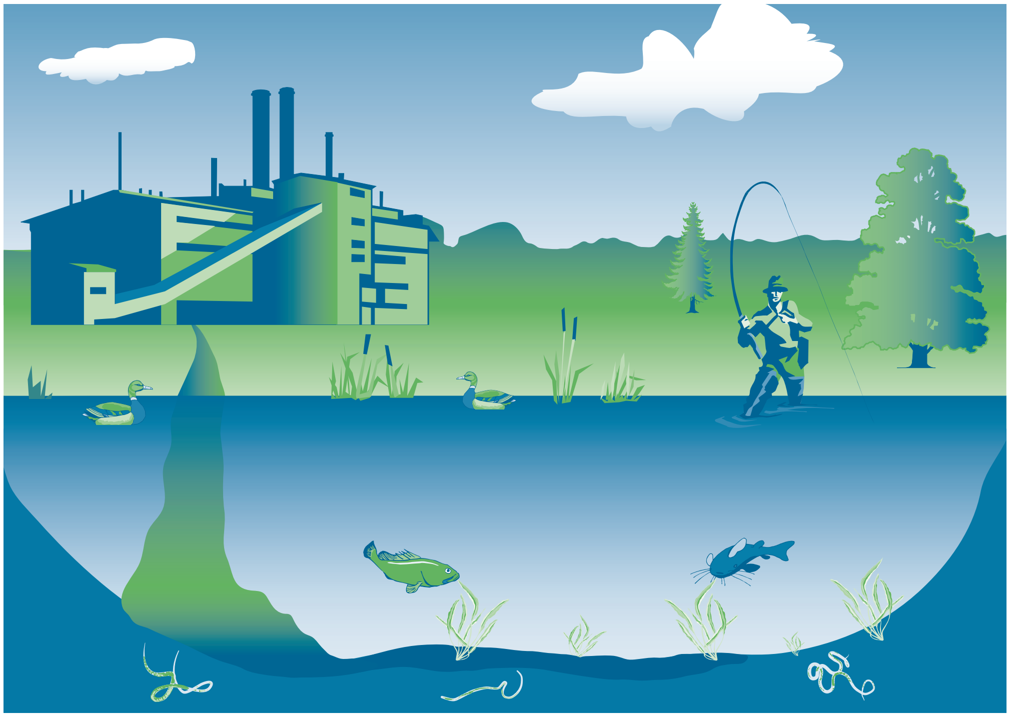
Technical/Regulatory Guidance

Incorporating Bioavailability Considerations into the Evaluation of Contaminated Sediment Sites



February 2011

Prepared by
The Interstate Technology & Regulatory Council
Contaminated Sediments Team

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EXECUTIVE SUMMARY

> The U.S. Environmental Protection Agency estimates that approximately 10 percent of the sediment underlying our nation's surface water is sufficiently contaminated with toxic pollutants to pose potential risks to fish and to humans and wildlife that eat fish. This represents roughly 1.2 billion cubic yards of contaminated sediment (representing the upper five centimeters of sediment) where many bottom dwelling organisms live.
>
> *EPA's Contaminated Sediment Management Strategy* (USEPA 1998a)

According to current average costs for managing contaminated sediments, this volume of material could cost several trillions of dollars to dredge. In addition, state regulatory agencies are increasingly responsible for the identification, investigation, oversight, and management of contaminated sediment sites throughout the United States. More than 25% of the contaminated sediments sites addressed to date in the United States have had state drivers. As activity accelerates, this percentage will likely grow.

Methods to assess the potential effect of sediment contamination on human or ecological health are historically based on total contaminant concentrations in the bulk sediment. Unfortunately, the relationship between contaminant concentration in sediments and risk from exposure is not linear. Research conducted over the past 15 years has shown that the bioavailable concentration of many of these contaminants causing a toxic response in the receptors is much less than the total concentration of these contaminants in the sediment.

The National Research Council defines "bioavailability processes" as "individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments." (NRC 2003). Only the bioavailable fraction of an environmental contaminant may be taken up and subsequently result in an effect on an organism. If contaminants are present but not physically accessible or chemically or biologically available, they should not be included in the calculation of risk. The principal objective of bringing bioavailability considerations into sediment risk management is to reduce the extent of cleanup required to that which is necessary to be protective of the environment. Incorporating bioavailability information in the calculation of risk can also be an important factor in balancing the risks *caused* by remedial action with the risks *addressed* by remedial action.

This web-based ITRC technical and regulatory guidance is intended to assist state regulators and practitioners in understanding and incorporating the fundamental concepts of bioavailability in contaminated freshwater or marine sediment management practices.

The intended users of this guidance are individuals who have a working knowledge of contaminated sediment management but seek additional information about bioavailability.

The objectives of this guidance are as follows:

- provide a basic understanding of bioavailability

- provide direction as to where bioavailability considerations may be pertinent in the human health and ecological exposure assessment processes
- describe the pertinence of assessing bioavailability during risk assessment process
- describe the tools available for bioavailability assessment and their application
- describe how bioavailability considerations can be used in risk management of contaminated sediment sites
- provide case studies that highlight the application of bioavailability assessment tools and methodologies in contaminated sediment site risk management

This guidance is constructed to assist the user in identifying the most relevant places within an exposure assessment that bioavailability can be assessed and which tools and methods are most useful and appropriate. As described in Chapter 2, the assessment of bioavailability is an iterative process that is carried forward through scoping and screening and in the evaluation of each applicable receptor pathway (benthic invertebrates, fish and aquatic invertebrates, wildlife, plants, and human health). Scoping activities are often revisited after completing a screening-level risk assessment (Chapter 3), as part of the planning for a remedial investigation and baseline risk assessment. Chapters 4–8 describe the ecological receptor pathways (benthic invertebrates, fish and aquatic invertebrates, wildlife, and plants) and the human health pathway. Bioavailability tools are identified in these chapters and organized according to whether they involve chemical analyses, biological analyses, or modeling. Case studies on their application are referenced as pertinent in these chapters as well as summarized in Chapter 9 and Appendix D. Chapter 9 describes how bioavailability assessment can be and has been incorporated into the contaminated sediment management process and indicates advantages and challenges to doing so.

Overall, this guidance establishes that bioavailability considerations should be incorporated in the exposure assessment process to obtain a clearer understanding of contaminant toxicity and exposure pathways such that remedy selection decisions can be focused and resources efficiently used. By incorporating bioavailability considerations into the early stages of site characterization, the risk assessment process, and remedy selection, a more effective remediation may be accomplished, which may well optimize overall cost. This web-based technical and regulatory guidance can help the user understand the proper application of these tools to assess bioavailability and more effectively protect human health and the environment.

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INCORPORATING BIOAVAILABILITY CONSIDERATIONS INTO THE EVALUATION OF CONTAMINATED SEDIMENT SITES

1. INTRODUCTION

As defined by the National Research Council (NRC 2003), "bioavailability processes" are the "…individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments" (Figure 1-1). Specifically, bioavailability addresses the fact that only a fraction of a contaminant present in the environment may be taken up and subsequently result in an effect on an organism. Exposure of a chemical in soil, sediment, or pore water requires that the chemical come in contact with a biological membrane. The chemical can migrate through the membrane and enter the bloodstream, or a particle can come into contact with the membrane and the chemical can move from within the particle into the aqueous phase and subsequently move though the membrane to the blood (NEPI 2000). Based on this principle, the U.S. Environmental Protection Agency (USEPA) has defined "bioavailability" as the "state of being capable of being absorbed and available to interact with the metabolic processes of an organism" (USEPA 1992a), meaning that the chemical must (1) be released from the sediment (either in the natural environment [desorption] or after ingestion [bioaccessibility]), (2) come in contact with a membrane (e.g., stomach, intestine, lung, or skin), and (3) be distributed to an organ or cell. Bioavailability assessment tools aid in the assessment of human and ecological exposure and development of site-specific remedial action objectives (RAOs). An appropriate consideration of the degree of bioavailability, therefore, supports risk assessment and risk management decision making.

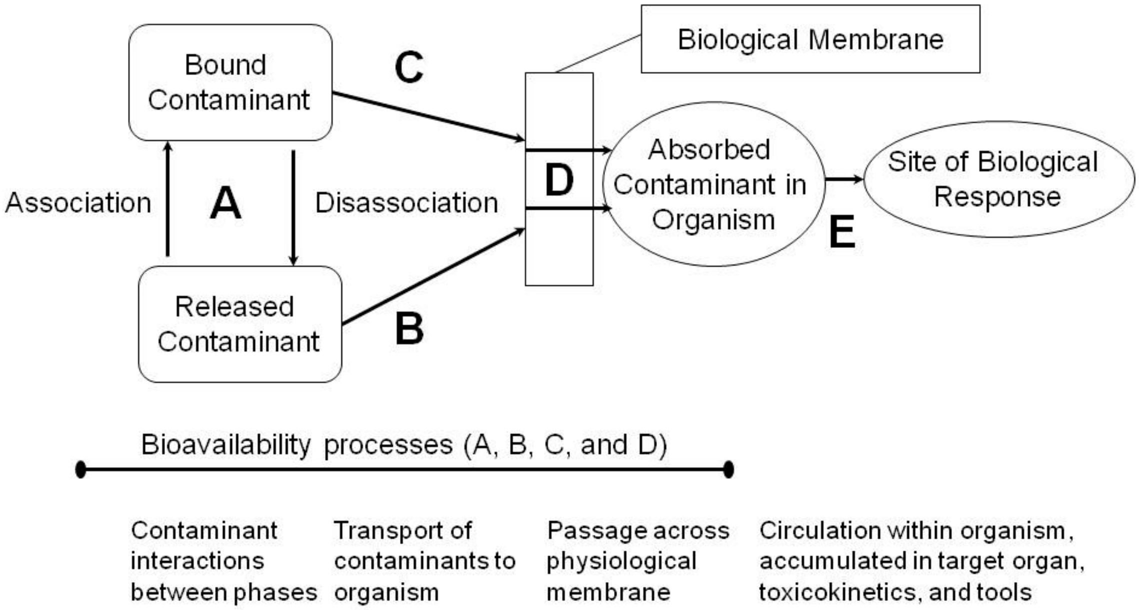


Figure 1-1. Bioavailability processes in soil or sediment. Includes release of a solid bound contaminant and subsequent transport, direct contact of a bound contaminant, uptake by passage through a membrane, and transportation into a living system. A, B, and C can occur internal to an organism such as in the lumen of the gut. (*Source:* NRC 2003)

This Web-based Interstate Technology & Regulatory Council (ITRC) technical and regulatory guidance on the use of bioavailability to evaluate exposure at contaminated freshwater or marine sediment sites describes the mechanisms affecting contaminant bioavailability, the tools used to assess bioavailability, proper application of those tools, and how bioavailability information is incorporated into risk management decisions at contaminated sediment sites. This guidance contains case studies presenting examples of the application of bioavailability in the establishment of remedial goals.

The ITRC Contaminated Sediments Team expects that this guidance will be used by responsible parties, state and federal regulators, practitioners, consultants, and public and tribal stakeholders, as a tool to understand how bioavailability can be useful in managing risk to ecological and human receptors at contaminated sediment sites. Because of the complexity of some of the material discussed in this document, the team assumes that the user has a reasonable understanding of the following:

- the risk assessment process
- contaminated sediments
- the potential value of using bioavailability assessment information
- basic knowledge of human health and ecological risk assessment terminology, methods, and approaches

The team recommends that, at a minimum, the user become familiar with USEPA ecological risk assessment guidelines (USEPA 1992b, 1997b, 1998c) before reading this document.

1.1 Background

State regulatory agencies are increasingly responsible for the identification, investigation, oversight, and management of contaminated sediment sites. The regulatory framework for management decisions for sediments is generally based upon USEPA's human health and ecological risk assessment and remedial investigation (RI)/feasibility study (FS) guidance (Ehrlich 1988, USEPA 1989a, 1989d, 1992b, 1997b). States differ in the level of regulations or guidance for managing contaminated sediments. Currently, nine states (California, Florida, Minnesota, New Jersey, Ohio, Oregon, Texas, Washington, Wyoming) have developed detailed processes for assessing and designating sediments for management actions, while other states either rely on USEPA guidance or are developing specific guidance.

How can bioavailability make a difference?

If contaminants are present but not bioavailable, they should not be included in the calculation of risk. This approach can optimize the extent of cleanup required to be protective and can be an important factor in balancing the risks caused by remedial action with the risks addressed by remedial action. This balance is particularly important for sediment sites where two of the primary remedial options, capping and dredging, can significantly alter physical, chemical, and biological conditions and disrupt or destroy existing habitat. At the Tektronix site in Oregon (see Appendix D), even though metals concentrations in stream sediment exceeded screening levels, a no further action determination was made based on evaluation of the bioavailability of the metals.

The current process used to assess sediment toxicity has included one or more elements of the Sediment Quality Triad (SQT, or "Sediment Triad") approach (Long and Chapman 1985; Chapman, Dexter, and Long 1987; Chapman 1996; VonStackelberg, Thompson, and Patton 2008; Wenning et al. 2005). The Sediment Triad attempts to relate measures of bulk sediment chemistry, benthic community, and sediment bioassays to characterize contaminated sediments. Sediment quality guidelines (SQGs) evolved as an effort to identify thresholds for individual sediment chemicals that, when exceeded, adversely affect benthic communities and/or bioassay endpoints (Barrick et al. 1988; Chapman 1989; Chapman and Mann 1999; Long and Morgan 1991; MacDonald et al. 2003; Persaud, Jaagumagi, and Hayton, 1993; Barrick et al. 1988). Currently, SQGs are frequently used to determine the need for cleanup at many federal and state sites (VonStackelberg, Thompson, and Patton 2008). Additional discussion of these types of benchmarks appears in Chapter 3.

While the existing SQGs offer simplicity and utility (Wenning et al. 2005), those values are thresholds that focus only on benthic organisms. Unfortunately, SQGs generally do not address food-chain risks associated with bioaccumulation of sediment contaminants. SQGs often have low reliability or predictive value, and they are generally set on the conservative side (WDOE 2003) to ensure environmental protection. There is an increasing scientific and regulatory acknowledgement of the need to consider bioavailability processes of sediment contaminants in exposure assessments. Site-specific field measurements have clear scientific precedence over generic or literature-derived values. Based on sediment testing results for the Ashtabula Harbor site, MacDonald et al. (2005) found little site-specific evidence of PCB bioavailability or toxicity and much higher evidence of metals availability and toxicity, yet they dismissed the latter and concluded that the former drove toxicity and therefore management decisions based on generic literature-based "expected effects" concentrations, which their own data contravened at the particular site. Such a procedure weakens—in fact, practically eliminates—the technical credibility of the methodology in application. Ankley (1996), Di Toro et al. (2005a, 2005b), and Hawthorne et al. (2007) present evidence that identifies mechanisms that control contaminant bioavailability. The application of bioavailability in contaminated sediment management has lagged behind the still-growing body of evidence that confirms that at many sites sediment contaminants may be less "available" to cause harm to humans or ecological receptors than is suggested by extrapolating effects based on bulk (total) sediment concentration measurements (NRC 2003, SERDP and ESTCP 2008, USEPA 1998c).

An overwhelming body of scientific evidence points to the fact that physical, chemical, or biological properties can reduce the potential for sediment exposure and/or uptake of contaminants by living organisms. Processes affecting bioavailability are often not addressed when setting risk-based cleanup levels. Explicitly, assessing contaminant bioavailability can achieve more technically defensible cleanup goals and establish more accurate cleanup priorities while still ensuring protection of human health and the environment.

This document offers a compilation of the existing concepts, tools, and measures for assessing bioavailability. Case studies and examples of how those tools and measures have been used in decision making are also included. The ITRC Contaminated Sediments Team notes that the application of the tools described in this document may depend on a variety of project constraints, such as the following:

- schedule
- number of contaminants of potential concern (COPCs)
- investigation resources
- acceptance by the regulatory agency and regulated community

1.2 Objectives of this Document

The objectives of this guidance are as follows:

- provide a basic understanding of bioavailability
- provide direction as to where bioavailability considerations may be pertinent in the human health and ecological exposure assessment processes
- provide a direction to the pertinence of bioavailability during risk assessment process
- describe the tools of bioavailability assessment and their application
- describe how bioavailability considerations can be used in risk management of contaminated sediment sites
- provide case studies that highlight the application of bioavailability assessment tools and methodologies in contaminated sediment site risk management

This guidance assists state regulators and practitioners in understanding and incorporating fundamental concepts of bioavailability in contaminated sediment management, including communicating risk and the need for potential remedial action(s) to the public and other parties involved in the decision-making process.

The intended users of this guidance are individuals who have a working knowledge of contaminated sediment management but seek additional information about bioavailability.

An overview of the physical, geochemical, and biological mechanisms involved with assessing bioavailability is presented in Chapter 2. This technical and regulatory guidance does not provide a comprehensive description of those processes. For this level of detail, please refer NRC's *Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications* (NRC 2003). Additional specific references are listed in Appendix A.

1.3 Sediment Assessment Approach

Inclusion of bioavailability during a sediment assessment should proceed as part of the overall planning of a site investigation. Procedures for conducting a site investigation are described in several federal and state documents (see Appendix A). Those documents describe how to scope, plan, and execute sediment site investigations, risk assessments, and evaluate remedial actions. While there are differences in how each of those documents approaches site investigation, most generally adhere to the following four steps (see Figure 1-2):

- Development of a conceptual site model: Review site history, define initial COPCs, develop the conceptual site model (CSM), and identify initial RAOs and cleanup levels (Chapter 2).

- Screening-level assessment: Perform a screening-level evaluation that compares existing site sediment and/or fish/shellfish tissue concentrations to background and conservative screening criteria to finalize the COPC list and determine whether additional investigations or actions are needed (Chapter 3).

- Characterization of exposure and effect: Identify receptors of concern, assessment and/or measurement endpoints, exposure pathways, and data quality objectives (DQOs), refine nature and extent of COPCs, and conduct baseline human health and ecological risk assessments (Chapters 4, 5, 6, 7, and 8).

- Response action/risk management: Use the information gathered in the investigation and risk assessment stage to make an informed risk management decision and set defensible cleanup goals; identify and evaluate potential RAOs (Chapter 9).

While sites typically enter the assessment process at the scoping stage, they can exit at any point provided the following:

- the results indicate acceptable risk(s) to human health and ecological receptors
  OR
- based on a risk assessment of all pathways, there has been a determination of unacceptable risk to human health and/or ecological receptors, but a site-specific remedial alternative is chosen that will manage or reduce risk(s) to acceptable levels

Incorporating bioavailability in the scoping process is an iterative process that is carried forward through each tier, as shown in Figure 1-2. For example, scoping activities are often revisited after completing a screening-level risk assessment as part of the planning for a remedial investigation and baseline risk assessment. Inclusion of bioavailability considerations as a project scoping activity allows for the evaluation of existing processes, available data, and the data needed for moving forward.

Figure 1-2 displays the general flow of an assessment of exposure at a contaminated sediment site. This flow diagram and related diagrams throughout this guidance help users identify where to consider bioavailability in the site investigation process and the tools and approaches that are available**.** The numbers in each box refer to the chapter of this document where the topic is discussed.

1.4 Roadmap to this Guidance

This guidance provides a description of bioavailability considerations in the site investigation process. The following topics are described in each chapter of the document:

- Chapter 2 describes the process of ***scoping a contaminated site, characterizing the nature and extent of contamination, and risk assessment.*** The chapter identifies processes that can affect bioavailability in specific exposure pathways.

