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Monitored Natural Recovery at Contaminated Sediment Sites

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TECHNICAL GUIDE

Monitored Natural Recovery at Contaminated Sediment Sites

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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

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.

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

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 ...

Monitored 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

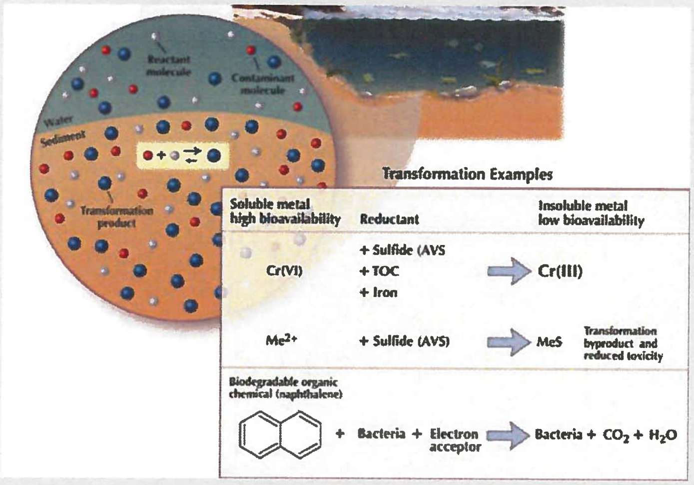
⇨Refer to Chapter 4 for more information about natural recovery processes.

The 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)

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

Description	**Effectiveness**
Change in chemical structure or valence state. Mechanisms include: • Abiotic chemical reaction or biological degradation • Mineralization • Redox transformation	Achieves risk reduction to the extent that transformation processes eliminate, detoxify, or reduce the bioavailability of the contaminant. 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).



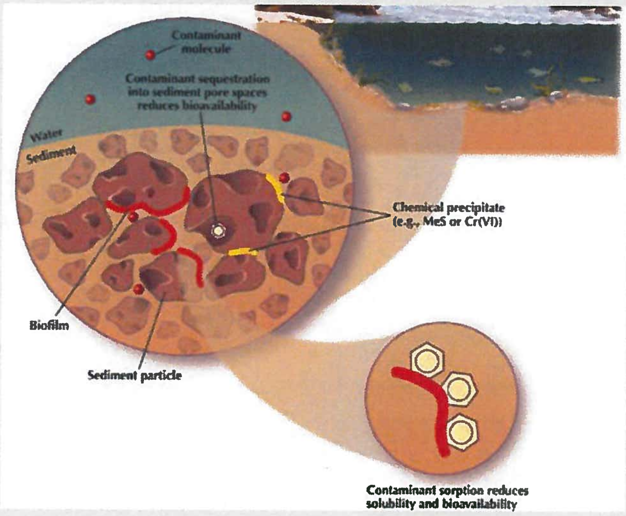
Examples

- 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	Effective in achieving risk reduction to the extent that reduced mobility and bioavailability minimize the potential for human or biological exposure and uptake. Because contamination is left in place, these processes may require a more comprehensive effort to verify permanence in support of MNR.

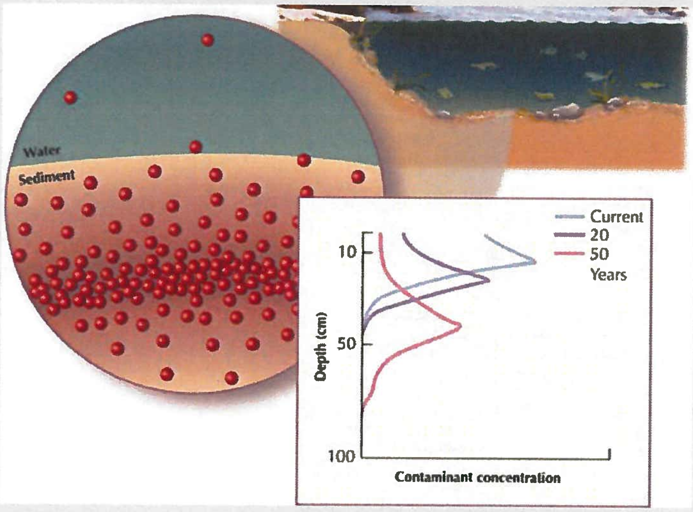


Examples

- 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
Physical containment via deposition of clean sediment that segregates contaminated sediment from benthic and pelagic organisms. Mechanisms include: • Burial via natural sedimentation • Surface sediment dilution via mixing with clean sediment • Consolidation and cohesion of sediment bed. • Natural sediment winnowing and bed armoring.	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. Because contamination is left in place, these processes may require a more comprehensive effort to verify permanence in support of MNR.

