	Simon Fraser University (Frank P. Gobas)
ELM	Everglades Landscape Model	SFWMD (H. Carl Fitz)
EXAMS II	Fate and exposure model for assessing toxics in receiving waters	USEPA/CEAM
FGETS	Food and Gill Exchange of Toxic Substances Fish bioaccumulation model	USEPA/CEAM
HEP/HS	Habitat Evaluation Procedures/Habitat Suitability Indices evaluates the quality and quantity of available habitat and measures the impact of land or water use changes	USEPA/CEAM
HES	Habitat Evaluation System used to assess the impacts of development projects for aquatic and terrestrial habitat evaluations	USEPA/CEAM
HGM	Hydrogeomorphic Assessment used to determine the integrity of physical, chemical, and biological functions of wetlands as they compare to reference conditions	USEPA/CEAM
IFIM	Instream Flow Incremental Methodology used to assess riverine habitats	USEPA/CEAM
MNSTREM	Minnesota Stream Temperature Model	USEPA/CEAM
PHABSIM	Fish-Habitat Preference and Discharge-Habitat Model that determines the Weighted Usable Area under a variety of channel configurations and flow management conditions	USEPA/CEAM
PVA	Population Viability Analyses for aquatic and terrestrial populations	USEPA/CEAM
RBPs	Rapid Bioassessment Protocols used to characterize biological integrity of riverine habitat	USEPA/CEAM
SAGEM	Saginaw Bay Ecosystem Model	USEPA
SNTMP	Stream Network Temperature Model simulates mean daily water temperature for stream networks for multiple time periods	USEPA/CEAM
SSTEMP	Stream Segment for a Single Time Period model simulates mean daily water temperature	USEPA/CEAM
TSLIB	Time-Series Library creates habitat time series and habitat-duration curves using habitat discharge relationships produced by PHABSIM	USEPA/CEAM
WET II: Wetland Evaluation Technique, version 2.0	A community-based habitat evaluation that can provide a broad overview of potential project impacts on wetland habitat functions	USEPA/CEAM

Adapted from LimnoTech, 2002. Descriptive Inventory of Models with Prospective Relevance to Ecological Impacts of Water Withdrawals. Prepared for the Great Lakes Commission.