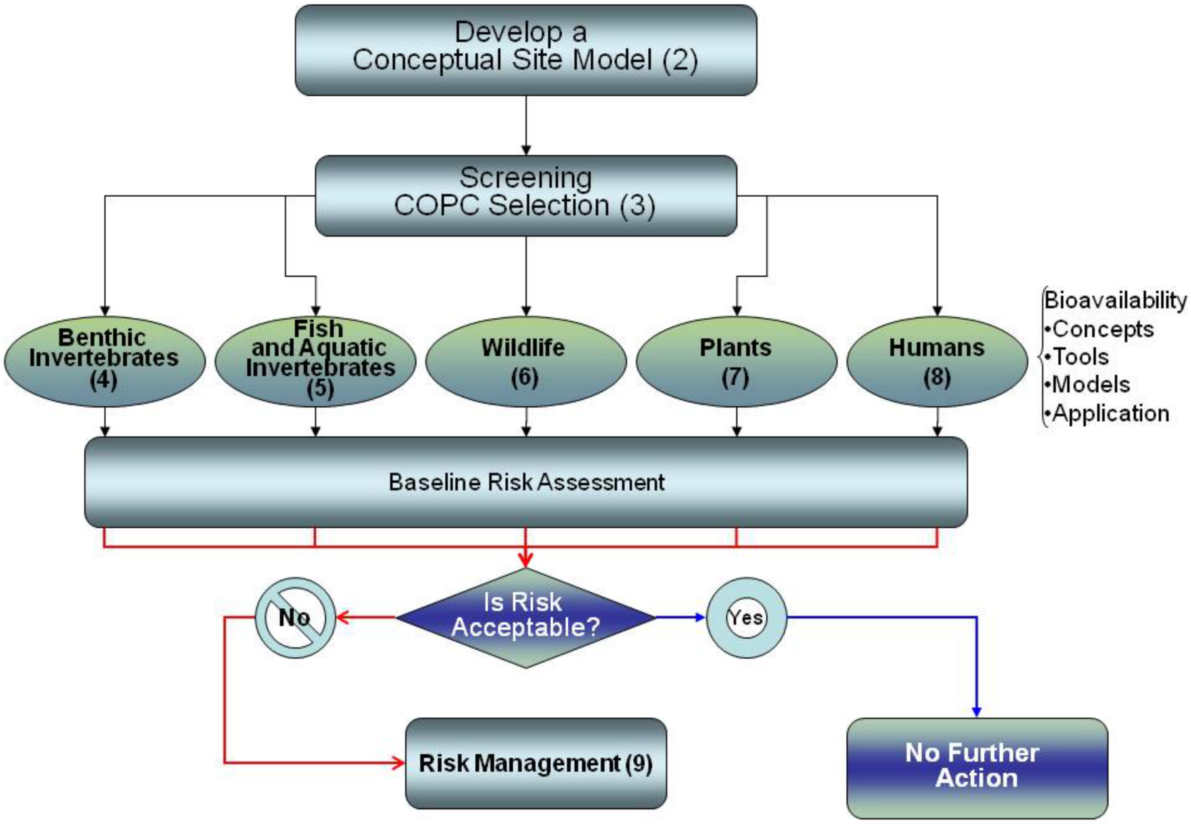


Figure 1-2. Sediment assessment process followed in this guidance.

- Chapter 3 describes the use of ***background and screening criteria*** for ecological and/or human health. While traditional screening criteria have been developed empirically, more recent criteria are being developed using models that incorporate into estimates of endpoints bioavailability concepts other than toxicity, such as bioaccumulation.

- Chapters 4, 5, 6, 7, and 8 introduce and discuss the current ***in situ and ex situ measures and models*** used to assess bioavailability for specific exposure pathways. These tools assess exposures in sediments (e.g., benthic organisms) and the estimation of sediment-related contaminant transfer to water-column organisms (e.g., fish, amphibians), aquatic-dependent wildlife (piscivorous birds and mammals), and humans.

- Chapter 9 describes the role of bioavailability in ***risk management decisions***, including examples of weight-of-evidence approaches, development of numeric cleanup criteria, and the state of the practice in evaluating long-term performance of bioavailability-assisted management actions.

2. OVERVIEW OF PROCESSES AFFECTING BIOAVAILABILITY THAT SHOULD BE CONSIDERED IN DEVELOPING A CONCEPTUAL SITE MODEL

Incorporating bioavailability into risk assessments and management decisions requires recognition during the scoping phases of how bioavailability fits within the state or federal regulatory process for characterizing the level of exposure to contaminants in sediments. Bioavailability concepts are implicit in USEPA's risk-based approaches used for assessing both human health and ecological risks and are encouraged throughout the contaminated sediment management process (Greenberg and Sprenger 2008). Use of bioavailability in the sediment management process varies by state, although many use USEPA's ecological risk assessment guidance for Superfund (USEPA 1998c, 1997b, 1992b) and for human health (USEPA 1989a, 1989d).

Consideration of bioavailability begins during the scoping or problem formulation step by linking the source release(s) to potential receptors through the development of a CSM. The CSM becomes the descriptive framework in which to insert specific exposure pathways and subsequent bioavailability measures and/or models into the site characterization and risk assessment process.

While consideration of processes affecting bioavailability should be an integral part of a risk assessment and/or the risk-based management of contaminated sites, it is often neglected due to a perceived greater burden of proof for incorporating bioavailability into decision making (NRC 2003). Bioavailability information can, however, help to alleviate concerns, provide greater transparency in decision making, and allow for setting more technically defensible cleanup goals and realistic cleanup priorities.

Scoping Bioavailability in Contaminated Sediment Site Management

- Defines the extent of the site exposure boundaries, the potential chemicals of concern, and the target human health and ecological receptors
- Develops a conceptual site model that defines the source term, expected exposure pathways, and fate and transport processes from sediments to ecological and human receptors
- Identifies what tools (biological, chemical, and physical) and/or models may be available to measure whether chemicals may be bioavailable to the site receptors
- Initially considers potential site remedial alternatives and how bioavailability may be applied to determine acceptable remedial goals
- Determines how information on bioavailability can be reliably communicated, especially to the public

The following sections provide an overview of how bioavailability measures and endpoints can become an integral part of the CSM when scoping the initial investigation(s). A brief description of the process is provided, supported by links and references to important and relevant supporting information and websites. Chapters 4–8 of this document provide more detail on the tools and mechanics available for assessing the bioavailable component for each ecological or human health pathway.

2.1 Processes Affecting Bioavailability

Management of COPCs requires an understanding of how they are released from the sediment matrix, transported, and taken up by a target organism. Bioavailability tools are methodologies applied to evaluate the magnitude of release of contaminants from the solid to dissolved phase (bioaccessibility) and assess the uptake of a COPC into receptor organisms (bioavailability).

Figure 2-1 is a representation of some example contaminant transport pathways between environmental compartments and native ecological receptors in a freshwater system:

- movement or transport to and into an organism by absorption of the dissolved form from sediment pore water or by the degree of accumulation through the food chain
- transport of COPCs bound to sediment particles through the skin or gut following dermal contact or ingestion
- movement of the COPC across biological membranes
- subsequent transport to the site of biological response

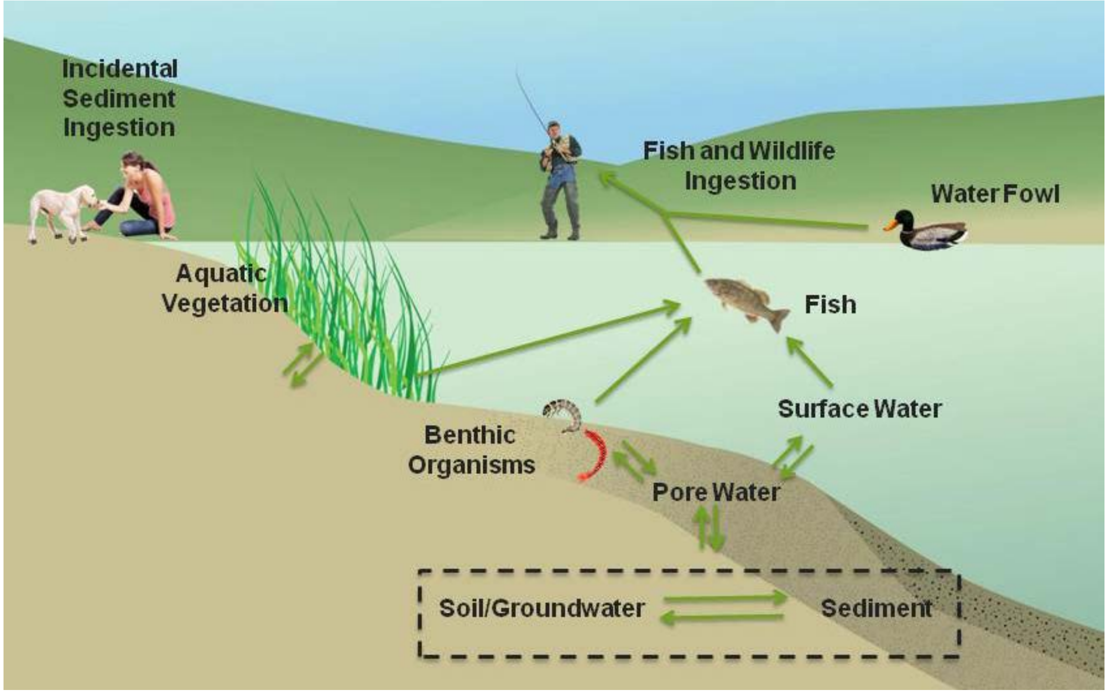


Figure 2-1. Key exposure pathways for human health risk at contaminated sediment sites.

For most aquatic risk assessments, COPC movement is either directly measured, estimated using models, and/or measured as tissue residues within the target organism.

The complexities of the sediment and aquatic systems make accurate tracking impractical, but reasonable estimates can be made. Fortunately, the ability to measure the dissolved and particulate phases of COPCs has improved considerably, and the tools described in the specific pathway chapters have a documented basis for applying these values to exposure evaluation. The general scoping process described in this section is intended to help the user understand when relatively simple considerations are adequate and where more complex tools may be required.

General processes that are important in sediment characterization can be categorized as physical, chemical, or biological. Processes that affect the bioavailability of COPCs in aquatic systems are those individual physical, chemical, and biological interactions that affect the degree of exposure and uptake of receptors to COPCs originating in the sediments. Note that some of these processes can vary due to seasonal changes. This variability should be considered in the assessment of bioavailability. A brief overview of physical, chemical, and biological processes active within sediment/surface water systems follows. These processes are also discussed in greater detail in the relevant chapters of this document dealing with different types of receptors.

2.1.1 Physical Transport Processes

Physical transport processes in sediments may include any of the following:

- advection/diffusion
- resuspension/deposition
- burial
- bioturbation
- ebullition (gas transport)

Physical processes (Figure 2-2) are generally responsible for the transport of a COPC within the sediment. Physical contaminant transport within sediment can be upward (advection/diffusion, ebullition), downward (advection/diffusion, burial), or lateral (resuspension/deposition). In water overlying the sediments, COPCs can move by the same advective and diffusive forces operating within the sediment, by sorption to/from sediments resuspended by currents or scour events, or through bioturbation caused by benthic organisms. Transport of COPCs to a site from sources such as groundwater, surface soil erosion, and outfall discharges can be considered physical processes. Hydrodynamics directly affects sediment and associated COPC transport in several ways. Sediment transport typically varies in a nonlinear fashion with hydrodynamic energy. This energy can be in the form of water flow in a river or tidal estuary or in wind-driven waves in a large lake or bay.

Advective flux in groundwater can transport COPCs directly into and through the sediment-associated pore water, as well as influence redox conditions in the sediments (USEPA 2008a). Diffusive mixing due to temperature, salinity, or pressure gradients can change COPC sorptive behavior (i.e., equilibrium partitioning) over short or long periods of time. COPC redistribution due to bed-shear caused by currents, ice scour, waves, propeller wash, or anchor drag can result in suspension of bulk sediments and can also alter partitioning relationships so that COPCs may be desorbed into the water column. These same processes can result in the release of buried nonaqueous-phase liquids (NAPLs). Finally, ebullition (gas bubble transport) may result in the upward movement of COPCs within the sediment.

2.1.2 Chemical Processes

Just as physical processes impact the distribution of sediments and COPCs in aquatic systems, so do chemical processes. It is critical that chemical processes be considered in conjunction with physical and biological processes in developing a CSM and subsequent site investigations. The bioavailability of COPCs is directly affected by the interplay of these processes.

This document considers the following chemical characteristics or processes in sediments:

- sorption/desorption

- transformation/degradation
- oxidation/reduction

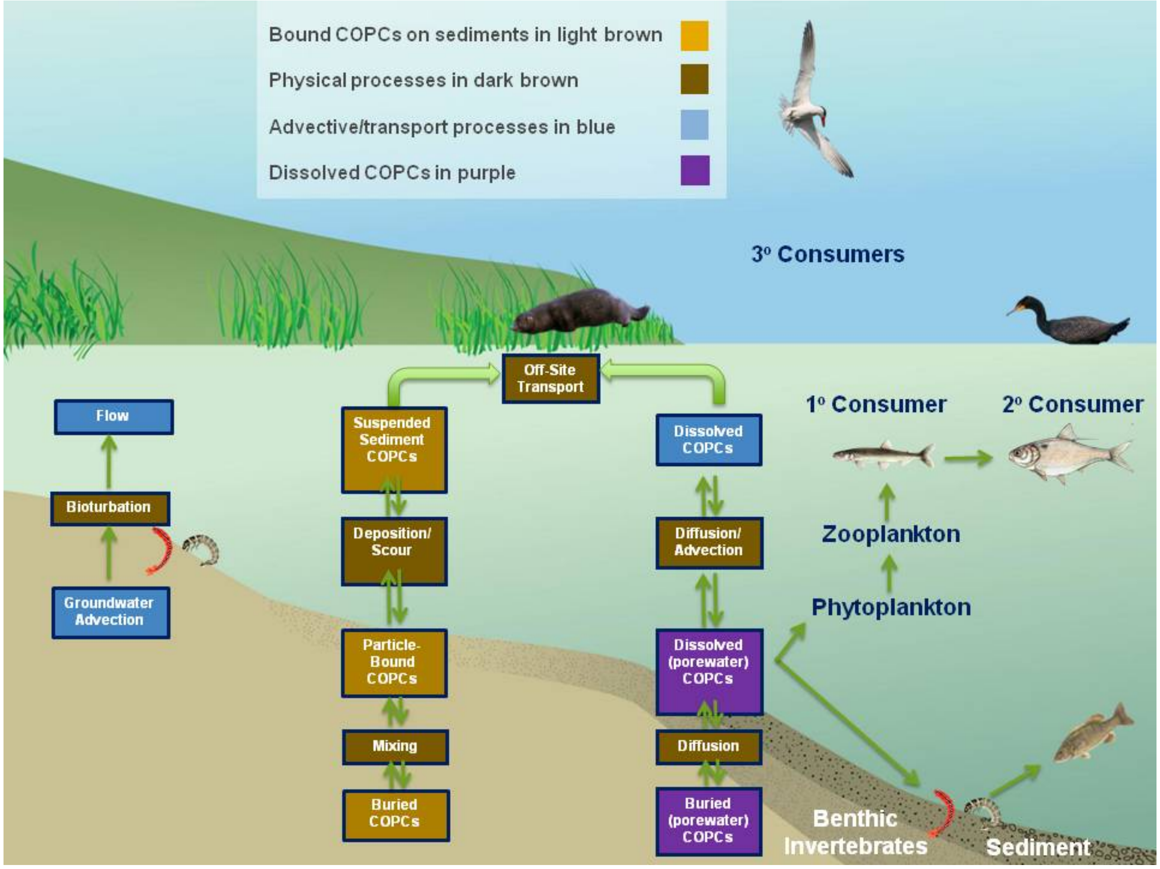


Figure 2-2. Physical transport and ecological receptor processes in a freshwater system.

Sorption/desorption processes are important in defining what "compartment" of the sediment matrix a COPC will reside in. Sediment bioavailability is often mediated by the movement of a COPC from the bulk sediment matrix (desorption) into an aqueous phase. The transfer mechanism can be either via pore water or through the gut of the organism. An example of a sorption/desorption process affecting bioavailability is the binding of polycyclic aromatic hydrocarbons (PAHs) to black carbon at a former coal gas site, rendering these compounds less bioavailable than would have been predicted (Hawthorne et al. 2007). Geochemical processes (e.g., redox/pH) are generally more important when considering inorganic COPCs. An example is the reduction of soluble Cr(VI) to the less soluble Cr(III) species (Borch et al. 2010, Graham and Bouwer 2010).

Sediment geochemical parameters—such as the quantity and type/quality of organic carbon (OC), the presence of acid volatile sulfides (AVS), the redox state of the sediment, salinity, or pH—can also influence whether a COPC is tightly bound within the sediment and unavailable for uptake, or whether it is freely dissolved and can be absorbed into organisms.

Mixing in the hyporheic zone (i.e., the region where surface water and shallow groundwater mix) can result in a release of COPCs due to changes in pressure, oxygen, temperature, oxidation state, and/or salinity. In some cases this process has resulted in increased sequestration of metals or increases in the flux of reduced metals at higher concentrations than would otherwise be expected in oxygenated surface water (e.g., arsenic in a contaminated Montana stream) (Bencala 2005). Thus, the chemical environment is a controlling determinant of potential bioavailability associated with a specific physical transport process.

2.1.3 Biological Processes

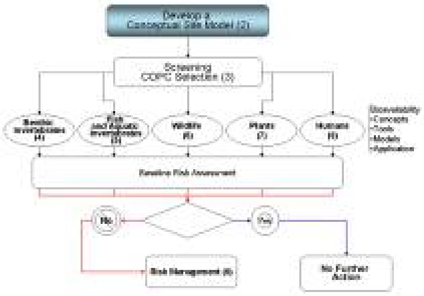
As discussed above, infaunal benthic organisms may take up COPCs from sediments and then serve as prey for higher-level organisms. Biological processes in sediments discussed in this document include the following:

- uptake
- bioconcentration or bioaccumulation
- biotransformation

"Uptake" refers to processes whereby a COPC in sediment is transported into an organism. These processes can include movement of the COPC through the gut, external surfaces (e.g., gills), or the integument (skin) of an organism. The COPC must be bioavailable to be absorbed and subsequently transported to a site of action to have an adverse effect. The COPC may also be metabolized (biotransformed) by the organism, or it may bioaccumulate within the organism (generally within lipids or fatty tissues although some compounds preferentially bind to proteins). Finally, microbial activity within the sediment matrix may play a large role in the biotransformation or degradation of a COPC (e.g., inorganic mercury biotransformed to the more toxic and bioavailable form of methylmercury).

These processes depend on where and how an organism lives and feeds in the sediment or water column, the rate and route of COPC uptake, the relative levels of fats (lipids) within the organism, the ability of the organism to metabolize and/or excrete the chemical, as well as other factors like the age, growth life stage, and gender of the organism.

2.2 Scoping the Problem



During site assessment, one begins identifying the questions that need to be answered to evaluate and manage site risks. An initial site walkover reveals the nature of the aquatic habitat, which is important as the disposition of various COPCs may differ with the type of water body and benthic substrate (e.g., freshwater vs. saltwater, lotic vs. lentic). The scoping process identifies the early CSM, initial site COPCs, and sometimes the initial narrative remedial alternatives for a site (USEPA 1988). Fundamental steps in the scoping process are as follows:

- determine site boundaries
- review site history
- develop an initial list of COPCs
- identify ecological and human receptors and exposure pathways
- develop the early CSM

Table 2-1 lists considerations within the scoping process that are introduced in this section and discussed in more detail in subsequent chapters.

2.2.1 Determine Site Boundaries

Boundaries for a sediment site include the source release area and the extent of flow-facilitated transport of COPCs, ice scour, wind, fetch, boat disturbance, construction activities, navigational dredging, and uptake and subsequent senescence of plants. It is recommended that, if not already performed, a wetland delineation be performed by a certified wetlands biologist at applicable sites to segregate operable units. Adjacent sites, particularly upgradient sites that may also have contributed COPCs, should be identified. In addition to identification of the types of COPCs present, the vertical and horizontal extent of the COPCs must be established.

The vertical and horizontal extent of the COPCs provides an indication of the areas that may contribute to an organism’s potential exposure. In this sense, bioavailability could define a physical limit on the amount or duration of exposure that could occur. For example, at small sites, sessile organisms living within the sediments would be continually exposed to COPCs. Fish, birds, or mammals, all of which have larger home ranges, would be exposed to the contaminated area (or forage on contaminated prey) only during that time period that they (or their prey) are physically within (or foraging within) that contaminated area.