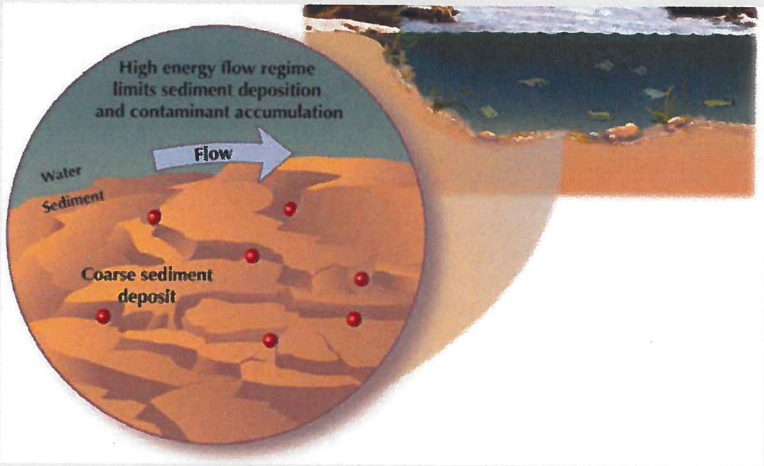


Examples

- Isolation of polychlorinated biphenyl (PCB)-contaminated surface sediments at Bremerton Naval Complex (USEPA 2000a).
- Burial of Kepone-contaminated sediment in the James River, VA (Luellen et al. 2006).
- Burial, isolation, and reduced surface sediment PCB concentrations at the Sangamo Weston/Twelve-Mile Creek/Lake Hartwell Superfund Site, SC (Brenner et al. 2004).
- Burial of PCB-contaminated post-dredging residuals in Manistique Harbor, MI (NRC 2007a).
- Burial of mercury-contaminated sediment in Eight-Day Swamp in the Hackensack Meadowlands, NJ (Weis et al. 2005).

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

Description	Effectiveness
Disturbances that physically transport sediment or otherwise disperse contaminants into the overlying water column, where they are transported away from the contaminated area: • Resuspension • Pore water advection and contaminant diffusion • Bioturbation/biomixing	Effective in achieving risk reduction to the extent that dispersion processes reduce exposure and bioavailability at the site without resulting in unacceptable offsite risk. 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.



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.

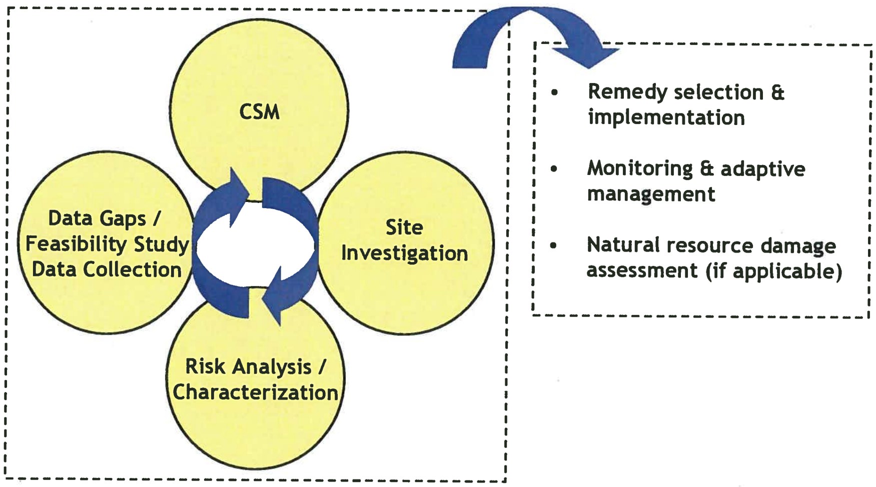


FIGURE 1-1. Conceptual site model as the basis for developing a remedial strategy.

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.

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.

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

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**
RI/FS and Baseline	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			
Long-term Monitoring	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
Chemical Transformation	• Historical trends in chemical concentrations and loadings • Chemical indicators of previous or potential chemical weathering and biodegradation • Characterization of factors that may regulate chemical transformation, including: o Chemical solubility, hydrophobicity, or volatility o Oxidation/reduction potential o Electron donors/acceptors o Microbial community o Other general aqueous geochemical and physiochemical conditions • Modeling of long-term trajectories balancing source control vs. dominant chemical transformation processes
Reduction in Contaminant Mobility and Bioavailability	• Historical trends in chemical mobility, bioavailability and uptake • Chemical partitioning into sediment pore water • Chemical solubility, hydrophobicity, or volatility • Age of contamination and degree of sequestration • Geochemical precipitation (metals) • Sediment and aqueous geochemical and physiochemical conditions • Modeling
Physical Isolation	• Sediment core profiles demonstrating burial of historical contaminant deposits and reductions in surface sediment concentrations over time • Hydrodynamics (water depth and velocity) under a range of flow conditions • Geophysical conditions such as bathymetry or subbottom profiling • Radiogeochemistry (e.g., lead-210 or cesium-137) to measure historical deposition and deposition rates • Sediment critical shear strength to predict sediment scour potential under a range of flows • Benthic biological activity and the role of benthic organisms in surface sediment mixing and transport (bioturbation) or as a vector for food-web uptake • Modeling

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

Natural Recovery Process	Lines of Evidence
Dispersion	• Desorption or dissolution processes and kinetics • Upstream and downstream water column analyses • Hydrodynamic conditions • Sediment critical shear strength to predict sediment scour potential under a range of flows • Empirical evidence of sediment transport, such as the absence of sediment deposits followed by historically formed deposits downstream of the source • Modeling

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.

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

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

Remedy 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.

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

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.

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

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

Lines 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.

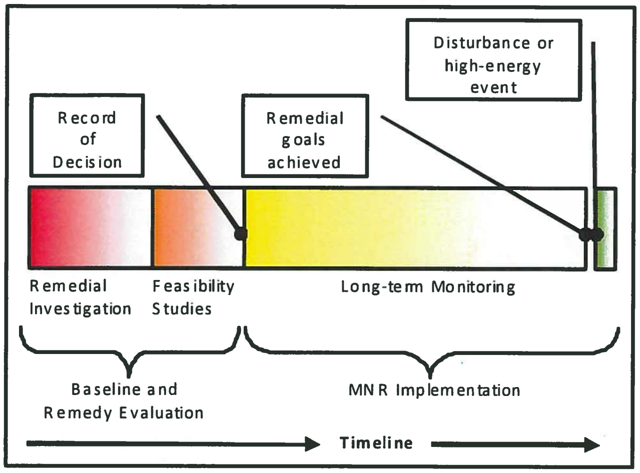


FIGURE 4-1. MNR timeline for a contaminated sediment site.

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.

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

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)	■ Improve accuracy of risk estimates for organic compounds and selected metals by supporting a basic assessment of bioavailability. ■ Investigate bioavailability reduction as a natural recovery mechanism for selected metals.
Sediment coring and vertical profiling	■ Determine whether risk estimates based on surface sediments would apply if subsurface sediments became exposed. If not, sediment stability investigation is needed.

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

Tool	Applications
Sediment coring and vertical profiling	▪ Characterize depth of contamination to assess requirements for dredging alternatives. ▪ Evaluate occurrence of physical isolation through burial, based on concentration profiles. ▪ Visually identify bioturbation depths. ▪ Estimate sediment deposition rates (particularly if geochronological parameters analyzed). ▪ Characterize geochemical parameters influencing transformation processes or bioavailability/mobility.
Model effects of statistically relevant storm events on sediment resuspension.	▪ Identify engineering requirements for capping alternatives. ▪ Evaluate high-energy conditions such as storms or waves and their influence on flood potential or sediment erosion. ▪ Estimate whether naturally buried contaminants are likely to become exposed or, conversely, whether storm-related deposition is likely to augment contaminant isolation. ▪ Estimate the likelihood and duration of geochemical changes that might release sequestered metals through oxidation. ▪ Simulate where resuspended sediments would be deposited.

⇨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.

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).

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

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

Evidence Type	Line of Evidence
Literature and historical data	▪ Assemble information on historical contaminant releases, transport pathways, and source control measures, and confirm effectiveness of contaminant source control. ▪ Review historical records, including historical aerial photographs, industry records, data on outfalls, and permitted or non-permitted releases. ▪ Determine whether groundwater source control would address sediment and water column contaminants. ▪ Identify background sources or sources from off-site contributors that may slow recovery.

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

Evidence Type	Line of Evidence
Modeling	▪ 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. ▪ Use modeling to understand historical chemical releases and chemical transport to sediments.
Site-specific investigations	▪ 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. ▪ Measure contaminant concentrations in upgradient sediment loads using water column, bedload, or sediment trap samples. ▪ Use chemical forensics to associate the chemical fingerprint of sediment contaminants with that of suspected sources. ▪ Conduct site-specific investigations as needed to verify onsite source control. ▪ 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.

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.

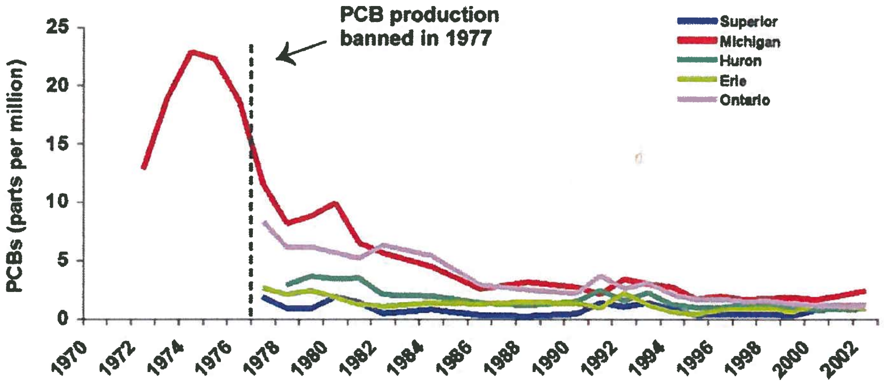


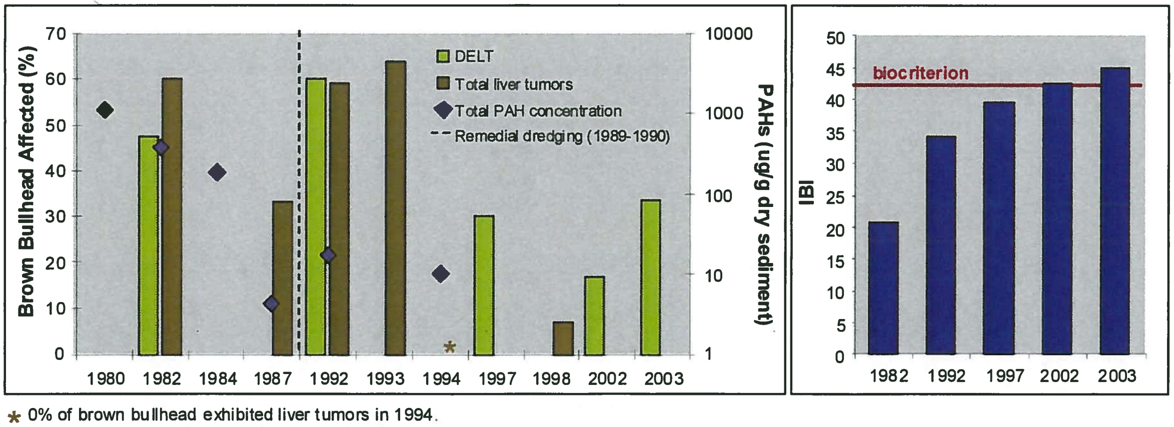
FIGURE 4-2. Temporal trends of PCB concentrations in Great Lakes open water predatory fish document historical natural recovery (Illinois-Indiana Sea Grant 2005). Concentrations declined dramatically during the decade following the PCB production ban but have tended to plateau more recently.

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).



* 0% of brown bullhead exhibited liver tumors in 1994.