2.2.2 Review Site History

The initial site scoping involves evaluation of existing information on the site background, site use, source release histories, potential COPCs released, area(s) of release, and site-specific and/or regional information available to help identify surface, subsurface, atmospheric, and biotic transport pathways (Ehrlich 1988). MacDonald and Ingersoll (2002) describe the type of information that should be identified from a review of the site history and that is needed for a site investigation. The following elements are helpful in formulating a CSM that includes an assessment of bioavailability:

- nature and quantity of COPCs released
- length of time contamination is estimated to have been in the sediment
- control or elimination sources of COPC(s)
- site or release conditions that may impact bioavailability
- other (i.e., non-site-related) potential source(s) of contamination
- physical and geochemical conditions of the site sediments
- hydrodynamic conditions at the site that may influence sediment transport
- historic and current use of the site by potential human and ecological receptors

Table 2-1. Bioavailability[1] considerations within the scoping process of a contaminated sediment site

Scoping element	Source of information	Activity	Bioavailability related analyses/considerations (Appendix C)
Review site history	• Available data in preliminary site assessment • Hazard ranking documents	• Establish site boundaries, identify adjacent facilities • Identify initial COPCs • Identify geochemical parameters • Understand reference (background) conditions	• Nature and extent of COPCs and exposure pathways • COPC mobility forms and pathways • Data gap analysis (OC, simultaneously extracted metals [SEM]/AVS, SEM – AVS, redox, salinity, and pH, which are available or which may be needed)
Identify site transport processes	Groundwater data	• Understand direction and flow • Understand hyporheic zone mixing	• Flux measures into sediments via piezometers, direct pore water, solid-phase microextraction (SPME)/polyethylene (PE)/polyoxymethylene (POM) or diffusive gradient in thin films (DGT)
	Surface water data	• Identify upstream sources • Characterize surface runoff	• Type and nature of wetland habitat (e.g., freshwater, brackish, saltwater) • Analyses of total and dissolved COPCs
	Sediment data	Assess bulk sediment	• Analyses of COPCs, total organic carbon (TOC), SEM/AVS, SEM – AVS, and metals speciation and grain size in bulk sediment
		Assess pore water	• Sample and analyze COPCs via piezometers, direct pore water measurement, dissolved organic carbon (DOC), SPME/PE/POM or DGT • Estimate pore-water fraction by equilibrium partitioning (EqP), SEM – AVS, or other appropriate model(s)
		Assess diffusive flux	• Analyses of dissolved COPC immediately above sediment/water interface • Estimate flux based on models
	Potential sediment hydrodynamics	• Assess flood or ice scour • Assess wave/current-induced resuspension • Assess boat propeller wash • Assess tidal dynamics • Assess resuspension flux	• Estimates and/or analyses of COPC desorption from resuspended sediments • Redeposition of contaminated sediment • Measures of total and dissolved COPCs, TOC, and DOC estimates and/or analyses of COPC desorption from resuspended sediments • Resuspension of contaminated sediment • Exposure to buried contaminated sediments • Nonequilibrium conditions for organics • Oxidation of metals • Direct measures of COPCs in overlying waste and newly exposed sediments • Changes in oxidation conditions • Changes in salinity; estuarine/tidal wedge

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[1] The processes affecting bioavailability are defined in the Glossary (Appendix F). The tools and methodologies used to assess bioavailability are described in subsequent chapter and Appendix C.

Scoping element	Source of information	Activity	Bioavailability related analyses/considerations (Appendix C)
Evaluate ecological and human health pathways and endpoints	Ecological receptor–based information	Evaluate receptor and exposure pathways: • Benthic invertebrates • Fish and water-column invertebrates • Wildlife • Plants	• Plant tissue residue analysis, plant bioassays • Community analyses, bioassays, tissue residue analysis, EqP, and biota-sediment accumulation factor (BSAF) uptake models • Tissue residue analysis (COPC and lipid), BSAF, kinetic uptake models • Tissue residue analysis (COPC and lipid), oral dose models, laboratory bioassays, field assessment of fecundity • Animal testing for bioavailability (e.g., swine), tissue residue measure (COPC and lipid), oral dose models, laboratory bioassays
	Human health–based information	Evaluate receptor and exposure pathways: • Direct contact • Ingestion	• Water analysis for COPCs, partitioning variables (e.g., octanol-water partition coefficient [K_{ow}]), oral dose models • In vitro/in vivo testing for bioavailability (e.g., swine), bulk sediment analysis, partitioning measures (e.g., organic carbon–water partition coefficient [K_{oc}]), oral and dermal dose models • Tissue residue(s), fraction of COPC available for uptake (bioaccessibility) • Identification of ingestion rates
Develop conceptual site models	• Source disposition • Ecological receptor–based pathways • Human health–based pathways	• Evaluate geochemical, physical, and hydraulic pathways • Evaluate critical receptors and exposure pathways • Evaluate exposure routes and sensitive user groups	• Identify physical processes and data needs to assess COPC availability • Identify routes of uptake into biota, transfer through the food web • Characterize consumption rates, area use factors, uptake factors, fish consumption, etc.

Text Box 2-1 presents an example of the importance of site history review. At the Mocks Pond site in Muncie, Indiana, the use of a former quarry site as an effluent settling pond for a wire-galvanizing plant resulted in the deep accumulation of a fine, heavy metal–rich sludge. While the benthic conditions in the pond bottom were not conducive to support benthic infauna or fish, the overlying water supported a diverse and healthy fish and wildlife community. In evaluating the site history, it was determined that the spent sludge was treated with lime prior to discharge, which resulted in insoluble metal hydroxides. The CSM was developed and tested based on the hypothesis that these metal hydroxides were not biologically available through dissociation in pore water or surface water and that the sediment would not support aquatic life. Confirmation of the CSM allowed for a remedial alternative that included some removal, followed by capping to improve benthic habitat.

2.2.3 Develop List of Contaminants of Potential Concern

A critical element of the CSM is the identification of the chemicals that may have been released at a site or may occur for other reasons within or beyond the identified site boundaries. This initial list of COPCs is evaluated in more detail and refined during the screening process that is described in Chapter 3. Understanding the potential processes affecting bioavailability associated with different classes of compounds (e.g., PAHs, chlorinated organic compounds) may lead to a better understanding of analytical requirements, exposure pathways, COPC mobility testing, and relevant toxicity (e.g., critical body residue thresholds or species sensitivity distributions).

2.2.4 Identify Ecological and Human Health Exposure Pathways

A complete CSM requires an integration of the physicochemical conditions with each of the complete ecological and human health exposure pathways. The exposure pathways for screening assessment should be set up without consideration for bioavailability (Figure 1-2), then refined with bioavailability estimates in the baseline risk assessment. For example, fish could potentially ingest sediment in an impacted lake (so this would be a potentially complete pathway), but concerns of bioavailability of COPCs would be made in the text supported by empirical data. Considerations for bioavailability assessments in exposure pathway analyses are identified in Table 2-1 and described in more detail in Chapters 4–8.

2.2.4.1 Ecological exposure pathways

Numerous federal and state guidance documents that discuss the process for conducting sediment investigations are available to download (Table 2-2). These documents should be used to obtain background information on how to scope a sediment investigation. Additional references are also provided in each individual pathway chapter as it relates to how bioavailability may fit into the exposure evaluation.

Text Box 2-1. Case Study: Mocks Pond Area, Muncie, Indiana (see Appendix D)

The importance of understanding site history in the formulation of a CSM is illustrated by the investigation and remedial actions undertaken at the Mocks Pond Area in Muncie, Indiana. Mocks Pond is an abandoned limestone quarry which had formerly received treatment sludge related to the manufacture of galvanized (zinc-coated) wire products. Review of site history determined that lime was added to neutralize the waste solutions before discharge, forming insoluble metal hydroxides. The resultant "sediment" was a very fine iron-rich material with low TOC. While constituents of interest in the pond included heavy metals (i.e., lead, zinc) at concentrations exceeding their respective sediment screening values, previous testing suggested that the materials deposited in the bottom of the pond were stabilized and not biologically available.

Ecologically, the pond bottom consisted principally of unconsolidated sediment that was largely devoid of organic material and bottom-dwelling insects. As a result, bottom-feeding fish species (e.g., carp, catfish) were not common in the pond. Also, despite the presence of shallow, permanently submerged habitat, the margins of the pond were devoid of rooted or floating vascular vegetation (e.g., cattails). In contrast to the sediment conditions, the pond contained a relatively diverse and healthy water-column aquatic community, including a variety of pelagic fish, snapping turtles, and other turtle species. Belted kingfishers, great blue herons, and other aquatic-dependent birds were observed foraging on and nesting within the area. Mammals using the pond included raccoon and potentially river otter. Institutional controls for human exposure were in place in the form of a large fence surrounding the site.

The CSM was formulated and tested based on the hypothesis that sludge-sediment itself would not support aquatic life and that the metal hydroxides were not biologically available through dissociation in pore water or surface water. While the physical/chemical conditions in the deposited materials were not conducive for benthic-dependent insects or fish, metals in the sediments were biologically unavailable to upper trophic level organisms. A remedial goal of the project was to demonstrate that the metals present in the impacted sediment were biologically unavailable following dredging to a clear water depth of 10 feet and placement of a sand cap over the entire pond bottom to improve aquatic habitat for future recreational use.

Bioavailability was evaluated as part of a human health and ecological risk assessment by measuring metals in the whole bodies and filets of pelagic fish species. The risk assessment activities determined that select metals tissue were identified in fish tissue at concentrations that may pose a significant consumption risk to recreational anglers.

Bioavailability was subsequently evaluated following implementation of the remedy as part of a post-remedial monitoring program designed to monitor cap performance (i.e., ability to restrict the migration of constituents into the biotic zone) by measuring metals concentrations in pore water. Large-volume "peepers" were used to collect pore-water samples. These devices consisted of dialysis tubing filled with reagent grade water placed into a protective sheath, and then inserted to a depth of 10 cm into the sediment. Results from the post-remedial monitoring confirmed that metals were tightly sequestered and not partitioning into pore water or surface water.

Peeper sampler (l), sampler installation (r).

Table 2-2. Links to guidance on conducting sediment investigations and risk assessments

USEPA	
Contaminated Sediment Evaluation Guidance	
EPA's Contaminated Sediment Management Strategy (USEPA 1998a)	http://itrcweb.org/contseds-bioavailability/References/PCBContaminatedSedimentsStrategy.pdf
"Contaminated Sediments In Superfund"/ "Guidance Documents, Fact Sheets and Policies"	www.epa.gov/superfund/health/conmedia/sediment/documents.htm
Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual (USEPA 2001c)	http:\\itrcweb.org\contseds-bioavailability\References\EPA_823_F_01_023.pdf
Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA (USEPA 1988)	www.epa.gov/superfund/policy/remedy/pdfs/540g-89004-s.pdf
A Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems, 3 vols. (MacDonald and Ingersoll 2002)	Vol. I. *An Ecosystem-Based Framework for Assessing and Managing Contaminated Sediments*: www.clu-in.org/download/contaminantfocus/sediments/guidance-assessment-freshwater-epaVolumeI.pdf Vol. II. *Design and Implementation of Sediment Quality Investigations*: www.clu-in.org/download/contaminantfocus/sediments/guidance-assessment-frehwater-epa-VolumeII.pdf Vol. III. *Interpretation of the Results of Sediment Quality Investigations*: www.clu-in.org/download/contaminantfocus/sediments/guidance-assessment-freshwater-epa-VolumeIII.pdf
Contaminated Sediment Remediation Guidance for Hazardous Waste Sites (USEPA 2005a)	www.epa.gov/superfund/health/conmedia/sediment/pdfs/guidance.pdf
Risk Assessment	
Wildlife Exposure Factors Handbook, 2 vols. (USEPA 1993)	Vol. I.: http://www.itrcweb.org/contseds-bioavailability/References/10004SMD.pdf Vol. II.: http://www.itrcweb.org/contseds-bioavailability/References/WEFHV2.PDF
"Superfund Risk Assessment" Home Page	www.epa.gov/oswer/riskassessment/risk_superfund.htm
Guidelines for Ecological Risk Assessment (USEPA 1998c)	http://www.itrcweb.org/contseds-bioavailability/References/ECOTXTBX.pdf
Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments (EPA 1997b)	www.epa.gov/oswer/riskassessment/ecorisk/ecorisk.htm
ECO Update Bulletin Series	http://epa.gov/oswer/riskassessment/ecoup
State	
Guidance for Applying the Sediment Sampling and Analysis Requirements of Chapter NR 347, Wisconsin Administrative Code	http://www.itrcweb.org/contseds-bioavailability/References/nr347guidancefinal.pdf
Guidance for Sediment Quality Evaluations (NJDEP 1998)	http://www.itrcweb.org/contseds-bioavailability/References/ecological_evaluation.pdf

Sediment Sampling and Analysis Plan Appendix: Guidance on the Development of Sediment Sampling and Analysis Plans Meeting the Requirements of the Sediment Management Standards (Chapter 173-204 WAC) (WDOE 2008)	http://www.itrcweb.org/contseds-bioavailability/References/0309043.pdf
Overview of Freshwater and Marine Toxicity Tests: A Technical Tool for Ecological Risk Assessment (California Office of Environmental Health Hazard Assessment, 2004)	http://oehha.ca.gov/ecotox/pdf/marinetox_2004.pdf
"Spatial Analysis and Decision Assistance" (University of Tennessee Institute for Environmental Modeling)	www.tiem.utk.edu/~sada/index.shtml
Guidance for Ecological Risk Assessment: Levels I, II, III, IV (Oregon Department of Environmental Quality, 1998)	www.deq.state.or.us/lq/pubs/docs/cu/GuidanceEcologicalRisk.pdf
Guidance for Assessing Bioaccumulative Chemicals of Concern in Sediment (ODEQ 2007)	www.deq.state.or.us/lq/pubs/docs/cu/GuidanceAssessingBioaccumulative.pdf
Guidance for Conducting Ecological Risk Assessments, Revised (OEPA 2008)	http://www.epa.state.oh.us/portals/30/rules/RR-031.pdf
A Guide to the Interpretation of Metal Concentrations in Estuarine Sediments (Florida Department of Environmental Regulation, 1988)	www.dep.state.fl.us/water/monitoring/docs/seds/estuarine.pdf
"Frequently Asked Questions Concerning the Florida Coastal Sediment Quality Guidelines" (Florida Department of Environmental Protection, n.d.)	www.dep.state.fl.us/water/monitoring/sedsfaq.htm
"Interpretative Tool for the Assessment of Metal Enrichment in Florida Freshwater Sediment" (Florida Department of Environmental Protection, n.d.)	www.dep.state.fl.us/water/monitoring/fwseds.htm
Development and Evaluation of Numerical Sediment Quality Assessment Guidelines for Florida Inland Waters (MacDonald et al. 2003)	www.dep.state.fl.us/water/monitoring/docs/seds/sqags_for_florida_inland_waters_01_03.pdf
Technical Guidance for Screening Contaminated Sediments (New York State Department of Environmental Conservation, rev. 1999)	www.dec.ny.gov/docs/wildlife_pdf/seddoc.pdf
Department of Defense	
Contaminated Sediment Evaluation Guidance	
Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S.—Testing Manual: Inland Testing Manual (USEPA 1998b)	http://www.itrcweb.org/contseds-bioavailability/References/Evaluation-Analytical-methods-USACE-EPA.pdf
Dredged Material Evaluation and Disposal Procedures (Users' Manual) (U.S. Army Corps of Engineers, 2008)	http://www.itrcweb.org/contseds-bioavailability/References/aqr_dmmp_user_manual.pdf

Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments at U.S. Navy and Marine Corps Facilities, Part 1: Overview of Metals Bioavailability (NFESC 2003b)	http://www.itrcweb.org/contseds-bioavailability/References/bioavailability01.pdf
Critical Issues for Contaminated Sediment Management (Apitz et al. 2002)	www.clu-in.org/download/contaminantfocus/sediments/critical-sediment-mgt-sedmgt.pdf
Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities (NAVFAC 2003)	http://itrcweb.org/contseds-bioavailability/References/ug-2053-sed-rev-2.pdf
Risk Assessment	
"Navy Guidance for Conducting Ecological Risk Assessments"	https://portal.navfac.navy.mil/portal/page/portal/NAVFAC/NAVFAC_WW_PP/NAVFAC_NFESC_PP/ENVIRONMENTAL/ERB/RISK
Department of Energy	
"RAIS: The Risk Assessment Information System." (Oak Ridge National Laboratory) Several guidance documents can be found on this site describing the use of ecotoxicological benchmarks.	http://rais.ornl.gov
Data Quality Objectives	
Guidance on Systematic Planning Using the Data Quality Objectives Process (USEPA 2006a)	www.epa.gov/quality/qs-docs/g4-final.pdf
QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations: Chemical Evaluations (USEPA Office of Water, 1995)	http://water.epa.gov/polwaste/sediments/cs/upload/evaluationguide.pdf

While specific wildlife and exposure pathways are site dependent, four general receptor groups are evaluated (see Chapters 4–7 for more detail):

- Chapter 4: benthic invertebrates
- Chapter 5: fish and aquatic invertebrates
- Chapter 6: wildlife (aquatic dependent)
- Chapter 7: plants (aquatic)

Organisms that live in or on the sediment, generally referred to as "benthic invertebrates," are in direct contact with the sediment and in some systems form the foundation of the aquatic food web. COPCs that are bound to sediment particles may partition to pore water and be absorbed across gill membranes or may be ingested and absorbed in the gut. Fish and other organisms that prey on benthic infauna are exposed in turn to those same COPCs. Processes that govern uptake by benthic infauna are discussed in Chapter 4.

Resuspension of bedded sediments can result in release of COPCs to the water column, where the chemicals can partition to a freely available (i.e., dissolved) form and be absorbed by phyto- and zooplankton. Fish and other water-column (pelagic) organisms that consume phytoplankton or prey on zooplankton are exposed in turn to these same COPCs. Processes affecting bioavailability and measures for pelagic food webs are discussed in Chapter 5. Aquatic-dependent wildlife (e.g., birds or mammals) are principally exposed through incidental ingestion of sediment (e.g., during foraging) or consumption of contaminated fish or shellfish. Processes affecting bioavailability and measures for these receptors are discussed in Chapters 6 and 7.

2.2.4.2 Human health exposure pathways

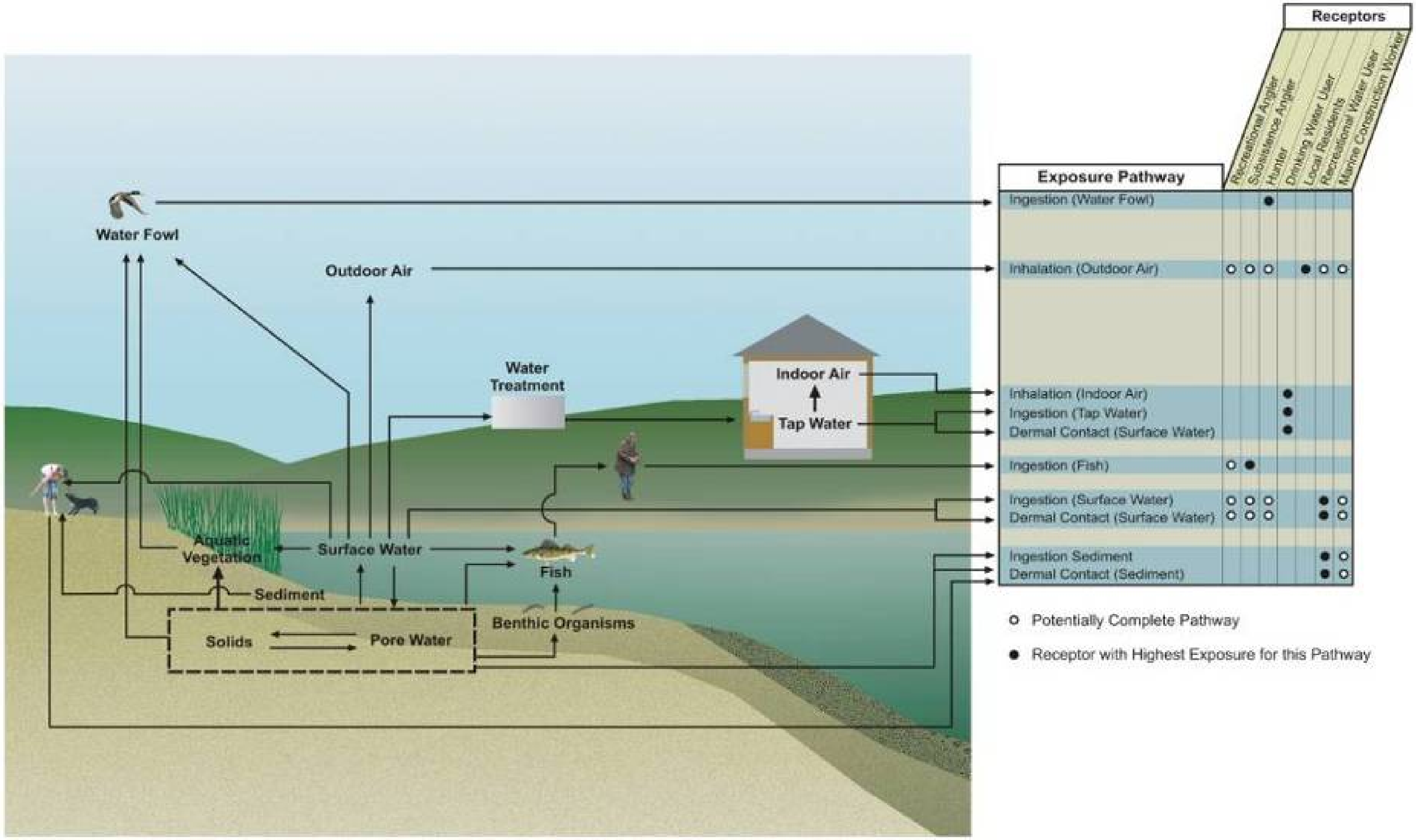
The primary and secondary exposure pathways for human health exposures from contaminated sediments typically include direct contact with sediments and surface water and ingestion of contaminated shellfish, fish, or less often plants (e.g., wild rice) and wildlife (waterfowl). Figure 2-3 shows an example of a human health food-web model. Chapter 8 discusses processes affecting bioavailability and measures for humans in more detail.