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

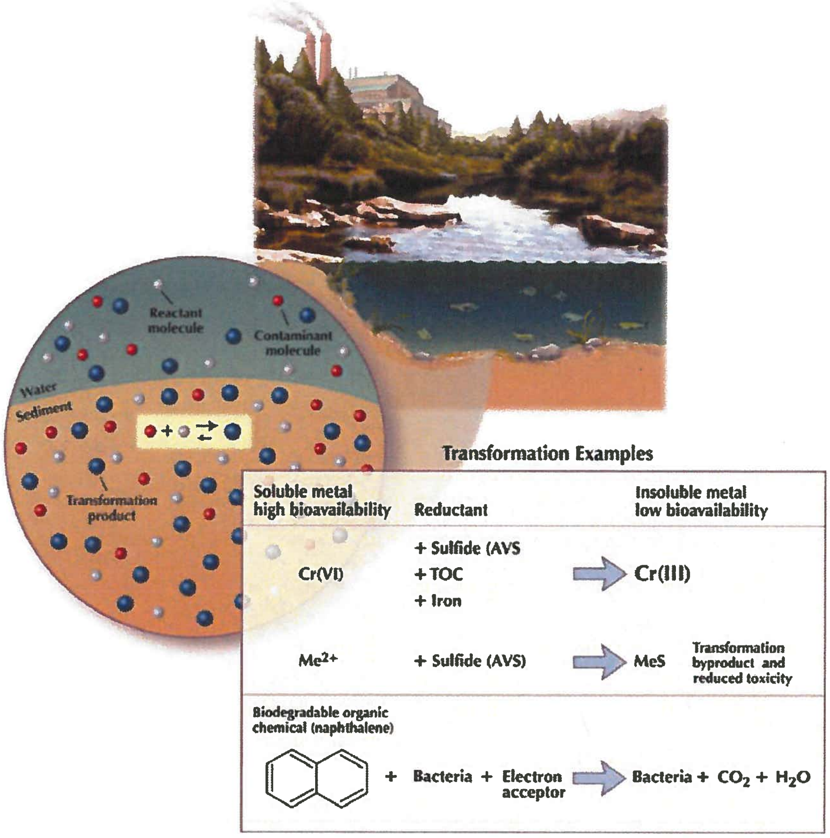


FIGURE 4-3. Chemical transformation. Note: Me^{2+} represents a generic divalent metal.

4.5.1 Chemical Transformation

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

Transformation 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_2, H_2O, Cl^-) (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 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.

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

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).

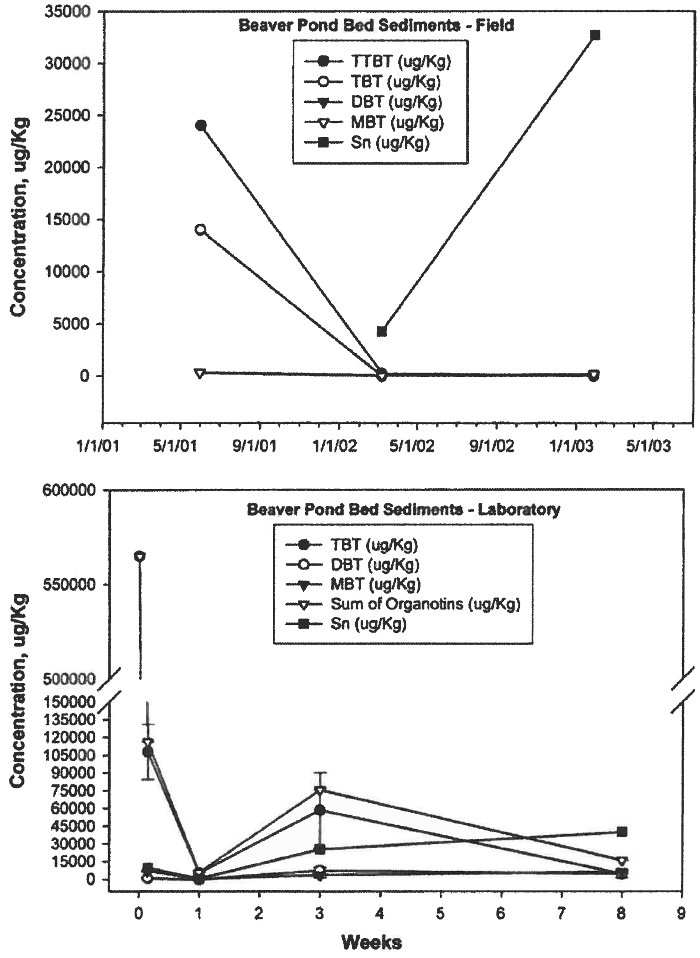
Key considerations for investigating transformation processes at any site include:

- 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 (µg/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
Likelihood of transformation	Literature review: ▪ Identify established contaminant transformation pathways and biological or geochemical conditions under which they occur. Site-specific investigations: ▪ 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). ▪ Measure the presence or absence of parent compounds and/or transformation byproducts in situ. ▪ Conduct laboratory studies to demonstrate the presence or absence of transformation processes, intermediate byproducts, and end products.
Potential of transformation to reduce risks	Literature review: ▪ Assemble findings on toxicity, bioavailability, and mobility of transformation products. Site-specific investigations: ▪ For poorly studied chemicals, conduct controlled experiments to directly measure toxicity of parent compounds and/or transformation products. ▪ Model impact of transformation on bioavailability using relevant partitioning models. ▪ Measure impact of transformation on bioavailability via direct in-situ or laboratory pore water or biota tissue measurements. ▪ Refer to Table 4-4 for additional lines of evidence related to bioavailability and mobility. ▪ 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).
Transformation rate	Literature review: ▪ Assemble findings of contaminant transformation kinetics under relevant physiochemical conditions. Site-specific investigations: ▪ Identify and measure sediment physiochemical characteristics that impact transformation kinetics.

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

Consideration	Lines of evidence
Transformation rate	■ Conduct laboratory and/or field experiments to directly measure transformation kinetics. ■ Measure transformation products or metabolites to compare to original contaminant mixture. ■ 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.
Reversibility of metal transformations	Literature review: ■ Assemble findings on contaminant transformation pathways with respect to permanence. Modeling: ■ Model likelihood and duration of geochemical changes that could cause transformation reversals (such as sediment erosion). ■ Model relative kinetics of transformations and transformation reversals. Site-specific investigations: ■ Identify and measure sediment physiochemical characteristics with an impact on the reversibility of transformation processes. ■ Conduct laboratory and field experiments to detect the occurrence and extent of actual transformation reversals under relevant geochemical conditions.

4.5.2 Reduced Bioavailability and Mobility

Evidence 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

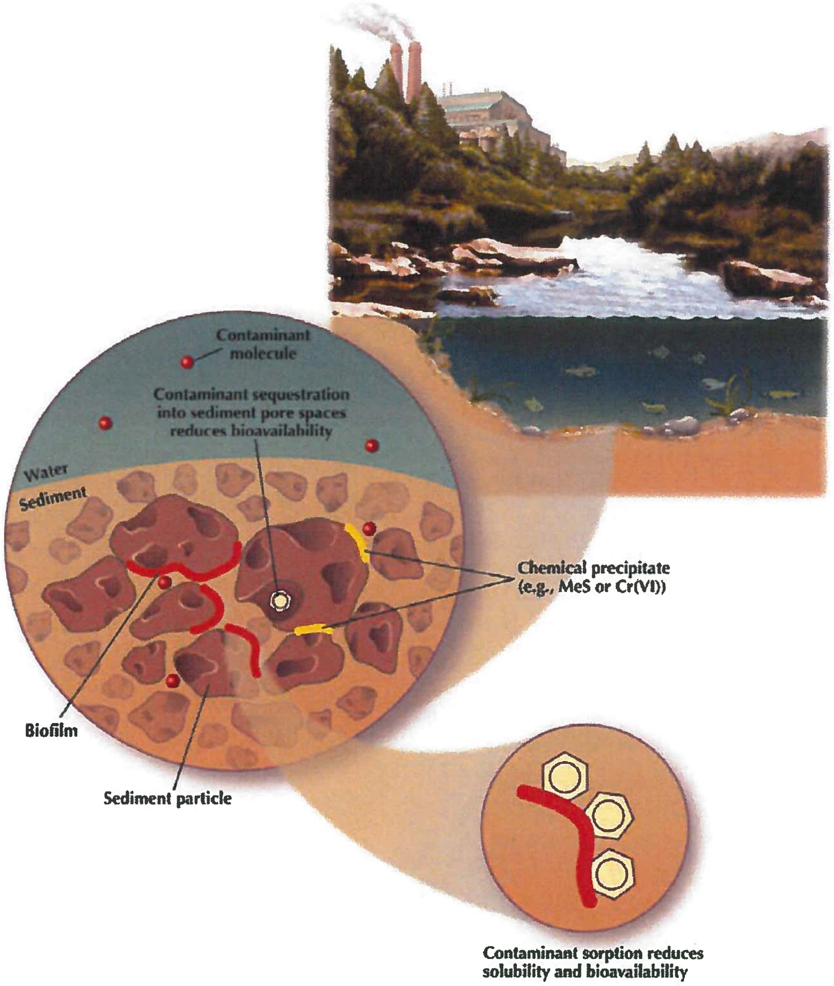


FIGURE 4-4. Processes that reduce mobility and bioavailability. Note: Me represents a generic divalent metal.

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.

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

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
Degree of contaminant bioavailability	Literature review: ▪ Assemble findings on contaminant-specific properties that influence mobility and bioavailability. Modeling: ▪ Incorporate contaminant-specific properties into equilibrium partitioning models that predict contaminant solubility, mobility, and bioavailability. ▪ Develop a site-specific equilibrium partitioning model that describes sediment- and contaminant-specific behaviors. Site-specific investigations: ▪ Measure pore water concentrations in situ or in the laboratory for direct measures of contaminant bioavailability. ▪ 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. ▪ Develop contaminant- and site-specific laboratory partitioning coefficients. ▪ Identify influences of chemical speciation, precipitation, or sorption on contaminant mobility and bioavailability.
Sorption kinetics	Literature review: ▪ Assemble findings on rates of bioavailability and mobility reduction for COCs and their relevance to natural recovery. Modeling: ▪ Develop predictive models that incorporate kinetics.

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

Consideration	Lines of evidence
Sorption kinetics	Site-specific investigations: ▪ Conduct laboratory and field work to collect data that describe reduction rates. (Measuring sorption kinetics can be very slow and time-consuming.)
Reversibility	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.

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

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).

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

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.