RAOs for human health exposure at contaminated sediment sites are most often based on the management of unacceptable lifetime cancer or noncancer risks from the consumption of fish or shellfish. Sediment cleanup levels are back-calculated from unacceptable tissue concentrations using models that range in complexity from simple BSAFs to sophisticated toxicokinetic models that are linked to systemwide fate and transport models. Because the primary risk pathway to humans is ingestion of organisms that have accumulated contaminants from the sediment, the most significant processes affecting bioavailability are addressed in that initial uptake. The processes and tools for evaluating this initial uptake are covered in more detail in this guidance in the chapters addressing risk to those receptors. Chapter 8 summarizes the human health exposure assumptions in more detail, with references to pertinent sections of Chapters 4–7.

2.2.5 Develop CSM

Assessing exposure and uptake requires formulating a CSM that considers the individual exposure pathways linking sources to potential receptors. Site-specific investigations of contaminated sites, as defined in USEPA’s *Risk Assessment Guidance for Superfund* (RAGS) (USEPA 1989d), are structured to incorporate measures of site-specific bioavailability through each step of the assessment process.

A CSM is especially important at sediment sites because the interrelationship of soil, surface water, groundwater, sediment, and human and ecological receptors can be complex. Sediment and soil may be subject to erosion, and both can be transported by natural events (e.g., floods) or man-made disturbances from engineering changes in a waterway. Because sediment is a dynamic medium subject to a wide range of natural phenomena, it is important to understand what chemicals may be bound and what may be bioavailable to human and ecological receptors.



Exposure Pathway	Recreational Angler	Subsistence Angler	Hunter	Drinking Water User	Local Residents	Recreational Water User	Marine Construction Worker
Ingestion (Water Fowl)			●				
Inhalation (Outdoor Air)	○	○	○		●	○	○
Inhalation (Indoor Air)				●			
Ingestion (Tap Water)				●			
Dermal Contact (Surface Water)				●			
Ingestion (Fish)	○	●					
Ingestion (Surface Water)	○	○	○			●	○
Dermal Contact (Surface Water)	○	○	○			●	○
Ingestion Sediment						●	○
Dermal Contact (Sediment)						●	○

○ Potentially Complete Pathway

● Receptor with Highest Exposure for this Pathway

Figure 2-3. Potential source media, chemical migration routes, receptors, and exposure pathways relevant to human health (Lower Fox River).

The importance of a CSM in identifying the significance of bioavailability considerations in sediment management decision making is illustrated by the Lake Hartwell polychlorinated biphenyl (PCB) Superfund site in South Carolina (Text Box 2-2). The CSM identified the important physical, chemical, and biological processes for PCB transfer through the food chain that may cause risk to human health and ecological receptors. Based on the CSM, the natural burial of PCBs by clean sediment coming into the system was demonstrated to be reducing the bioavailable concentrations in bedded lake sediments. Based on this mechanism of decreased PCB bioavailability, USEPA selected monitored natural recovery (MNR) with long-term monitoring as the preferred remedy.

2.3 Data Quality Objectives

Incorporating bioavailability considerations into a CSM supports the development of testable hypotheses around which field data collection, laboratory testing, and modeling activities can be structured. Formulation of DQOs provides a systematic structure for defining the criteria that a data collection design should satisfy, whether or not they include bioavailability considerations. DQOs include when and where to collect samples, what parameters need to be tested, the tolerable level of decision error for the study, and how many samples to collect. Balancing risk and cost in an acceptable manner should be considered at this step in the process (see http://vsp.pnl.gov/dqo, DOE 2009). USEPA also provides an example DQO process germane to planning bioavailability assessments in the document *Systematic Planning: A Case Study for Hazardous Waste Site Investigations* (www.epa.gov/quality1/qs-docs/casestudy-final.pdf, USEPA 2006b).

After completion of a CSM wherein the preliminary COPCs and potential exposure pathways have been identified and the DQOs have been established, the screening process should occur. Chapter 3 briefly describes the application of a screening process to determine whether additional investigations are required to refine the CSM, the list of COPCs, and the exposure pathways at the site.

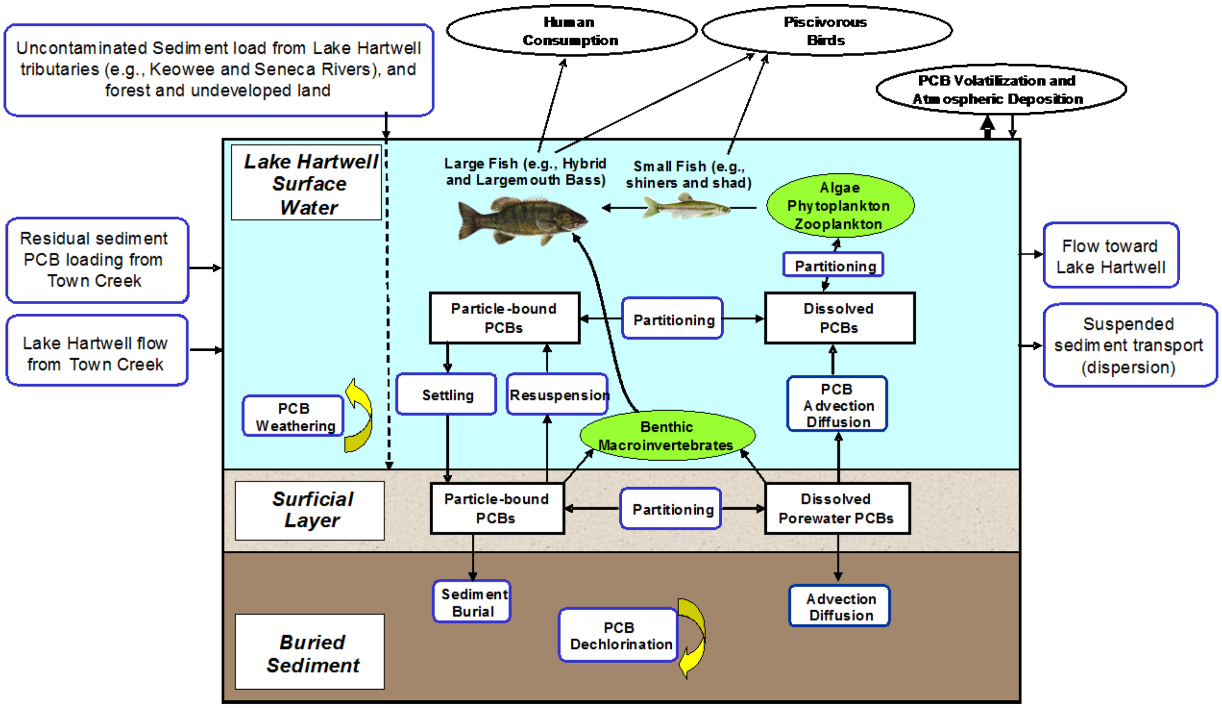
2.4 Community Stakeholder Identification, Engagement, and Contributions

This section provides information to help affected individuals and groups participate more effectively in the site evaluation and remediation process for sites in which bioavailability processes are pertinent. In this document community stakeholders (stakeholders) include affected tribal sovereign nations, community members, members of environmental and community advocacy groups, and local governments.

Affected stakeholders are not necessarily limited to those on or immediately adjacent to the site. In the case of contaminated sediments in a river, affected stakeholders may include parties far removed from the source of contamination. Tribal sovereign nations may have treaties or other pacts with the federal government that grant them fishing, hunting, or access rights in places that are not necessarily near their present-day communities. This consideration is especially important in the identification of affected tribal sovereign nations.

Text Box 2-2. Application of a CSM at Lake Hartwell PCB Superfund Site

Monitored natural recovery was the selected remedy for PCB-contaminated surface sediments in approximately 730 acres of the Twelve Mile Creek Arm of Lake Hartwell, South Carolina. The Sangamo-Weston Plant, situated on Town Creek, was responsible for PCB discharges from plant effluent and improper waste-disposal practices. Particulate-sorbed PCBs were transported through Town Creek to Twelve Mile Creek and were deposited into the Lake Hartwell sediment bed. The CSM developed for the remedial investigation identified the important physical, chemical, and biological processes affecting the bioavailability of PCBs in the Lake Hartwell food chain. The CSM (below) highlights the pathways PCB contamination follows from sediment to humans.



(*Source:* ESTCP 2009)

An important component of the CSM identified deposition of clean up-river sediments into the lake as a mechanism that would bury contaminated sediments, making them physically unavailable. Monitoring studies confirmed a steadily decreasing surface sediment PCB concentrations due to burial, mixing, dispersion (Brenner et al. 2004) and dechlorination (Magar et al. 2005a, 2005b). Sediment age dating indicated that the majority of surface sediments in the Twelve Mile Creek arm of Lake Hartwell would reach the 1 mg/kg cleanup goal between 2007 and 2011 (USEPA 2004b). Based on these data, the EPA selected MNR with long-term monitoring as the remedy.

The CSM was also instrumental in assisting with the design of the long term monitoring program. PCB concentrations are measured in surface sediment samples, caged freshwater clams (*Corbicula* spp.) exposed for 28 days, forage fish (gizzard shad/blueback herring, threadfin shad, and bluegill), and game fish (largemouth bass, channel catfish, and hybrid bass) (USEPA 1994d). Although surface sediment PCB concentrations have declined as predicted, PCB concentrations in fish tissue remain elevated, suggesting incompletely characterized and controlled exposure pathways. Additional investigation of exposure pathways are planned to update the CSM (ESTCP 2009).

For contaminated sediment sites, effective evaluation and treatment of environmental contamination require community engagement early in the process. Community involvement is particularly important for technically challenging situations where bioavailability assessments associated with contaminated sediments have not yet been well established and the approach will therefore necessarily involve some uncertainties. The contamination itself may involve a complex environment with many coupled systems and processes, and the relevant natural phenomena such as bioavailability, bioaccumulation, and biomagnification may be difficult to understand. Furthermore, the number of communities, states, and tribal sovereign nations affected by a contaminated sediment site may be large, encompassing a wide geographic area.

For effective community stakeholder identification and involvement, several important questions should be asked early in the process of investigating a site:

- Who are the stakeholders, and what is their interest in the site cleanup?
- What resources are the stakeholders trying to protect?
- What is the best method to communicate with the stakeholders?
- In what manner are these resources at risk, and can that risk be quantified?
- How will stakeholders be involved in deciding what is acceptable risk?
- Historically, what was the use of the site, and is this culturally significant to the stakeholders?
- What is the current use of the site, and what is the vision for the future use of the site?
- How will stakeholders be involved in the assessment, project planning, evaluation, and closure processes?

Individual states and the tribal sovereign nations may also recognize Native American tribes that are not currently recognized by the federal government. A list of federally recognized tribal sovereign nations can be found at http://edocket.access.gpo.gov/2008/E8-6968.htm. A list of Native American tribes not federally recognized can be found at www.kstrom.net/isk/maps/tribesnonrec.html.

2.4.1 Engagement Considerations

It is desirable to establish early and frequent communication between the project team and the stakeholders. As a project evolves and the scope of the project becomes better defined, stakeholder roles may change. Nevertheless, it is valuable to define roles and responsibilities early in the process and to agree on the methods that will be used for effective communication. Stakeholders must have an active role in the decision-making process.

Building effective relationships with stakeholders and involving stakeholders in collaborative decision making are essential components of a successful cleanup effort. All interested stakeholders must have access to critical information and the opportunity to be partners in technology development decisions during the planning, evaluation, and implementation processes. Stakeholders often have valuable information about site characteristics and history that can enhance the evaluation process and improve the quality of remediation decisions. Technology development and deployment decisions need to take into account the uses of affected water bodies, including fishing patterns, consumption of aquatic species, and cultural and ceremonial practices. It is important to achieve consensus with stakeholders about the intended end use of the site.

In the evaluation of the impact of the contamination and cleanup, it is important to keep in mind that not all of the affected communities may have comparable lifestyles. Lifestyle choices lead to different levels of risk, and communities may be disproportionately affected. For example, stakeholders with high ingestion rates of fish may be subject to greater risk than others. It is essential to establish what species are being fished and the methods used in their preparation for consumption. Certain stakeholders may have rights to fish by traditional methods that are prohibited for commercial fishermen. These may include dragnet fishing, which pulls up sediments. Thus, risks associated with contaminated sediments may be greater for those who fish by this traditional method than for commercial or sport fishermen.

2.4.2 Contribution Considerations

Stakeholders are likely to ask questions about the risks associated with specific technological solutions. Concerns might include questions about whether the remedy will lead to mobilization of the contaminants and how much contamination is being left in place. Stakeholders may also be concerned about making sure that there are sufficient data/support that any residual contamination will not pose an unacceptable risk (because it is not bioavailable) and will remain so in the future.

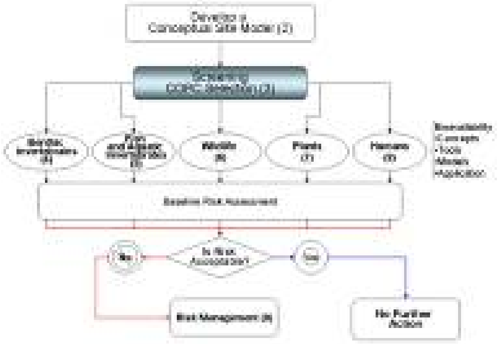
The most effective way to respond to such concerns and build public trust is to include stakeholders in the evaluation of the contamination problem and in the formulation of a remediation strategy. Open public discussion is particularly important in the evaluation of the problem and of potential technological solutions because the approaches to contaminated sediment problems are still under development and technological uncertainties remain. Stakeholders also need to be involved in the on-site observation and evaluation of the cleanup process.

Stakeholder involvement contributes to the overall success of a sediment management decision. Involvement of stakeholders in all stages of the process helps to build support for the cleanup effort and also helps to reduce the possibility of political and legal barriers to successful remedies.

3. SCREENING ASSESSMENT

Screening is the process by which the universe of COPCs and exposure pathways is evaluated and those that are below a threshold of concern are eliminated from further evaluation. Proper screening is critical because it focuses resources on key site issues, optimizing risk assessment and risk management.

To avoid eliminating potentially relevant exposures, screening is deliberately designed to be inclusive and overly conservative. For this reason, the incorporation of



bioavailability at the initial screening stage of sediment evaluation is limited. However, a brief section on screening has been included here because of the importance of this step in the overall site evaluation process. Where bioavailability-related factors can be considered, these are highlighted. Note that screening typically occurs in a tiered fashion, with site-specific considerations integrated as the initial component of pathway evaluation. These types of more focused screening tools are covered in the pathway-specific chapters of this document, Chapters 4–7.

The screening process for sediments occurs when the initial COPC selection process and CSM development are complete. Thus, COPCs and pathways have generally been identified. The purpose of the screening process is therefore to assist the user in determining the need for, and nature of, further investigation and to facilitate further refinement of the CSM and COPC list.

As discussed in Section 2.2.3, COPCs are initially selected based on general knowledge about the site's current and historic activities. This initial list of COPCs is distinguished from final list of chemicals, which may be subject to further detailed evaluation. Screening is the process by which the universe of chemicals that are known or suspected to be released from a site are reduced to a final list of COPCs that require further evaluation.

Screening is often treated as a mechanical process structured to err on the side of inclusion to provide conservatism. In practice, however, this approach tends to pull in contaminants that are secondary or may even be insignificant. As the number, complexity, and cost of sediment assessment tools rapidly expands, the most important site contaminants need to be identified so that finite resources can be optimally allocated. Thus, the screening process is a critical step in sediment assessments and must be undertaken with care and judgment. Refining the COPC list increases the efficiency and relevance of subsequent studies and thus contributes to better risk-management decisions.

Text Box 3-1. Wisconsin Department of Natural Resources Sediment Quality Guidelines (2003)

Nonpolar Organic Compound and TOC Relationships

In the case of nonpolar organic compounds such as PAHs, PCBs, dioxins/furans, and chlorinated pesticides, the bulk sediment concentrations can be normalized to the TOC content for site-to-site comparison purposes by dividing the dry weight sediment concentration by the percent TOC in the sediment expressed as a decimal fraction. This normalization helps account for differences in contaminant bioavailability among sites due to varying sediment concentrations of TOC.

Example

TOC-normalized PCB concentration of 7 mg/kg with 3.5% TOC is 200 mg PCB/kg TOC (i.e., 7 mg PCB/kg ÷ 0.035 kg TOC/kg = 200 mg PCB/kg TOC).

The Wisconsin sediment quality guidelines for total PCBs range 6–67.6 mg/kg TOC.

Normalization of nonpolar organic compounds to TOC content is valid only if the TOC content in the sediments is >0.2%. At TOC concentrations <0.2%, other factors that influence partitioning to the sediment pore waters (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important (Di Toro et al. 1991). This number is then compared to the appropriate screening level.

Although screening benchmarks do not typically account for bioavailability, some screening levels do consider binding properties that affect the degree of exposure associated with a particular bulk sediment concentration. For organic compounds, concentrations may be normalized to TOC content; extractable metals concentrations can be normalized to AVS. These tools are summarized in Section 3.1 and described in more detail in Chapter 4. TOC-adjusted screening levels can be applied within the screening process under many state regulatory programs (e.g., Text Box 3-1).

3.1 Screening Approaches

There are two major categories of screening. The first compares site-related concentrations to concentrations that are representative of prevailing conditions in the site area. Background evaluations may not always be successful at eliminating nonsite contributions because of specific provisions of the applicable regulatory framework, which may prohibit these considerations or require consideration of total risk. The second involves comparison of observed concentrations to one or more sets of reference values. Typically, these sets of benchmarks are specified by the overseeing agency. In some cases where benchmarks are not available, it may be appropriate to seek literature.

Figure 3-1 provides an overall flowchart for the screening process. State environmental agencies are encouraged to provide as much flexibility as possible to enhance the value of the screening process.

The following discussion provides an overview of the screening benchmarks commonly in use; these benchmarks typically apply only to benthic endpoints (i.e., protection of benthic invertebrates). Additional screening approaches for other endpoints and pathways appear later in this document where the respective pathways are discussed.

3.1.1 Background Evaluations

A critical step in refining a COPC list, which can also be useful at later stages of site assessment, is the determination of background values. By definition, COPCs are chemicals that are present due to some release that results in concentrations that are distinct from prevailing conditions. Therefore, the process of identifying COPCs must include a mechanism to distinguish elevated concentrations from background. This step should occur early in the site assessment, before other types of screening techniques are applied.