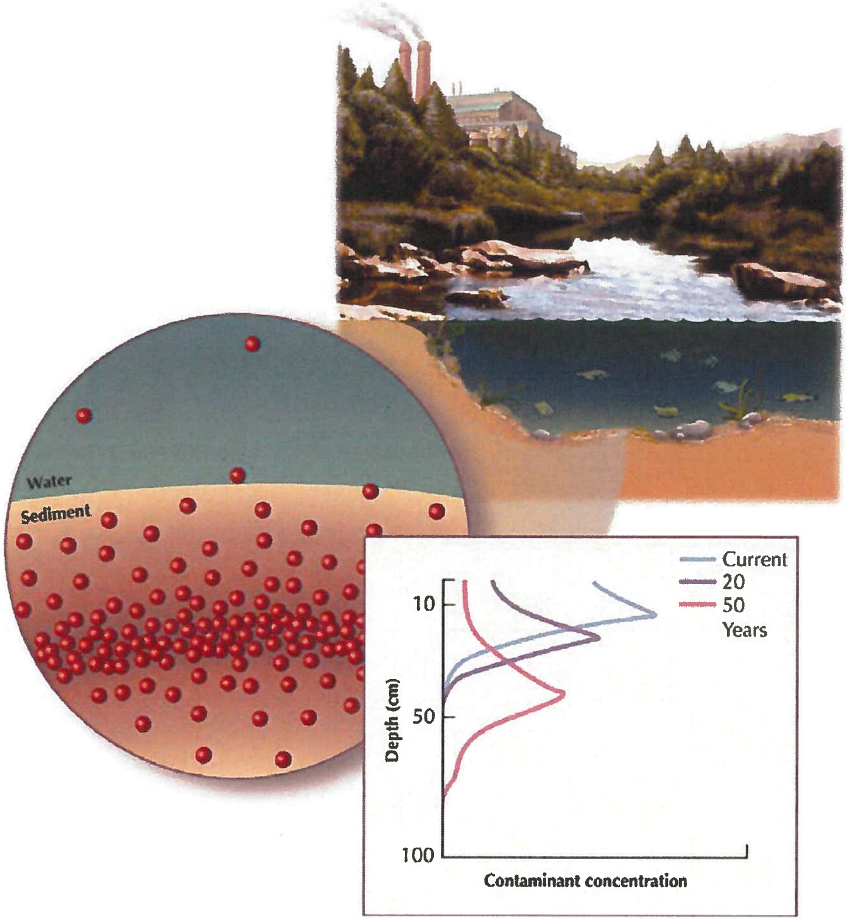


FIGURE 4-5. Physical isolation processes.

As deposited sediments contribute to isolating contaminants from biological receptors, contaminants will be diluted though 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).

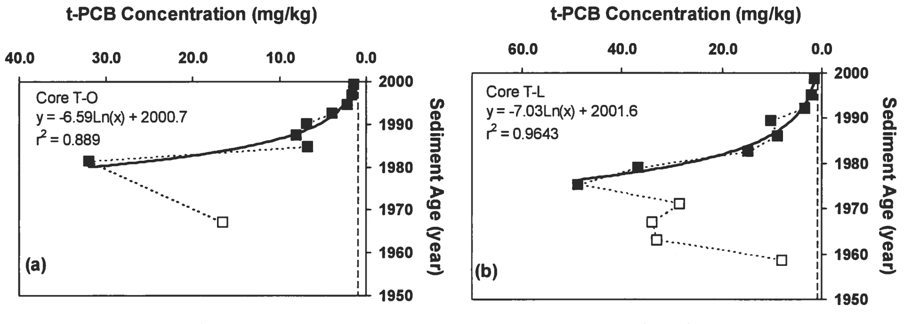
Impact on transformation processes and bioavailability. Physical isolation of sediments and the mixing of contaminated surface sediments with cleaner materials could alter physiochemical conditions (e.g., redox gradients) that promote transformation. For example, only surface sediments are oxic in many 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}Pb) and cesium-137 (^{137}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 ± 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 ± 3.7 cm, 11 ± 4.2 cm, and 33 ± 11 cm, respectively. Using the age-dating results, the average recovery dates to meet these goals were determined to be 2000.6 ± 2.7 years, 2007.4 ± 3.5 years, and 2022.7 ± 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.

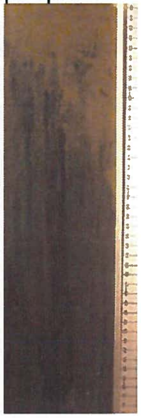
Erosion potential. Sediment erosion potential is determined by sediment properties (e.g., sediment grain size, bulk density, cohesiveness, organic content, gas content, burial depth, and age) and hydrodynamic conditions (e.g., current flow rates and wave energy during normal- and high-energy events, 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).

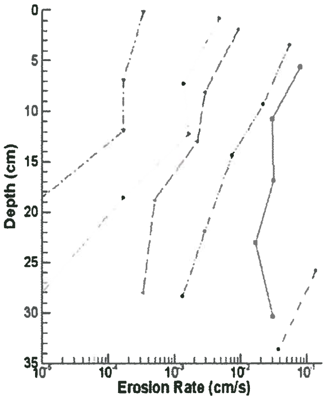
Factors that can limit contaminant erosion potential include burial of contaminated sediments beneath cleaner sediments, as well as bed armoring, a natural process by which sediment erosion potential decreases over time. Armoring can occur regardless of whether the bed consists predominantly of cohesive (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

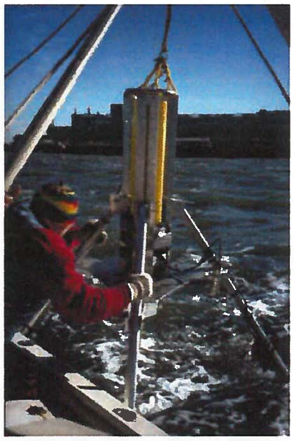
The sediments in Hunters Point Shipyard (HPS) in southeast San Francisco are contaminated with metals, PAHs, and PCBs (NOAA, 1997). An important component of the evaluation of MNR processes for HPS was to determine whether contaminated subsurface sediments are below the depth where sediments are considered 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.