The process of determining a background sediment concentration can be complex and depends on the type of contaminant, the similarity between the background area sediments and site sediments, and confirmation that site sources are not negatively affecting the area(s) used to establish background concentrations. Consideration of background is important at several stages of the site evaluation process. In addition to serving a screening role, characterization of background is necessary for the appropriate identification of reference/control areas in almost any kind of toxicity study. In the risk management phase, the sustainability of a proposed mitigation must be evaluated in the context of background concentrations of COPCs. Background samples can be collected from any sediment not affected by site activities but should include areas with similar physical, chemical, geological, and biological characteristics as the site being investigated (USEPA 2005a). Some agencies will allow the elimination of a COPC by comparing it to background. Be sure to confirm the requirements with your regulatory agency.

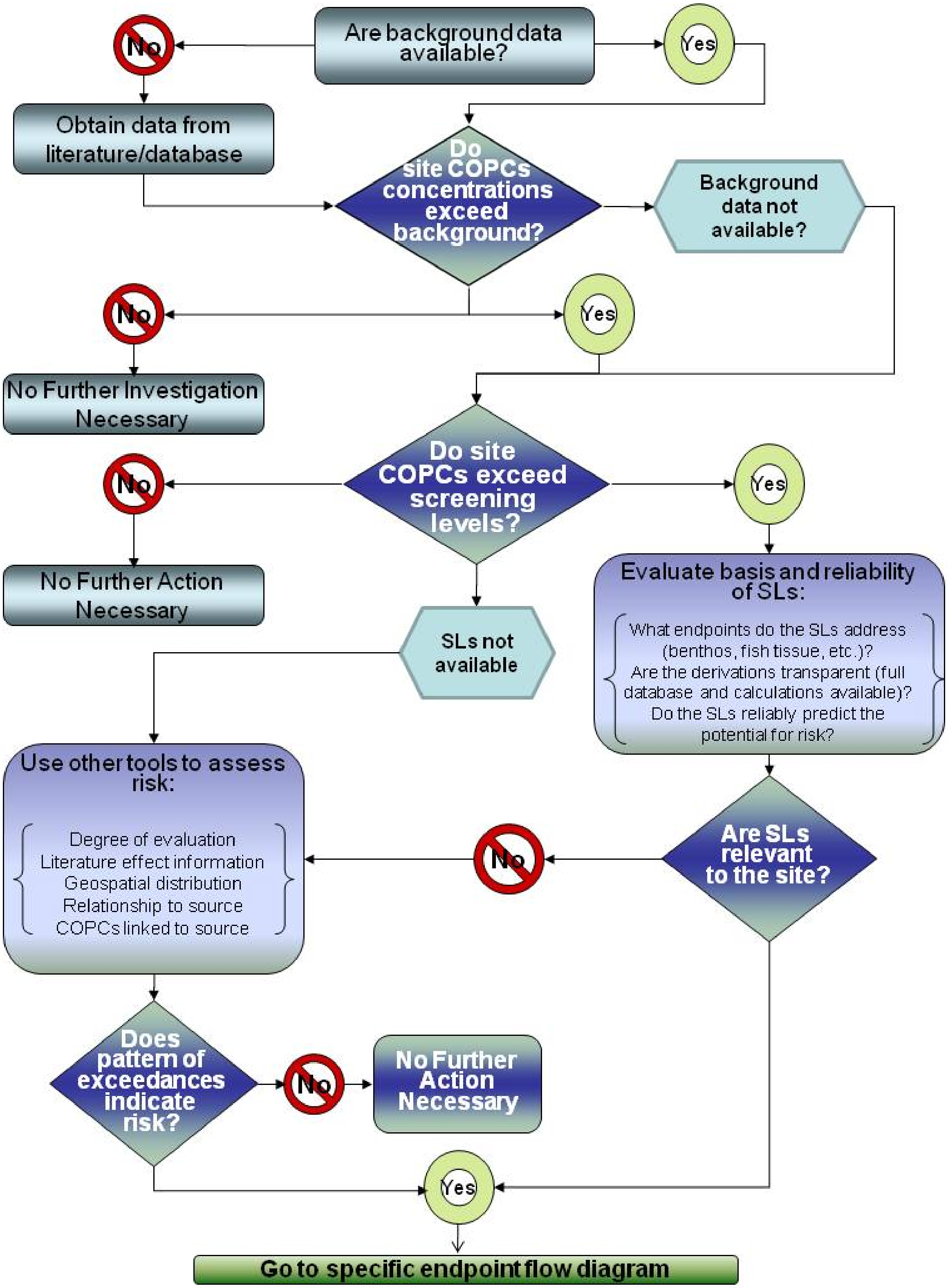


Figure 3-1 Sediment screening process.

When used in sediment characterization studies, the term “background” refers to both the concentrations of COPC that are not a result of the activities at the site undergoing assessment and the locations of the background areas (MacDonald and Ingersoll 2002). USEPA and many states recognize two types of background. According to USEPA (MacDonald and Ingersoll 2002), compounds are naturally occurring or anthropogenic based on the following definitions:

- **Naturally occurring** background compounds are present as a result of geochemical processes that have not been influenced by human activity. Naturally occurring organic and inorganic background chemicals in soil and groundwater are attributable to the natural physicochemical characteristics of the area.

- **Anthropogenic** background compounds are synthetic constituents or natural substances that have been released to the environment as a result of human activities that are not related to specific activities conducted at the site. USEPA (1991) considers the following to be sources of anthropogenic background compounds: agricultural runoff, septic systems, irrigation (former agricultural and residential application of pesticides), air pollution, historical industrial discharges and landfills not associated with the site, and urban pollution (lead and PAHs from automobiles and combustion process).

Users should investigate whether their state and/or USEPA region has different definitions and requirements for assessing background conditions as part of environmental site assessments.

The selection and analysis of background sediment samples is important in the determination and use of bioavailability within the site characterization process. Background comparisons often necessitate analysis of hydrodynamic conditions as well as the fate and transport potential of COPCs at the investigated site. *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites* (USEPA 2002b) provides guidance on the determination of background concentrations and how to compare these to site concentrations. Although this document was originally intended for soils, it also has applications for sediments.

DQOs should be established and followed when preparing a background comparison (USEPA 2006a). Regardless of the intended use, it is critical to determine data needs prior to conducting the background assessment. This document is not intended to provide a recipe for conducting these types of investigations. The references and links provided in this section will inform and guide the user in making the appropriate decisions regarding background for a particular scenario.

It is up to the user to decide what type of background evaluation is necessary for the scope of the assessment and whether the collection of site-specific data is justified. The user must also decide whether the background evaluation is necessary only as a screening step or whether the data will also serve in the scoping of later evaluations, such as identifying a reference/control area for, say, a toxicity study. In cases where site-specific background data are not available or practical to obtain, regulatory agencies may allow use of representative concentrations obtained from the literature or agency sources, e.g., National Oceanic and Atmospheric Administration (NOAA)

Screening Quick Reference Table (SQuiRT) values (see http://archive.orr.noaa.gov/faq_topic.php?faq_topic_id=6#7).

3.1.2 Numeric Screening Criteria for Sediments

A number of agencies have established sets of quantitative screening values for contaminated sediments, including USEPA (federal), USEPA regions, foreign environmental agencies, NOAA, U.S. Department of Defense agencies, Oak Ridge National Laboratory (ORNL), and some state environmental agencies. Screening values vary widely and can apply to freshwater or marine but not both. In most cases, states have adopted one set of values; however, some states (e.g., Oregon) apply more than one screening value per analyte to address multiple endpoints (i.e., receptors). Other agencies provide tables containing multiple ecological screening values (see www.esd.ornl.gov/programs/ecorisk/tools.html).

The USEPA (2001a) states that, since screening values "are based on conservative endpoints and sensitive ecological effects data, they represent a preliminary screening of site contaminant levels against these screening values to determine if there is a need to conduct further investigations at the site. Ecological screening values should not be used as remediation levels." Although these measures alone might not always accurately reflect risk to the environment, SQGs have been developed as numerical chemical concentrations intended to be either protective of biological resources, predictive of adverse effects to those resources, or both (Wenning and Ingersoll 2002).

3.1.2.1 Screening values in relation to bioavailability

There are generally two types of screening values currently in use by states and other regulatory agencies: site specific and benchmark based (i.e., established screening levels). Site-specific values generally capture critical variables related to bioavailability and rely on back-calculation to sediments from identified ecological or human health endpoints to determine the need for further evaluation. This type of screening is not common as an initial step because it is labor-intensive and costly, although it may be applied later in the process.

The vast majority of agencies use benchmarks for screening purposes. Most benchmarks are based on bulk sediment concentrations (total individual COPC concentrations in sediment). Benchmark values are generally based on observational studies that correlate biological effects (i.e., biological response) with concentrations (i.e., exposure) in samples potentially affected by multiple chemical and physical stressors. These benchmarks do not provide causal links between individual contaminants and effects but do indicate whether a potential correlation exists between individual contaminants concentrations in sediments and effects on benthic organisms. Some sets of benchmark values do include some laboratory-derived values representing effects of a single contaminant on a single species (such as spiked sediment bioassays) or are based on predicted interstitial concentrations of specific contaminants that have been studied under controlled laboratory conditions (such as USEPA's equilibrium sediment benchmarks [ESBs]). For the most part, screening benchmarks are not valid for *predicting* effects associated with individual contaminants. They can, however, be used as conservative, lower-bound estimates of individual contaminant concentrations in sediment that are likely to cause effects on benthic organisms.

Benchmark values are typically based on effects to benthic organisms; however, some state agencies have benchmark values for multiple potential receptor groups, including aquatic invertebrates, wildlife, plants, birds, and humans. Bioaccumulation- or food web–based benchmarks are typically calculated on an individual contaminant basis. Approaches using these types of benchmark values are discussed in more detail within Chapters 6 and 8.

All benchmarks are by nature simplistic since they are intended to apply to a universe of sites with vastly different characteristics. Factors generally not considered include the following:

- site setting (i.e., heterogeneous populations, dietary changes, weather conditions)
- multiple chemical exposures (i.e., distinguishing effects of individual contaminants or considering additivity/synergism)
- sediment physiochemical characteristics (i.e., changes in OC, redox, pH, etc.)

As a result, the screening process rarely incorporates site-specific bioavailability of COPCs.

Most of the published sediment screening tables are cross-referenced to two basic sets of values: the lowest effects levels (LELs) and severe effects levels (SELs) published in *Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario* by the Ontario Ministry of the Environment (www.ene.gov.on.ca/envision/gp/B1-3.pdf, Persaud, Jaagumagi, and Hayton 1993) and the effects range low (ER-L) and effects range median (ER-M) values published by Long et al. (1995). While it has been argued that these screening levels were partly derived from laboratory aquatic toxicity studies (some using sediments spiked with the COPC of interest), none of these benchmarks account for site-specific conditions that may influence the bioavailability of individual contaminants. In fact, sediment screening levels are derived to conservatively predict *the absence of a toxic effect* and generally do not provide adequate information to predict toxic effects. The prediction of toxicity is better addressed through the incorporation of bioavailability in subsequent stages of the site investigation. A brief discussion of the background and basis of the most commonly used sets of screening benchmarks for sediments, including LELs/SELs, ER-Ls/ER-Ms, and the USEPA ESBs, is presented below.

3.1.2.2 Screening values commonly used by the states and federal agencies

A variety of sources of screening benchmarks are applied by states and other jurisdictions for evaluation of contaminated sediments; however, many cite the same basic sets of screening levels or other compilations that are cross-referenced to these screening levels. The following provides a brief basis and background summary of the most popular benchmarks. The use of a particular set of benchmarks should consider the basis and background of that set of benchmarks in determining the weight to assign to the result provided by the benchmark value.

Lowest Effects Levels and Severe Effects Levels. Persaud, Jaagumagi, and Hayton (1993) described a methodology for developing LELs and SELs for metals,[2] nutrients, polar organics, and nonpolar organics. The authors reviewed a range of protocols for setting SQGs, including

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[2] By convention and for convenience, the nonmetal arsenic is considered as part of the metals group.

background, EqP, apparent effects threshold (AET), screening level concentration (SLC), and spiked bioassay. To set the LELs and SELs, only the SLC method was considered. This method involves first plotting the frequency distribution of the contaminant concentration across multiple (at least 10) sites where an individual benthic species is present. From this plot, the 90th percentile of the concentration distribution, or species screening level concentration (SSLC), is estimated; that is, 90% of sediment concentrations where the species was observed are lower than this SSLC. Then the 90th percentiles for all species are plotted in order of increasing concentrations. The LEL and SEL are set at the 5th and 95th percentiles, respectively, of this distribution. Nonpolar organics are normalized to OC, thus incorporating a component of the EqP process.

The application of the SLC approach in setting chemical-specific criteria was detailed by Jaagumagi (1993), and three sets of companion documents addressing metals, PCBs and organochlorine pesticides, and PAHs ultimately led to the Ontario screening benchmarks (*Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario*, www.ene.gov.on.ca/envision/gp/B1-3.pdf, Persaud, Jaagumagi, and Hayton 1993). The data were derived from several hundred samples collected in and adjacent to the Great Lakes region. The SLC method provides an overview, within the Great Lakes area, of statistical associations between concentrations of COPCs and absence of species but does not address toxicity (causality) due to any specific constituent. The method does not accommodate integration of other variables that are important for benthic organisms, such as dissolved oxygen concentrations or substrate particle size. Furthermore, no consideration was given to the fact that LELs for most of the metals (cadmium, copper, chromium, iron, and nickel) are below the identified background concentrations for these metals identified from the Great Lakes area.

Effects Range-Low and Effects Range-Median Concentrations. The most frequently cited set of benchmarks for saline/estuarine sediment was published by Long et al. in 1995. The criteria were developed by assembling a biological effects database consisting of studies in which both sediment concentrations and adverse biological effects were reported. For each target constituent, concentrations were arranged in ascending order. The ER-L and ER-M were identified as the 10th and 50th percentiles, respectively.

The 10th percentile (ER-L) represents the COPC concentration that was associated with a low probability of effects. The ER-L therefore serves as a useful indictor of a concentration below which toxicity from that contaminant is not likely to occur. However, the ER-L cannot be used to infer whether impacts due to that constituent would occur at a higher concentration since any number of toxicants or conditions could be the cause of observed effects in those samples. The ER-M is the COPC concentration below which 50% of the samples did not exhibit toxic effects. Given the presence of multiple contaminants in the samples used to develop the ER-L/ER-M benchmarks, the inference that the median concentration of any specific contaminant is associated with "probable effects" is not supported. Without a detailed understanding of the toxicity of other COPCs in any sample in conjunction with the physical characteristics of the sample, no conclusion regarding effects from an individual contaminant is possible. Rather, the ER-M is simply the median concentration of a COPC developed from a spectrum of contaminated sediments.

Threshold Effects Concentrations (TECs) and Probable Effects Concentrations (PECs). MacDonald, Ingersoll, and Berger (2000) evaluated several sets of SQGs. The final sets of values include the LECs/PECs and ER-Ls/ER-Ms discussed above, as well as three other sets of values: threshold effects levels/probable effects levels (TELs/PELs) (Smith et al. 1996), minimum effects thresholds/toxic effects thresholds (METs/TETs), and USEPA sediment quality advisory levels (SQALs) (USEPA 2008b). Of these, the METs and TETs were developed using a screening level concentration approach and field effects–based approach, respectively. TEC/PEC-HA28 values are based on 28-day *Hyalella azteca* toxicity tests from sites affected by multiple contaminants. The SQAL values (used by MacDonald, Ingersoll, and Berger [2000] for only the TECs) were derived based on EqP theory to predict interstitial water concentrations of COPCs. Of the methods above, only the SQAL values consider bioavailability (i.e., through the use of organic carbon normalization), but these values are available for only a limited number of nonionic organic contaminants.

MacDonald Ingersoll, and Berger (2000) derived the TECs and PECs by calculating the geometric mean of three to five other benchmarks. They reported them to three significant figures, suggesting a 99.9% confidence in the validity of these resulting screening levels. In fact, these “consensus” benchmarks are a variable combination of other values and do not have a consistent background and basis. Furthermore, the data sets are not strictly independent, since the TELs were developed using data from datasets that were also used to develop the ER-Ls/ER-Ms by Long et al. (1995). The consensus values of MacDonald, Ingersoll, and Berger (2000), as well as other sets of benchmarks, are overlapping in basis and background and ultimately are derived from many of the same datasets.

Overall, “field effects–based” screening levels imply a statistical association/correlation between COPC concentrations and the likelihood of a benthic species presence/effect in samples containing multiple contaminants. However, these types of benchmarks do not reflect causality between any individual contaminant and observed effects. While in situ effects naturally reflect the bioavailability of COPC in sediments, there is no way for the field effects–based benchmarks to determine which of the many COPCs present in contaminated sediment sites may account for the observed effects or whether physical-chemical factors such as dissolved oxygen concentrations or substrate particle size distribution could account for toxicity or species presence/absence. Furthermore, as stated by Long et al. (1995), factors that are typically likely to influence bioavailability, such as grain size, sulfides, and carbon, were not reported in most of the studies used to develop the field effects–based screening benchmarks.

Overall, therefore, the following caveats apply to the use of these field effects–based benchmarks:

- The thresholds values are conservative and useful to help eliminate individual constituents from further consideration.
- The values do not indicate causality between any individual contaminant and biological effects.
- Since contaminants co-occur, “probable” or “likely” effects levels of individual contaminants are not necessarily predictive of effects and should not be used to infer toxicity by individual contaminants. These benchmarks are not appropriate for predicting effects at sites.

Apparent Effects Thresholds. AETs were developed (Beller and Simoneit 1986, Barrick et al. 1988) for the Puget Sound Estuary using four types of biological indicators: amphipod, oyster larvae, Microtox bioassays, and benthic infaunal abundance. Both impacted and nonimpacted stations were considered in establishing these values. Validation of the AETs indicated between 50% and 96% reliability in predicting effects in Puget Sound. However, the authors caution that the values are not necessarily applicable to other aquatic systems. The AETs are sediment management values and not intended as screening levels; however, they do provide a useful reference for concentrations that may associated with effects in estuarine systems.

Equilibrium Partitioning Sediment Benchmarks. USEPA used EqP to develop sediment benchmarks for selected hydrophobic organic chemicals (HOCs, e.g., PAHs, pesticides, etc.). ESBs for metals are based on binding to AVS. The partitioning equations assume that sequestration occurs by partitioning (binding) to OC or sulfides, rendering the contaminant unavailable for biological uptake. ESBs offer several advantages over field effects–based benchmarks because they are contaminant specific, address causal relationships between COPCs and the potential for toxicity, encompass site-specific conditions that affect bioavailability (e.g., binding ligands), and address additivity within contaminant groups (e.g., PAHs). However, ESBs address only direct toxicity. Other endpoints that may be more sensitive, such as bioaccumulation, require additional evaluation.

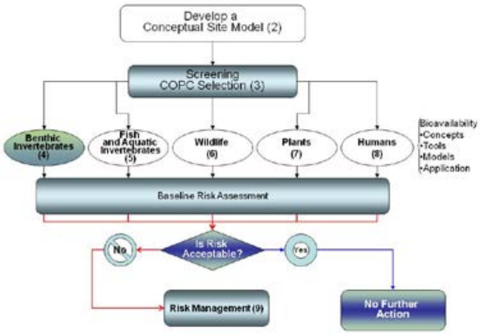
3.2 Screening Summary

Screening is a critical step in the sediment assessment process but does not offer much opportunity for bioavailability adjustments. The initial screening process is, in most cases, simply an approach to conservatively and cost-effectively determine whether additional site investigation is necessary. Screening should never be mechanical and must include professional judgment. The initial screening flow chart (Figure 3-1) suggests how users in jurisdictions that require consideration of specific benchmarks can enhance the process to obtain the most focused results and ensure that important endpoints are not obscured. States are encouraged to provide a flexible framework for site screening assessments and to collaborate with assessors in identifying COPCs so that resources can be directed to the most important contaminants.

An effective screening process focuses further evaluation on endpoints and pathways of concern and assists the user in refining the baseline CSM. In cases where benchmarks are set conservatively low and the screening process yields borderline results (marginal exceedances of benchmarks), decision makers need to carefully consider whether the site warrants the dedication of additional resources for further risk evaluation. Bioavailability generally becomes a more important factor and bioavailability assessment costs can be better justified *after* the initial screening process has determined that additional site investigation is necessary.

4. BIOAVAILABILITY TO BENTHIC INVERTEBRATES

This chapter presents the tools for assessing bioavailability to benthic macroinvertebrates that live in or on sediment. This pathway is often the first pathway assessed when sediment chemical screening levels are exceeded (see Chapter 3). Beyond the screening criteria, additional investigations may be conducted to determine whether the COPCs are affecting the benthic community. These investigations can include additional sediment chemistry analyses, bioassays, macroinvertebrate community surveys, or geochemical measurements that take into account site-specific conditions that may influence COPC bioavailability.



Benthic invertebrates are relatively sedentary organisms that inhabit or depend on the sediment environment to sustain life functions. Because they largely live on (epibenthic) or in (infaunal) the sediment, they are sensitive to both short- and long-term changes in sediment and water quality. Benthic invertebrates are frequently used as environmental indicators of biological integrity because they are found in most aquatic habitats; are of a size permitting ease of collection; reflect water quality conditions or sustainability of ecosystem components; are consumed by a wide range of wildlife species, including fish, amphibians, reptiles, birds, and mammals; and can be used to identify of impaired conditions (USEPA 1989d).

Assessment of exposure and bioavailability for benthic organisms depends on where they live and how they derive nutrition. Infaunal organisms living within the sediment can be exposed to COPCs through pore water, through ingestion of contaminated sediments or diet, or through COPCs released into the overlying water. (For some benthic organisms, such as clams, respiration and feeding are accomplished by siphoning the overlying surface water.) Exposure of epibenthic organisms is principally through ingestion of contaminated sediments or diet and COPCs released into overlying water.

This section identifies and describes the tools and measures that are available to assess bioavailability for the benthic invertebrate pathway. Text Box 4-1 presents a generalized roadmap for assessing bioavailability to benthos, which will be discussed throughout this section.

Text Box 4-1. Assessing Bioavailability to Benthic Invertebrates

Do bulk sediment concentrations of COPCs indicate potential for impact to benthos based on applicable SQGs?

If no, then probability of impact to benthos may be low.

If yes, then use weight-of-evidence approach that can include bulk sediment chemistry, laboratory-based toxicity tests, and/or macroinvertebrate surveys to gain information by the following:

- substituting pore-water measurements for bulk sediment chemistry:
    - estimate EqP or SEM – AVS
    - direct analysis through active or passive sampling
- estimating bioavailability from laboratory-based toxicity tests
- conducting laboratory bioaccumulation exposures
- conduct toxicity identity evaluation (TIE) to determine contaminant responsible for toxicity

4.1 Tools for Assessing Benthic Invertebrate Bioavailability

Benthic invertebrates may be prey for higher-level organisms and potentially transfer COPCs through the food web (Figure 4-1). If bulk sediment concentrations exceed state SQGs, the traditional procedure for evaluating the effect of sediment-based COPCs on benthic organisms is through the Sediment Quality Triad. The SQT is a weight-of-evidence approach that integrates results from sediment chemistry, aquatic toxicity testing, and benthic community analysis. MacDonald and Ingersoll (2002) provide an example of one method of interpreting the results of the SQT (see Table 4-1). For some states, sediment chemistry and aquatic toxicity testing may be given more weight than benthic community analysis because benthic metrics are often difficult to interpret, particularly for staff without formal training in benthic ecology. Additionally, there are other factors besides chemistry (e.g., grain size, depth, TOC, salinity, discharge) that may markedly affect the number and spatial distribution of benthic invertebrates in sediment and thus introduce bias during routine field sampling.

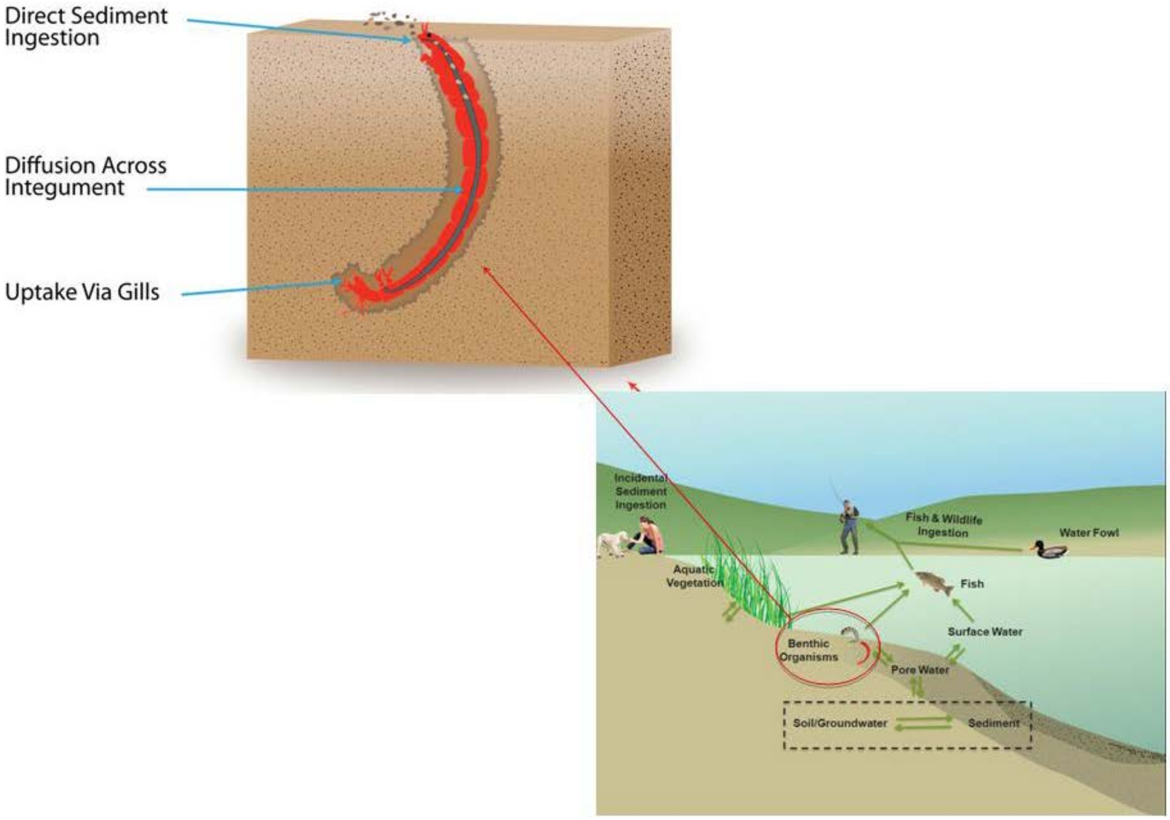


Figure 4-1. General bioavailability processes in the benthic pathway in sediments. (adapted after NRC 2003)

Table 4-1. Contingency table of possible outcomes using the Sediment Quality Triad (*Source:* USEPA 2002d)

Possible outcome	Sediment chemistry[a]	Toxicity test[a]	Benthic community[a]	Possible conclusions
1	+	+	+	Impact highly likely
2	-	-	-	Impact highly unlikely
3	+	-	-	Impact unlikely
4	-	+	-	Impacts possible
5	-	-	+	Impacts unlikely
6	+	+	-	Impact likely
7	-	+	+	Impact likely
8	+	-	+	Impact likely

[a] + indicates classified as affected; - indicates classified as unaffected.

In addition to bulk sediment chemistry, additional measures that can be used to assess whether sediment quality may be affecting benthic macroinvertebrates (or the benthic community as a whole) include the analysis of pore-water chemistry and macroinvertebrate tissue residue analysis (e.g., bivalves).

Sediment chemistry provides information on the types and levels of COPCs that may be causing an effect on the benthic community. Sediment toxicity testing provides a direct measure of the potential risk posed by the sediment. It does not provide any information about the source of that risk. Benthic community analysis may or may not be helpful in determining effects of COPCs. This parameter is highly variable and subject to influences other than COPCs (e.g., substrate or lack of food). It should be noted, however, that benthic macroinvertebrates have been assigned "pollution tolerance" scores (Section 4.1.2.2) so that the presence of a certain family, genus, or species can often inform the observer as to how disturbed the community is by human influence (Barbour et al. 1999).

Measures of Contaminant Bioavailability

- **Chemical measures** provide contaminant concentrations in sediments, water, or tissue.
- **Biological measures** provide inference about contaminant bioavailability.
- **Predictive measures** use models to estimate chemical and biological measurements that can be used to assess contaminant bioavailability.

Bioavailability concepts, tools, models, and/or applications should be considered when examining the physicochemical and risk-related aspects of sediments. Given the conservative risk assessment practice that assumes many exposure parameters may be "worst case" and independent of each other, simply assuming that a COPC is "100% bioavailable" will most likely result in an overestimation of risk and thus an uninformed decision. While there are suites of conventionally employed tests that are routinely used in federal and state site characterization programs, recent advanced tools and measures have made it possible to explore with more accuracy the degree to which a COPC is bioavailable by correlating the chemical activity with toxicological response in benthic invertebrates. Figure 4-2 presents a schematic to assist in examining tools, models, and/or applications of bioavailability within the benthic macroinvertebrates pathway. The various tools are linked to the section of the guidance that provides a description and application of the method.

The tools discussed in this section have been classified as chemical, biological, or predictive. As a matter of convenience, these subdivisions help to classify these tools and their application as described in Table 4-2.

4.1.1 Chemical Approaches

Chemical approaches are those techniques that provide COPC concentrations in sediments, pore water, surface water, and, if applicable, groundwater and tissue residues. Appendix B presents the major classes of chemicals found at contaminated sediment sites and specific bioavailability considerations for these classes of compounds. Appendix C provides more detailed descriptions and links to the tools described below. The following sections describe the concepts of assessing bioavailability with each tool or method and their application within the benthic pathway.

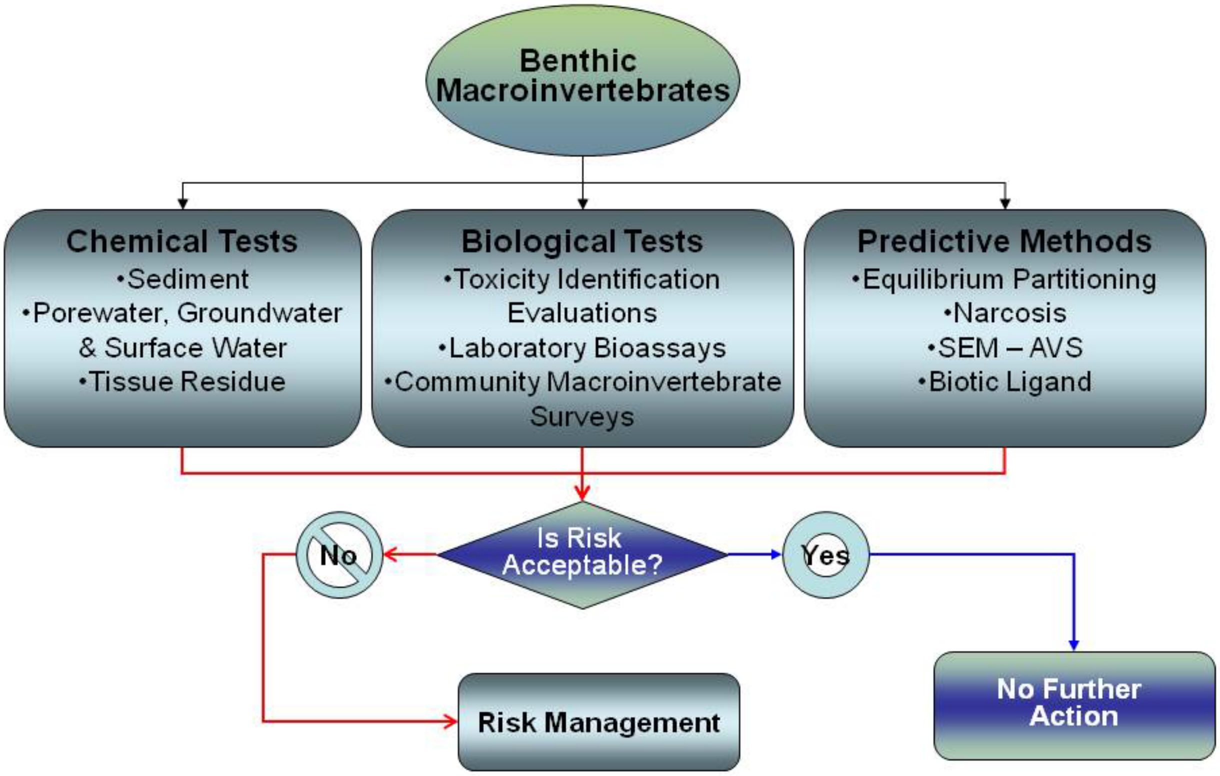


Figure 4-2. Tools and methods for evaluating benthic invertebrates for bioavailability.

4.1.1.1 Bulk sediment chemistry

Contaminated sediment sites require, at a minimum, an analysis of the total (bulk) concentration of the COPC(s) in sediment, as this measure is used for defining the nature and extent of site-related contamination, as well as for comparison to screening-level benchmarks, background comparisons, and/or local conditions (see Chapter 3). Screening of bulk sediment chemistry concentrations to SQGs is sometimes sufficient for risk management decisions, particularly when sites are small and/or there are prescriptive state sediment procedures for screening evaluations. Where background and relevant SQGs are exceeded, pore-water analysis, toxicity testing, and/or benthic macroinvertebrate surveys can be conducted to assess the actual impact to the sediment community. Confounding factors associated with benthic community assessments may include non-site-related factors (e.g., grain size, depth, TOC, salinity, discharge).

Bulk sediment chemistry is also used in predictive models of bioavailability to benthos and/or subsequent accumulation by fish, as well as to evaluate the potential exposure to higher organisms including humans. Horizontal (areal extent) and/or vertical (depth interval) assessments of bulk sediment chemistry with physical descriptions are needed for completing nature and extent evaluations under most site investigation programs, assessing COPC fate and transport, and planning and implementing remedial alternatives. With regard to spatial sampling, the scale (and budget) of the site determines the number of samples required to meet any predetermined degree of statistical power (Gilbert 1987). For vertical sampling, the depth of the bioactive zone is typically defined as 0–6 inches for freshwater sediment and a 0–1 foot interval for estuarine and marine habitat (USEPA 2001b). Most remote sampling grab devices, such as a clamshell type, typically obtain the 0–6 inch interval. Site specific conditions, however, may require alternative considerations of depth intervals (e.g., scouring).

Table 4-2. Approaches used to assess bioavailability in the benthic pathway

Measure		Standard approach	Advanced approach
Chemical measures	Bulk sediment chemistry	• Grab samples or core sediments in field, analyze chemicals, geochemical parameters (TOC, SEM – AVS, redox) • Grain size and pH • Compare to state, USEPA, or other sediment quality objective (SQO)/SQG values	• SEM – AVS or SEM/AVS/f_{oc} • ER-M quotients • TIE
	Groundwater (App. C-T2) Pore water (App. C-T1)	• Shoreline groundwater wells • Seep/direct samplers (e.g., piezometers, Trident, UltraSeep) • Geochemical parameters (TOC, DOC, humic acid, pH, salinity) • Compare to National Recommended Water Quality Criteria (NRWQC)	• Passive in situ samplers for nonpolar organics (e.g., SPMEs, PE, POMs) • Centrifuge sediments to recover pore water, analyze pore water ex situ using SPME • Passive samplers for metals (peepers, DGTs)
	Surface water (App. C-T7)	• Surface-water samples (grab, composite) • Total and/or dissolved COPCs • Geochemical parameters (total suspended solids [TSS], TOC, DOC, humic acid, pH, salinity) • Comparison to NRWQC	• Passive samplers for nonpolar organics (e.g., SPMEs, PE, POMs) • Passive samplers for polar organics (semipermeable-membrane devices [SPMDs], GORE® Module) • Passive samplers for metals (peepers, DGTs) • TSS, TOC, DOC
	Tissue residue analysis (App. C-T5)	• Direct collection and measurement of tissue COPCs and lipid • Comparison to ecological or human health screening toxicological effects concentrations • Calculation of BSAF	• Field bioaccumulation studies (e.g., caged mussels) • Field collection of invertebrates for chemical analysis • Laboratory bioaccumulation studies (*Macoma, Neanthes, Nereis*)
Biological measures	Toxicity testing (freshwater, App. C-T3 and marine, C-T3)	• Acute toxicity test (e.g., 10-day test) • Chronic toxicity test (e.g., 28–42-day test) • Sublethal development (e.g., 48-hour bivalve development) • Elutriate tests	• Pore-water toxicity (e.g., *Daphnia magna* lethality) • TIE testing (e.g., addition of chemical absorbent or metal chelating agent) • Reproductive endpoints • Life-cycle test (e.g., *Chironomus* larval development and hatch-out test)
	Macroinvertebrate surveys (App. C-T6)	• Rapid bioassessment protocols (qualitative kick-net sampling, drift nets) • Caged mussel surveys • Grab samples (e.g., 0.1 m^2 box cores or grabs) • Analysis and inference of bioaccumulation based on o identification to lowest practicable taxon o statistical comparison of populations to clean reference areas	• Sediment profile imaging (SPI)

Measure		Standard approach	Advanced approach
Predictive measures	Partitioning models (App. C-T4 and C-T8)	• Equilibrium partitioning for nonpolar organic compounds using TOC o Hydrocarbon narcosis–toxic unit approach • SEM – AVS (EqP applied to metals) • Logistical regression model	• Equilibrium partitioning for nonpolar organic compounds using TOC and sedimentary organic content • Biotic ligand model

Specific chemical and physical parameters to be measured when evaluating benthic exposure are site and/or program specific. These include the COPCs and may also include TOC, sediment grain size, ∑SEM – AVS parameters (sulfides), pH, salinity or alkalinity, ammonia, and redox potential. These parameters, their relevance, and test methods are described in USEPA 2001c (www.epa.gov/waterscience/cs/collectionmanual.pdf). Methods for the collection and analysis of COPCs in bulk sediment are described in multiple federal and state documents (USEPA n.d. “Measurement,” MacDonald and Ingersoll 2002, NFESC 2003a, NJDEP 1998, WDOE 2008, RSET 2006).

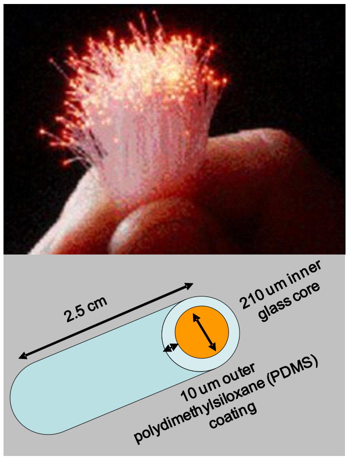
4.1.1.2 Pore-water and groundwater measures

Undisturbed sediment pore-water COPCs tend towards equilibrium with the solid-phase COPC concentrations (i.e., EqP, see Section 4.1.3.1 for explanation). Pore-water contamination, however, may also occur from groundwater discharge into the interstitial space.

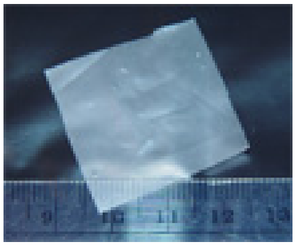
Measuring chemicals in groundwater that discharges into sediments has conventionally been done with groundwater monitoring wells or piezometers positioned along the shoreline and inferring or predicting attenuation and discharge concentrations with groundwater models (Winter 2002). More recently methods have been developed to sample tidal and subaqueous groundwater discharges to a water body (Chadwick and Hawkins 2008, Chadwick et al. 2003, Duncan et al. 2007a, 2007b). These tools include intertidal seep sampling, piezometers, and diver-deployed diffusion samplers. Text Box 4-2 illustrates several examples of samplers used to sample pore water (including passive groundwater samplers). For a complete list of available sampling tools of indirect and direct measurement of COPCs in pore water, see Appendix C-T1 (direct pore-water sampling devices) and C-T2 (indirect pore-water sampling devices). Those sections provide more details and descriptions of the tools and measures applicable to measuring COPCs in groundwater and pore water. USEPA (2008a) also provides information on the evaluation of the groundwater to sediment transport pathway.