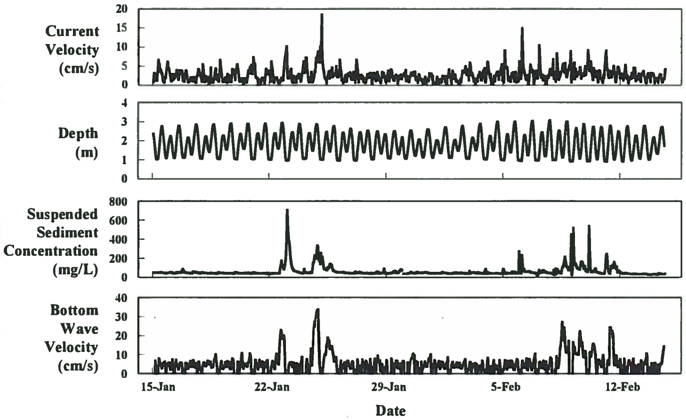




The Sedflume graph (left) shows measured erosion rates versus core depth at different applied shear stresses. The data show that the shear stress required to induce erosion increases with sediment depth. This characteristic is attributed to sediment consolidation and increased cohesion with depth and 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.

SEDIMENT CHARACTERISTICS

- ☆ 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.

Consideration	Lines of evidence
Occurrence and rates of sediment deposition	Literature and historical data ▪ Review literature and historical reports of sediment deposition, rates, and geochronology information. ▪ Review literature and historical reports of hydrodynamic conditions and sediment transport. ▪ Review historical bathymetric and profile analyses to qualitatively or quantitatively determine historical deposition rates. ▪ Review historical dredging records to quantify the amount of sediment removed routinely, for comparison with estimated sediment deposition rates. Modeling: ▪ Develop models to characterize and predict sedimentation and contaminant burial, including net deposition rates, bioturbation, diffusion, hydrodynamic mixing, geochronological age dating. Site-specific investigations: ▪ Vertically profile contaminant concentrations via coring and segmenting at appropriate intervals. ▪ Perform geochronological isotope analyses (e.g., ^{210}Pb and ^{137}Cs) to determine historic deposition rates and to develop an understanding of sediment stability in depositional environments. ▪ 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. ▪ Perform dendrogeomorphic analyses (based on tree root exposure) to establish sedimentation rates. ▪ Perform geophysical analyses (bathymetry, sidescan sonar, or subbottom profiling) to characterize sediment bed properties, establish baseline conditions, and contribute to hydrodynamic modeling.
Characteristics of freshly deposited sediments	Refer to Table 4-2 for lines of evidence to identify ongoing contaminant sources and/or verify source control. Additional lines of evidence include:

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

Consideration	Lines of evidence
Characteristics of freshly deposited sediments	Modeling: ▪ Develop models that account for current sediment characteristics and demonstrate the impact of deposition on contaminated surface sediments. Site-specific investigations: ▪ Analyze chemical and partitioning characteristics of recently deposited sediments.
Benthic bioturbation and hydrodynamic mixing	Literature review: ▪ Assemble findings on benthic community characteristics (habitat usage, burrowing depths, bioturbation rates). Modeling: ▪ Model benthic mixing and hydrodynamic mixing to demonstrate the impact of sedimentation and mixing on surface sediment concentration changes with time. Site-specific investigations: ▪ Collect surface grab samples to characterize the benthic community, including background locations. ▪ Use sediment profile imagery to identify surface sediment redox zones, bioturbating animals, and maximum site-specific bioturbation depths. ▪ Perform isotope analyses to characterize surface sediment bioturbation depths. This can be done by evaluating asymptotic changes in ^{210}Pb or ^{137}Cs profiles or by viewing the presence or absence of beryllium-7 (^{7}Be) in surface sediment.
Sediment Stability	Literature and historical data: ▪ Assemble information on site-specific sediment transport processes. ▪ Assemble sediment core data, identifying signs of depositional behavior, including historical contaminant trends and geochronological trends. Modeling: ▪ Develop models that account for current velocities and sediment shear strength behavior. ▪ Model sediment transport potential by integrating surface water hydrodynamic shear forces and sediment shear strength properties.

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

Consideration	Lines of evidence
Sediment Stability	Site-specific investigations: ▪ Conduct experiments to directly measure sediment critical shear strength. ▪ Characterize hydrodynamic conditions under normal and high-energy events (include storms, winds, prop wash, and other events, as appropriate). Measure sediment bed bathymetry over time using high-resolution multibeam techniques.

4.5.4 Dispersion

Dispersion 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.