Text Box 4-2. Some Examples of In Situ Pore-Water/Groundwater Tools

Field-deployable subaqueous sampling systems include both active and passive samplers. SPME fibers are thin silica fibers coated with an organic polymer. Polyethylene devices (PEDs) are polyethylene sheets. HOCs partition from the pore water onto the polymer/ plastic. SPMDs are polyethylene tubes that may be filled with laboratory-grade distilled water or triolein and deployed in the water column or sediments. Sediment "peepers" rely on a diffusion gradient across a dialysis membrane into a pure sampling liquid. With SPMDs, contaminants of interest passively diffuse and come into equilibrium in materials in the bag. The Trident probe is a simple, direct-push system equipped with temperature, conductivity, and water sampling probes and can collect water at specific depths. The UltraSeep Meter can be used to make continuous, direct measurements of the groundwater seepage rate using an ultrasonic flow meter (Chadwick et al. 2003, Chadwick and Hawkins 2008, Smith et al. 2003). The GORE® Module is a waterproof, vapor-permeable GORE-TEX® membrane tube containing hydrophobic adsorbents. Dissolved contaminants partition and diffuse through the membranes to the adsorbent (ITRC 2007). (SPME, PED, and SPMD photos courtesy of Dr. R. Burgess, USEPA; Trident and UltraSeep photos courtesy of Dr. B. Chadwick, U.S. Navy Space and Naval Warfare Systems Center; GORE Module photo courtesy W. L. Gore.)

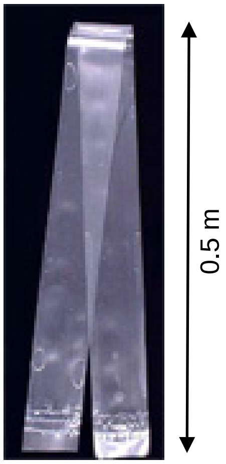


SPME



PED

PED and SPMD allow molecules <600 Daltons molecular weight



2.5 cm
SPMD
(containing triolien)


Trident Probe

GORE® Module

UltraSeep Meter

The principal routes of exposure for benthic infauna are through ingestion of sediment or direct exposure to contaminated pore water. Generally, there is a good correlation between biological effects and pore-water concentrations but not with total sediment concentrations (Di Toro et al. 1991). The bioavailability of a COPC from pore water is theoretically expressed as the "truly" dissolved phase and as such is separate from the COPC associated with suspended particulates and DOC (although the latter plays a role in phase equilibrium for organic compounds). Since the toxicity to benthic organisms is generally correlated to pore-water concentrations, the relationship of pore-water concentrations to established NRWQC (see USEPA n. d. "National") should theoretically provide a measure of the potential toxicity of the COPC. While the most common form of assessing COPC impacts is the comparison of bulk sediment concentrations to sediment quality criteria, this measurement does not provide information on site-specific bioavailability of the COPC. As a line of evidence assessing exposure to the benthic community, some states approve of the assessment of site-specific toxicity to benthos from sediments by the determination of the pore-water concentrations from bulk sediment concentrations using EqP theory. Recent advances in using solid-phase sampling devices (e.g., SPME, POM) would suggest that direct sampling of pore water would considerably increase accuracy while reducing the cost/benefit ratio of the site investigation (Hawthorne and Hawthorne 2009).

Pore-water measures are useful to apply when existing site data, based on bulk sediment chemistry and possibly aquatic toxicity testing or benthic community analysis, suggest that a specific contaminant may be responsible for an observed toxic response. Measurements of contaminants in pore water involve more advanced tools than evaluating total sediment concentrations, principally to collect the pore water and/or contaminants that are then measured by standard analytical techniques. There are several approaches to determine pore-water COPC concentrations:

- EqP to estimate pore-water concentrations from bulk sediment concentrations.
- Traditional sediment collection followed by centrifugation or core squeezing and filtration and/or flocculation of residual particulates. The resultant supernatant (pore water) can be chemically analyzed or used for toxicity testing.
- Sampling of pore water by use of suction devices, piezometers, or equipment such as the Trident probe. The resultant pore water can be chemically analyzed or used for toxicity testing.
- In situ or ex situ placement of diffusion or equilibrium-based samplers directly into the sediment or extracted pore water and measurement of either the sampler (e.g., SPME, PE, and POM) or the liquid contained therein (e.g., peepers).

Section 4.1.3.1 discusses EqP to estimate pore-water concentrations in detail. While pore-water concentrations of COPCs have shown to correlate with aquatic toxicity test results in relatively "clean" sediments, in sediments containing anthropogenic carbon (soot carbon, black carbon), estimates of pore-water concentrations from published EqP coefficients can overestimate pore-water concentrations by up to three orders of magnitude (Hawthorne, Grabanski, and Miller 2006). For this reason, other methods to measure pore-water concentrations of COPCs have been developed and are discussed below.

Advantages of Centrifugation Methods

- easy to implement
- relatively low cost
- have a track record of field studies where the methods have been used

Disadvantages of Centrifugation Methods

- require a large amount of sediment to extract sufficient pore water for chemical analysis for some compounds (e.g., PCBs, PAHs) but not for others (e.g., metals)
- typically have high chemical detection limits due to the small volumes of pore water extracted
- disrupt the integrity of the interstitial pore space
- may create conditions (e.g., altered redox or pH) whereby pore-water chemical form or speciation are altered

Centrifugation methods are well documented (USEPA 2001c, NFESC 2003) and are arguably the simplest and most commonly employed method for extracting pore water. Various types of sediment core squeezing devices have been employed in the past to obtain pore water. Suction devices that employ a syringe that is joined (via tubing) to an air stone or sintered glass filter have also been employed. The groundwater sampling systems described previously are also being used more frequently at contaminated sites to collect pore water. The box at right lists advantages and disadvantages of these pore-water collection methods (see Appendix C-T1).

In particular, the handling and disturbance of sediments that are reduced in situ can greatly increase the solubility of metals, resulting in false positive results. These methods are also not capable of completely removing COPCs associated with suspended particulates and DOC and thus do not report the truly bioavailable fraction of a COPC. A comparison of these types of pore-water collection methods can be found in Schults et al. (1992).

Advantages of Diffusion and Equilibrium-Based Samplers

- can be done in situ or ex situ
- measure the truly dissolved (bioavailable) fraction in pore water
- may act as biomimetic or surrogate for benthic organism exposure for some COPCs
- can be used to monitor COPCs in coarse sediments or in sand caps that might not be amenable to sampling by conventional sediment sampling methods
- can be used to support TIE

In situ and ex situ pore-water measurements can be made using samplers that rely on selective diffusion over time (e.g., sediment "peepers") or rely on a more rapid flux to attain equilibrium (e.g., POM, PED, SPMD, SPME). Diffusion samplers are routinely used for sampling HOCs. A number of the more commonly employed devices are described in Appendix C-T2. There are two general types of in situ samplers: passive diffusion samplers and equilibrium samplers. Some advantages of using these samplers are listed in the box at right. Diffusion samplers consist of a semipermeable membrane or dialysis tube filled with distilled water, a pure oil (triolein), or a gel, all of which rely on a diffusion gradient to establish equilibrium between the pore water and the sampler. Diffusion samplers are used for measuring metals, phosphates, and sulfides. Because diffusion samplers measure the bioaccessible (i.e., sediment extractable) fraction of COPCs, they require some knowledge of flux of a COPC across the membrane over time (e.g., by using internal permeability reference compounds) to correlate to biological uptake.

The pore-water sampler shown in Text Box 2-1 for the Mocks Pond site is one example of a passive diffusive sampling device. Another example is a sediment "peeper," which typically employs a rigid body into which open cells are milled. The peeper is laid flat, the cells are filled with distilled water, and the cells are covered with a semipermeable membrane. A perforated acrylic cover holds the dialysis membrane in place but allows exposure of the cells to sediment (USEPA n.d. “Measurement”). Section 4.2.1.2 offers another example of a diffusion sampler where COPCs coming into contact with the sampler and having sufficient volatility (Henry’s law) partition out of the pore-water solution and diffuse across the semipermeable membrane to the adsorbent for collection.

SPMDs are long (~1 m), flat, low-density polyethylene tubes typically filled with purified lipid (triolein) and sealed. The flat SPMD is wrapped around a metal “spider” that holds it in place. Four spiders are then placed in a perforated stainless steel deployment device to provide protection when deployed into surface water or sediment (USEPA n.d. “Measurement”). SPMDs uptake contaminants until they are at equilibrium among the phases (typically water and polyethylene/lipid). The membrane mimics a biological membrane in its ability to allow selective diffusion of organic compounds from sediment or surface water (Zimmerman, Thurman, and Bastian 2000).

Diffusive gradient in thin films, another type of diffusion sampler, refers to two similar tools for collecting metals from sediment pore water (Davison et al. 2000). DGTs differ from other diffusive samplers in that they are typically casings filled with gels that are specific to the target compound (e.g., a Chelex or acrylamide gel for metals, ferrous-oxide gel for phosphorus). The unique advantage of DGTs over other diffusive samplers is that after retrieval, the gel can be cut into segments for multiple analyses.

Equilibrium samplers are often used for the measurement of pore-water concentrations of HOCs such as PCBs and PAHs. These types of samplers can be divided into those that are used to extract small quantities of COPCs from extracted pore water and those that are inserted directly into the sediment and accumulate HOCs in proportion to their presence (Fernandez et al. 2009). Equilibrium samplers may be used as biomimetic devices because they may mimic uptake from the solid phase or pore water directly to the organism (NRC 2003, Wenning et al. 2005).

Equilibrium samplers include SPME, PEDs, POM, and polydimethylsiloxane (PDMS) samplers that provide a measure of freely dissolved HOCs in sediment pore water. In many cases, the results obtained from the use of these samplers correlate with aquatic toxicity test results and/or bioaccumulation of the compounds into benthic organisms (Zimmerman, Thurman, and Bastian 2000; Van der Heijden and Jonker 2009; Hawthorne et al. 2007). SPME fibers have been used for both in-laboratory measurements of pore-water chemical concentrations and as a field-deployed method for measuring in situ pore-water concentrations of HOCs (Zeng, Tsukada, and Diehl 2004; Mayer et al. 2000; Reible et al. 2008, Hawthorne et al. 2007). To date, most of the in situ work has evaluated PAH bioavailability in sediments, where several researchers have shown that PAH uptake into the SPME fibers is related to PAH uptake by tissue in some organisms (Reible et al. 2008, Van der Heijden and Jonker 2009). More recently, PCBs have been examined, but the time needed to achieve equilibrium rates for specific congeners is still an area of active research (Reible et al. 2008).

One innovative method has been developed to directly measure pore-water PAHs at low detection limits (pg/mL) from sediment samples as small as 40 mL (USEPA SW-846 Method 8272/ASTM Standard D7363-07). The field-collected sample is transported back to the laboratory and centrifuged. Dissolved solids in the supernatant are flocculated, and the sample is recentrifuged to eliminate the particulate and dissolved carbon–bound COPCs. An SPME fiber is added to the supernatant to adsorb pore-water PAHs and is then injected into a gas chromatograph/mass spectrometer (GC/MS) for analysis. The pore-water concentrations measured by this method have been found to be reasonably good predictors of toxicity (survival) to *Hyalella azteca*, a sensitive organism for evaluating toxic PAH response to benthic invertebrates. This method provides a more exact characterization of PAH impacts than found through the use of bulk PAH concentrations and EqP to estimate pore-water concentrations (Moles, Holland, and Andersson 2006; Hawthorne et al. 2007).

PE and POM samplers are similar to SPMEs in their ability to sequester organic compounds from sediments. These samplers have the advantages that (1) they come to equilibrium rapidly, (2) molecular tracers can be added prior to deployment that allow for a direct measure of equilibration, and (3) high concentrations of HOCs can be concentrated during short field deployments (Fernandez et al. 2009, Tomasaewski and Luthy 2008). Uptake of PAHs and PCBs by benthic organisms has also been shown to be correlated to uptake by PE and POM samplers (Vinturella et al. 2004, Tomasaewski and Luthy 2008). PE samplers have been used as part of toxicity identification evaluations (Perron et al. 2009) and also have been shown to provide a useful tool to measure very low levels of truly dissolved PAHs in surface water (Moles, Holland, and Andersson 2006; Carls et al. 2004; Fernandez et al. 2009).

4.1.1.3 Surface-water sampling

Surface water is a route of exposure for many benthic invertebrate species and may require careful sampling and consideration of what measured fractions might be bioavailable. For example, many states characterize the health of streams, creeks, and rivers based on surveys of the “EPT” species: *Ephemeroptora* (mayflies), *Plecoptera* (stoneflies) and *Trichoptera* (caddisflies). These species can be exposed to COPCs in surface water via the external gills and the integument. In marine systems, clams, oysters, mussels, and other invertebrates pump water through their siphons, extracting food, oxygen, and COPCs.

Bioavailability in surface waters can be addressed by many of the same tools described for groundwater and pore water. Centrifugation, diffusion, and equilibrium samplers have all been used for assessing the bioavailable fraction of COPCs in surface waters (Burgess et al. 1993, Cornelissen et al. 2008). Sampling of surface water is well established in most states and in federal programs and will not be covered in detail here. Table 4-2 provides water quality sampling and characterization measures and considerations.

4.1.1.4 Tissue residue analyses

The most direct method for determining whether COPCs are available to organisms is to directly measure the internal chemical concentration (tissue residue) either in organisms harvested from the field or by placing clean organisms into the contaminated sediment and allowing exposure to occur (see Appendix C-T5). Tissue residue concentration measurements integrate chemical bioavailability, multiple routes of exposure, and assimilation into organism tissue. Tissue residue values can be compared to observed toxic effects in the field such as pathological lesions, tumors, or other subcellular effects. Databases of tissue residue toxicity data have been compiled and are publically available (USEPA MED database, www.epa.gov/med/Prods_Pubs/ecotox.htm; U.S. Army Corps of Engineers (USACE) WES database, http://el.erdc.usace.army.mil/ered; Dillon and Gibson 1987; Beyer, Heinz, and Redmon-Norwood 1996; Jarvinen and Ankley 1999; Beyer and Meador 2011). Although these tissue residue toxic effects relationships can be used to estimate potential biological effects on benthic organisms based on tissue concentrations, it should be noted that the relationship between tissue residues and adverse effects is controversial, particularly for COPCs that are actively sequestered (e.g., metals via metalloproteins) or metabolized (e.g., PAHs). While measured tissue residues provide direct evidence that the chemical has indeed been accumulated, the disadvantage is that it is not necessarily possible to discern the route of exposure (e.g., sediments or surface water) and which is responsible for the adverse effects in the organism where multiple COPCs are measured.

Benthic organisms have been collected in situ as part of the Puget Sound Dredged Disposal Analysis Program, where the target species for measuring body burden are the sea cucumber *Molpadia intermedia* and the clam *Compsomyax subdiaphana*. Additional information on this study can be found at www.dnr.wa.gov/Publications/aqr_dmmp_monitoring_plan.pdf (Washington Department of Natural Resources 2007).

For human health risk assessments (HHRAs), field collection of clams, oysters, and mussels and the subsequent measurement of tissue residues in the laboratory provide a direct measure of exposure concentrations to recreational and subsistence shellfish consumers (see Chapter 8).

Certain contaminants possess the ability to bioaccumulate, the process by which chemicals are taken up by an organism either directly from exposure to a contaminated medium or by consumption of food containing the chemical. As discussed earlier, benthic organism tissue residue concentration can be compared to observed toxic effects in the field such as pathological lesions, tumors, or other subcellular effects or to literature values/databases that contain tissue residue toxicity criteria.

When a site is determined to contain contaminants of concern (COCs) that bioaccumulate, it is important to consider the potential for biological transfer of these contaminants from benthic organisms to fish and wildlife (birds and mammals). The simplest method for estimating contaminant loads in biota is the use of accumulation factors (AFs), which consist of ratios of the concentration of a given contaminant in biota (e.g., fish tissue) to that in an abiotic medium (e.g., sediment). For the evaluation of sediments, this is commonly presented as the BSAF. The concentration in biota may be estimated by multiplying the sediment concentration by the BSAF (Bechtel Jacobs 1998a). It should be noted that AFs are generally used to assess risk to upper trophic level receptors and not the benthic organisms themselves. Therefore, a more detailed discussion of AFs and how they are used to evaluate risk to fish can be found in Section 5.2.3.1.

Additionally, the potential for adverse effects from exposure to bioaccumulative chemicals can be evaluated by using food-chain models to estimate dose(s). Dose estimates are then compared to receptor-specific food chain–based benchmarks such as no observable adverse effects levels (NOAELs), for example, ORNL Toxicological Benchmarks for Wildlife (Sample, Opresko, and Suter 1996).

4.1.2 Biological Methods

Methods for inferring bioavailability of COPCs to benthic organisms include bioassays (i.e., toxicity tests), benthic macroinvertebrate surveys, and bioaccumulation studies. Bioassays are often conducted to provide a more site-specific measure of sediment bioavailability after bulk sediment COPC concentrations have been shown to exceed SQGs. Site-specific benthic infaunal measures of abundance and diversity (i.e., macroinvertebrate surveys) can also be used to evaluate the overall quality of the macroinvertebrate community and may indirectly assess the bioavailability of site COPCs through the observation of effects (Chapman, Dexter, and Long 1987; Long and Morgan 1991).

Laboratory (e.g., bioassays with *Lumbriculus* or *Nereis* spp.) and field (e.g., caged organisms) bioaccumulation studies provide a means to assess uptake under controlled or more realistic conditions (Lee 1998; Lee et al. 1993, USEPA 1994c). See Section 4.1.1.4.

4.1.2.1 Toxicity testing

Toxicity tests, widely used in the management of aquatic sites in the United States and throughout the world, compose the second leg of the SQT. These primarily laboratory-conducted tests (in situ toxicity tests are also possible) provide a measure of toxicity due to COPCs at a site. Toxicity tests integrate toxic effects of complex chemical mixtures in sediment and do not require knowledge of specific pathways or interactions among sediment and test organisms. Reproductive endpoints, which require chronic test periods, can also be tested.

Advantages of Toxicity Tests

- Provide a measure of toxicity resulting from one or several chemicals at a site.
- Indirect measure of the bioavailable fraction of contaminants.
- Can be conducted using organisms, life stages, and physical conditions of interest a particular site.
- Standardized methods (ASTM, USEPA) provide a legal and scientific precedence for use.
- Are promulgated in several federal and state sediment management programs.
- Can include TIEs to assess COPC responsible for toxicity.

Standard toxicity tests do not distinguish the particular COPC(s) responsible for the observed toxic effect(s). However, if a toxic effect is observed but the COPC(s) is unknown, a sediment TIE may help determine which COPC(s) is responsible for the observed toxic response. Along with bulk sediment chemistry measurements, toxicity tests are required in many state and federal sediment testing programs. As indicated above, these types of tests should be used with caution where the tests may alter chemical conditions such as redox potential, which may be controlling bioavailability in situ.

Types of Toxicity Tests. Various types of sediment toxicity test methods are available (see Appendix C-T3). A few types are listed below:

- Bulk sediment toxicity tests involve the exposure of test organisms to sediments that may contain known or unknown quantities of COPCs. At the end of a specific exposure period, the response of the test organisms is examined in relation to a "measurement endpoint" (e.g., percent mortality, growth, reproduction, etc.). These metrics are then compared to the same metrics from a control and/or reference sediment material to determine relative differences.

- Interstitial pore-water toxicity tests expose aquatic organisms to pore water extracted from sediments. The use of this methodology is based on the assumptions that pore water is at equilibrium with the surrounding sediment, the water phase provides a direct route of exposure to infauna, and the bioavailable fraction in pore water is most responsible for observed toxicity. A positive bulk sediment test and a negative pore-water test (using the same sample and organism) could imply that direct ingestion of sediment is the cause of the toxicity (i.e., COPCs are mobilized in the gut of the organism). It is important to note that the use of aquatic species (e.g., *Daphnia* spp.) is conservative as these sensitive organisms would never be exposed to interstitial pore water.