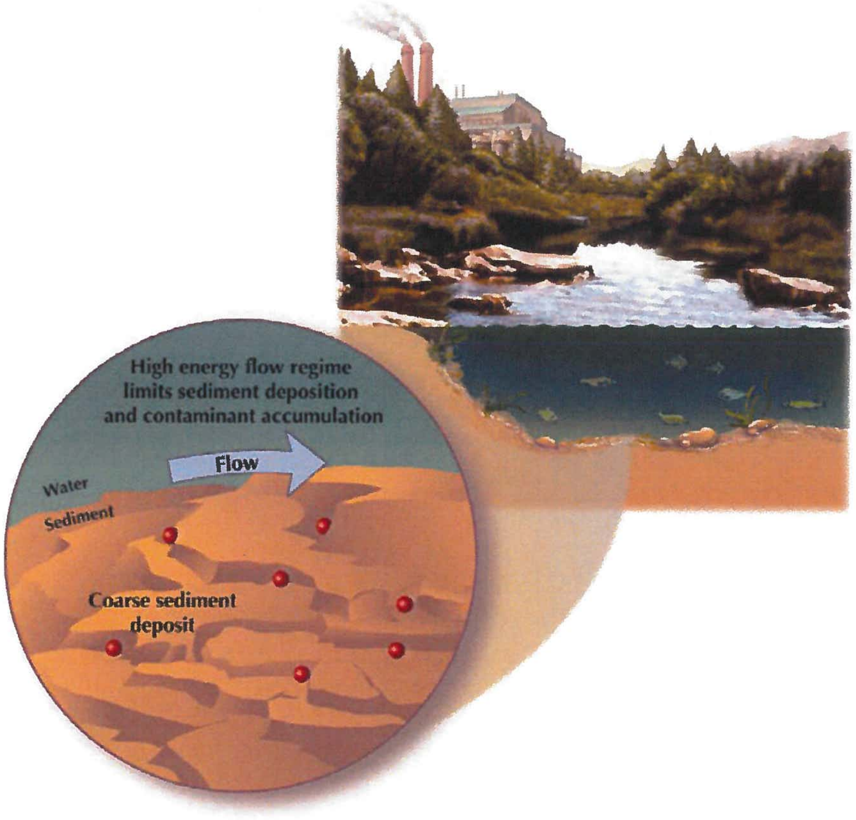


FIGURE 4-6. Dispersion and transport processes.

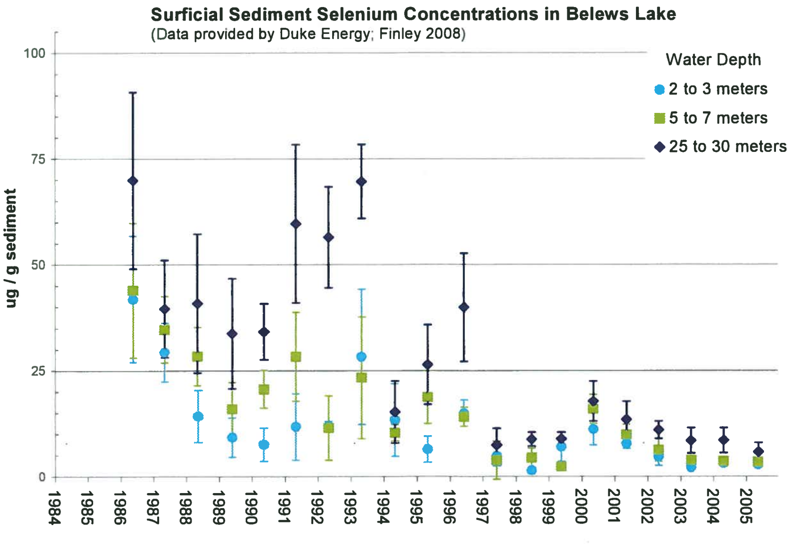
Whether sediment transport or chemical diffusion or advection contributes to reduced surface sediment exposures depends on the site physicochemical conditions and contaminant mobility. Sediment transport is most relevant to areas of relatively high hydrodynamic energy where contaminated sediment particles 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.


Surficial Sediment Selenium Concentrations in Belews Lake
(Data provided by Duke Energy; Finley 2008)

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

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.

PHYSICAL DISTURBANCES

- ☆ 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

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
Hydrodynamic conditions	Literature review: ▪ Assemble site-specific findings on hydrodynamic conditions. Modeling: ▪ Develop hydrodynamic models to capture the flow dynamics and the energy regime of the site, to support advective transport calculations and sediment transport characterizations. Site-specific investigations: ▪ Measure bathymetry to establish the morphology of the site, which controls the energy regime experienced and boundary flow conditions. ▪ 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.) ▪ Measure flow velocities to establish site-specific velocities in deep and relatively shallow areas. ▪ Measure near-bed current velocities to establish flow conditions at the sediment-water interface.
Sedimentation processes including deposition, erosion, and transport in the water column	Literature review: ▪ Assemble site-specific findings on sediment contaminant-specific fate and transport considerations. Modeling: ▪ Develop sediment transport models to simulate sediment erosion, deposition, and transport, to determine sources and sinks of sediment contaminants. ▪ Develop a sediment mass balance model to examine

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

Consideration	Lines of evidence
Sedimentation processes including deposition, erosion, and transport in the water column	■ inputs and outputs of sediment at major boundaries of the system. Site-specific investigations: ■ Characterize fluvial morphology and examine sediment bed forms to characterize depositional and erosional behaviors. ■ Conduct geochronological sediment core profiles to examine historical deposition rates, or lack thereof. ■ Measure vertical sediment contaminant profiles to determine whether persistent historical deposits exist. ■ Measure sediment loads and corresponding contaminant conditions entering and exiting site boundaries to understand contaminant fate and transport. ■ Measure sediment stability using sediment flumes that directly measure sediment shear strength and analytically compare with hydrodynamic shear forces.
Groundwater advection and contaminant transport	Literature review and historical data: ■ Assemble findings to establish the potential impact of groundwater advection on contaminant transport. ■ Identify site-specific studies that describe near-shore groundwater transport behavior. Modeling: ■ Incorporate results of site-specific investigations to assess the relative importance of groundwater advection to the transport of sediment contaminants. ■ If warranted, develop a groundwater transport model to describe contaminant transport. Site-specific investigations: ■ For mobile contaminants, measure groundwater flux rates, and use measured or estimated partitioning to establish desorption rates and corresponding aqueous concentrations and exposures. ■ Measure site-specific hydraulic conductivity values in consolidated sediment to calculate groundwater transport rates through the sediment bed. ■ 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.

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 210Pb and 137Cs) 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.