- Elutriate exposures are typically used for evaluating "potential" toxicity associated with dredged sediment resuspension. Elutriate testing involves mixing test sediment with an aqueous solution and then analyzing the supernatant. Elutriate testing is well defined in the two USEPA/USACE dredged sediment testing manuals for inland and marine water disposal:
    - Inland Disposal Testing Manual (USEPA 1998b) http://www.itrcweb.org/contseds-bioavailability/References/Evaluation-Analytical-methods-USACE-EPA.pdf
    - Ocean Disposal Testing Manual (USEPA 1991) http://www.itrcweb.org/contseds-bioavailability/References/gbook.pdf

In situ toxicity tests have been developed more recently to differentiate toxicity test responses in the laboratory from those conducted in the field. These tests use either surrogate organisms or indigenous species placed in chambers (cages, mesh bags, etc.). Since these chambers are placed in site sediment, organism exposure to sediments, pore water, and overlying waters is maximized. Compared with laboratory conditions, this type of test better represents real-world exposure (which may fluctuate dramatically), reduces sampling/experimental-related artifacts, integrates stressors over time, and allows for more natural interactions of potentially critical physical and chemical constituents. A disadvantage of this test is that impact to the test organisms from nonchemical stressors (e.g., low dissolved oxygen, redox, or high turbidity) are difficult to differentiate from COPC effects. These tests are also more expensive and time-consuming than laboratory toxicity tests.

Disadvantages of Toxicity Testing

- Imply bioavailability but do not provide a measure of which COPC is responsible for the observed toxicity.
- Test results not always translated into chemical cleanup levels.
- Bioavailability can be altered by sample collection, handling, storage, and laboratory exposure.
- Test organisms may not represent indigenous benthic organisms at the site.
- Laboratory test results have inherent limitations in predicting field ecological effects.

Test Organisms. A variety of standard methods have been developed by the USEPA, ASTM, and some states. These tests include exposures to bacteria, algae, macrophytes, macroinvertebrates, and fish. The selection of the organism can have a major influence on the ecological relevance, success, and interpretation of the test results. Furthermore, no one test species is always most sensitive or best suited for all applications over the wide range of sediment characteristics. Some factors to consider in the selection of the test organism(s) include relative sensitivity to the COPC in sediment, biological relevance to the subject site, life cycle, degree of sediment contact, ability to culture/maintain the organism in the laboratory, and tolerance of a wide range of physicochemical conditions. Appendix C-T3 provides citations for the more commonly used bedded sediment, pore-water, and elutriate tests.

It is generally recommended that sediment toxicity tests incorporate two different types of test organisms and at least two measurement endpoints (survival, growth, and/or reproduction). Testing multiple species reduces uncertainty and limits the probability of false positive or false negative results. The importance of testing multiple species increases with the level of ecosystem protection desired and the need to define "significant" contamination in the "gray" zone (marginally contaminated sites) (USEPA 1994a). However, the use of one species with multiple measurement endpoints may be justified if sufficient research has been conducted on the particular COPC. Because the costs of sediment tests are generally equivalent between test species, the choice to reduce the number from two to one test organism can allow twice the number of samples to be tested.

Test Endpoints. The endpoints typically measured with sediment toxicity tests are acute (mortality) and chronic (growth, reproduction, behavior) endpoints. Acute tests can be used to demonstrate a significant exposure and effect at a site but cannot account for sublethal exposure and effects. Concentrations of COPCs in sediments may not cause mortality but may interfere with the ability of an organism to develop, grow, or reproduce. Chronic toxicity test exposures more closely approximate the types of endpoints of concern for organisms in natural environments and can be used to better evaluate potential impacts to benthic communities in moderately contaminated areas (USEPA 1994a). Many state and federal regulatory agencies consider chronic endpoints to be ecologically significant and recommend the use of chronic sediment toxicity tests.

Toxicity Test Results. In most sediment toxicity tests, the organism response to contaminated sediments is compared with the response observed in a both a clean control and a reference sediment. Various methods are available to determine whether a statistically significant difference exists when comparing the results of field samples to reference samples. A detailed description of these statistical methods is beyond the scope of this document. For additional information, please consult USEPA (2002e), CETIS (2006), and Environment Canada (2007).

Toxicity Identification Evaluations. As noted above, one of the disadvantages of standardized toxicity tests is the inability to identify the particular contaminant(s) responsible for eliciting the toxic response observed. This shortcoming makes it difficult to translate toxicity test results into the development of chemical-specific cleanup goals, particularly when sediments are known to contain multiple contaminant classes (PAHs, metals, PCBs, etc.). A methodology termed "toxicity identification evaluation" has been developed to aid in identifying the contaminant responsible for the toxic response. A TIE consists of an iterative series of tests in which various physical/chemical modifications are made to the contaminated sediment that eliminate the potential toxic effects of a class of chemicals. By conducting a series of these tests, the COPC(s) class can be identified. For example, the addition of a carbon source to sediments will tend to sequester HOCs, eliminating or severely reducing their impact on the test species. If the toxic response is not observed with the amended sediments, then the TIE is a good indicator that HOCs are the class of COCS. However, if the impact to the test organism is still present, then another modification is made to further classify the COPC. USEPA (2007b) provides further information on designing and conducting sediment TIEs.

TIEs can be conducted on interstitial water (i.e., pore water) as well as whole sediments. Prior to designing a TIE, a decision should be made as to what medium the TIE will test. The toxicity test results from the manipulated sediment or interstitial water tests are compared to baseline toxicity test results from a sample tested prior to sample manipulation to estimate effectiveness of each sample manipulation in removing toxicity. Removal of sample toxicity by specific manipulations aids in the identification of the probable compound class causing the toxic effect.

Interstitial water TIE methods have been developed to classify five groups of toxicants commonly found in sediments (USEPA 2007b):

- Aeration tests evaluate volatile or easily oxidized toxicants.
- Reverse-phase solid-phase chromatography identifies nonpolar organic toxicants.
- Addition of ethylenediaminetriacetic acid (EDTA) identifies cationic metals.
- Addition of *Ulva lactuca* test or zeolite identifies ammonia.
- Graduated pH manipulation identifies pH-dependent toxicants.

Whole-sediment methods have been developed to classify three groups of toxicants commonly found in sediments (USEPA 2007b):

- addition of *Ulva lactuca* (algae) or zeolite tests for ammonia
- addition of cation exchange resin and sulfide addition tests for cationic metals
- addition of Ambersorb, powdered coconut charcoal, or carbonaceous resin tests for nonionic organic chemicals

4.1.2.2 Macroinvertebrate community surveys

Macroinvertebrates can be defined as invertebrates that are large enough to be seen by the unaided eye, can be retained by a U.S. Standard No. 30 sieve (0.5 mm), and live at least part of their life cycles in or on available substrate in a body of water. They are considered an important biotic component of most aquatic systems and play a significant role in the structure and function of ecosystems, including the processing and transfer of organic material and nutrient cycling. The macroinvertebrate community often represents most of the primary consumer biomass/production in an aquatic system food web, thus serving as the trophic base that supports upper trophic level species (e.g., fish, waterfowl, and other animals) (Thiel and Sauer 1999).

Changes or shifts in macroinvertebrate community composition could have significant implications for higher trophic levels and energy flow pathways in the food web.

Assessments of benthic macroinvertebrate community structure and function are sometimes used to provide evidence of COPC-related effects in the environment and as such provide the third leg of the SQT. In addition, they are practical to assess for the following reasons:

- They are found in most aquatic habitats and are of a size that can be easily collected.
- They have limited mobility and are less able to avoid unfavorable environmental conditions.
- They can be sensitive to both short- and long-term changes in sediment and water quality.
- They can respond to a broad array of potential pollutants.

Methodology. As they relate to ecological assessments, macroinvertebrate surveys are typically conducted to determine whether the sediments at a given location(s) (USEPA 1990; Lazorchak, Klemm, and Peck 1998; Schmitt et al. 1999) are impaired (benthic community alteration) in comparison to a reference/control location (see Appendix C-T6). A survey consists of macroinvertebrate collection and sorting, organism identification, and data analysis. Data analysis often involves the generation of various metrics, including community, population, and functional parameters such as species richness and tolerance indices (Barbour et al. 1999). The metrics selected for use in a survey may be specified by the method or a state/ federal regulatory program. Some of the more common metrics used include total abundance, species or taxa richness, and percent contribution of dominant taxa. Metrics can be integrated simultaneously to derive an index which represents a score (generally a single number) reflecting the overall quality of the area studied. Various benthic indices have been developed in recent years to assess environmental conditions and benthic habitat quality in both fresh and saltwater ecosystems (see Appendix C-T3).

Advantages of Macroinvertebrate Surveys

- Provide an in situ measure of the health of benthic community within an area of concern.
- Integrate interactions of multiple COPCs and not dependent on a single route of exposure.
- Readily related to ecosystem quality (e.g., quality of the prey base for higher trophic organisms that feed on benthos).
- Rapid bioassessment tools available for visual (qualitative) or metric (quantitative) evaluation of benthic integrity.

Disadvantages of Macroinvertebrate Surveys

- Imply bioavailability, but do not provide a measure of which COPC(s) (are) responsible for the observed toxicity.
- Survey results are often confounded by variables not related to COPC toxicity (predation, seasonal differences, physical/ chemical sediment characteristics, food availability).
- Can be difficult to obtain statistical power.

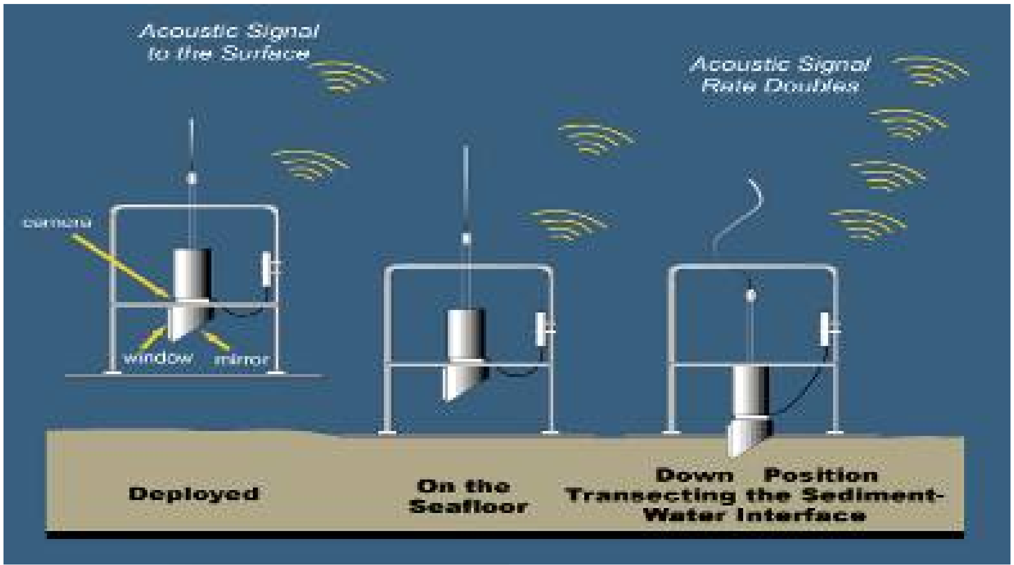
A detailed description of each component of a macroinvertebrate survey is beyond the scope of this document. Be aware that some states (e.g., Maine, Ohio) may have adopted state-specific guidance (Appendix A) tailored to unique habitats/program needs for how macroinvertebrate surveys are to be conducted.

Integration. The results of a well-conducted macroinvertebrate survey can provide direct evidence of impairment and an indirect implication of COPC bioavailability. Typically, macroinvertebrate survey results are used in conjunction with other tools, such as sediment chemistry and sediment toxicity tests (SQT), to provide a measure of ecosystem health. However, the results of a macroinvertebrate survey can also be used as a single line of evidence to determine environmental quality or the need for remediation.

Advanced Tools for Assessing Macroinvertebrate Health. An advanced reconnaissance tool for viewing benthic macroinvertebrate communities is sediment profile imaging (Text Box 4-3). While unable to provide the same level of detail concerning species and numbers present, sufficient studies have been done to be able to demonstrate the link between observed sediment conditions and the quality of the overall benthic infaunal population.

Text Box 4-3. Sediment Profile Imaging

SPI is an optical coring device that works like an upside-down periscope and takes cross-sectional images of the upper 20 cm of the seafloor. SPI has been used for more than 20 years as a tool for a number of benthic parameters, including sediment grain size, depth of the oxygenated sediments (apparent redox potential discontinuity), presence of methane gas bubbles, and placement of dredged or capped material. SPI has been used in dredged material characterization programs for the characterization of populations in contaminated sites, including the Hudson and Housatonic Rivers, a shipyard in San Diego, and at Soda Lake, Wyoming; in characterizing potentially deleterious organic debris at former log float areas or fish processing facilities in Washington and Alaska; and at numerous cap placement remedial programs, including the Eagle Harbor Superfund Site in Washington and the Permanent Shallow Water Habitat in Long Beach, California. Further information on SPI may be found at http://www.csc.noaa.gov/benthic/mapping/pdf/bhmguide.pdf.



4.1.3 Predictive Methods

Predictive methods have been used to estimate the bioavailability of COPCs based on modeling or toxicity identification evaluations. These include the following:

- equilibrium partitioning
- hydrocarbon narcosis model
- accumulation factors
- simultaneously extracted metals–acid volatile sulfide
- biotic ligand model

4.1.3.1 Equilibrium partitioning

EqP is a widely applied model for estimating bioavailability and toxicity to infaunal organisms for nonionic organic compounds (e.g., PAHs, PCBs and pesticides). EqP assumes that equilibrium exists between the COPCs sorbed to the bulk sediment (OC) and the sediment pore water and that toxicity in sediments can be estimated by comparing the derived pore-water COPC concentration to effects concentrations previously measured in water-only exposures (i.e., NRWQC). Considerable evidence concludes that measures of pore-water COPC concentrations more accurately predict toxicity and observed community level effects than do whole-sediment concentrations (Di Toro et al. 1991, 2005a; Di Toro 2008; Hansen et al. 1996; USEPA 1994a, 2003d).

The prediction of the sediment concentration that causes toxicity is based on a single coefficient partitioning model that relates the toxic pore-water concentration to the equivalent sediment concentration (Di Toro 2008). In the EqP model, the observed variation in sediment toxicity is ascribed to the variations in the partitioning between pore water and sediment particles. More complicated models are possible that represent various types of organic matter (e.g., "black" or "soot" carbon) in sediment as well as the occurrence of dissolved OC in water; however, the EqP model results are easily compared to water-only effects concentrations and frequently provide a better indication of potential toxicity than the traditional approach of comparing bulk sediment concentrations to a sediment screening level concentration (i.e., sediment quality criteria [SQC]). Since pore-water concentrations derived from bulk sediment concentrations are easy to calculate, the comparison of derived pore-water concentrations to effect-level concentrations is often used as a second-tier analysis if bulk sediment concentrations exceed SQGs.

Nonionic COPCs are assumed to partition to bulk sediment OC. The pore-water concentration (C_{pw}) is predicted from the measured bulk sediment concentration (C_{sed}) and TOC. In this regard, estimation of a site-specific K_{oc} is beneficial in that it effectively incorporates the various organic matter phases present in the sediment as well as the site-specific influence of DOC levels. Values in the literature for the K_{oc} of a specific chemical can vary due to the presence of multiple carbon phases. For example, Hawthorne et al. (2007) have shown that actual pore-water concentrations of PAHs can be overestimated by up to three orders of magnitude by using the EqP approach to derive pore-water concentrations. This error is due to the presence of anthropogenic carbon (e.g., soot or black carbon) in many sediments near urban and/or industrial systems, which have been shown to more tightly sequester HOCs than naturally occurring sediment OC. For this reason, USEPA (2003d, n.d. "Bioavailability") has indicated that direct measures of pore-water PAHs are more accurate than derived pore water in sediments. Modifications to the EqP model have been made which include an anthropogenic carbon phase in addition to the fraction of naturally occurring OC (EPRI 2009). However, it has been shown that even this addition to the predictive EqP model may not provide accurate estimates of actual pore-water concentrations when compared to toxicity tests using *Hyalella azteca* (McDonough and Azzolina n.d.).

Equilibrium Partitioning Calculation Example:

Calculation of pore-water concentration from sediment concentration. EqP is used to calculate C_{pw} of nonpolar organic compounds based on C_{sed}. The sediment-water partition coefficient (K_p) relates these two compartments through the following equation:

$$C_{pw} = C_{sed}/K_p$$

The K_p value is derived from the compound's K_{oc}, which can be obtained from published sources (see USEPA's EPI Suite quantitative structure activity relationship program, www.epa.gov/opptintr/exposure/pubs/episuite.htm) and the following USEPA ESB documents: PAHs—USEPA 2003d, nonionic organics—USEPA 2008b, and pesticides (dieldrin and endrin)—USEPA 2003c. In addition, K_{oc} values can be derived from published octanol-water partition coefficients. The K_p value is the K_{oc} adjusted by the fraction of organic carbon (f_{oc}) in the sediment:

$$K_p = K_{oc} * f_{oc}$$

Calculation of potential toxic effect based on pore-water concentration. Pore-water concentrations are compared to water quality criteria to indicate whether they might pose a threat of impact to benthic invertebrates. The appropriate water quality criteria are final chronic values (FCVs), which are listed in the USEPA ESB documents (2003d, 2005c, and 2008b). The comparison of pore-water concentrations to the FCV is a ratio called a toxic unit (TU), where

$$TU = C_{pw}/FCV$$

TUs are calculated for each individual compound in the sample (Table 4-3) , and then these TUs are summed into a final TU value. A TU of <1 indicates no probable toxicity; a TU of >1 indicates potential toxicity. An example calculation for PAHs in a sediment sample containing 1% TOC (f_{oc} of 0.01) shows that all individual PAH TUs are <1; however, the summed TU is >1, indicating potential toxic effects.

Table 4-3. Calculation of potential toxic effect based on pore-water and sediment concentration

Chemical	C_{sed} (mg/kg)	K_{oc} (L/kg)	K_p[a] (L/kg)	C_{pw}[b] (µg/L)	FCV (µg/L)	TU[c]
acenaphthene	0.29	8.79E+03	8.79E+01	3.29	55.8	0.06
acenaphthylene	0.28	1.47E+03	1.47E+01	19.1	307	0.06
anthracene	1.75	2.87E+04	2.87E+02	6.11	20.7	0.29
benz[a]anthracene	2.88	3.77E+05	3.77E+03	0.76	2.23	0.34
benzo[a]pyrene	3.77	1.01E+06	1.01E+04	0.37	0.96	0.39
benzo[b+k]fluoranthene	5.58	1.49E+06	1.49E+04	0.37	0.65	0.58
benzo[ghi]perylene	2.55	2.49E+06	2.49E+04	0.10	0.44	0.23
chrysene	4.47	4.13E+05	4.13E+03	1.08	2.04	0.53
dibenz[ah]anthracene	ND	ND	ND	ND	ND	ND
fluoranthene	5.85	9.95E+04	9.95E+02	5.88	7.11	0.83
fluorene	0.34	1.37E+04	1.37E+02	2.52	39.3	0.06
indeno[1,2,3-cd]pyrene	3.61	4.06E+06	4.06E+04	0.09	0.27	0.32
naphthalene	0.20	1.99E+03	1.99E+01	9.83	193	0.05
perylene	1.42	1.07E+06	1.07E+04	0.13	0.90	0.15
phenanthrene	3.18	3.12E+04	3.12E+02	10.2	19.1	0.53
pyrene	5.20	6.90E+04	6.90E+02	7.55	10.1	0.75
Sum	41.38					5.18

[a] $K_p = K_{oc} * f_{oc}$
[b] $C_{pw} = 1{,}000 * C_{sed}/K_p$
[c] $TU = C_{pw}/FCV$

The relationship between sediment, pore water, and biota is described schematically in Figure 4-3. Note that the organisms are not assumed to be at equilibrium—the arrows to the biota are unidirectional, and the pore water and sediment particles are assumed to be at equilibrium. In addition, COPCs associated with suspended particulates or DOC are in equilibrium with the bulk-sediment and pore-water phases. The assumption for this model is that pore water is a good representation of the chemical activity of the compound in the system and therefore is assumed to be representative of all routes of exposure to benthic organisms. However, an important issue with deposit-feeding organisms is whether conditions in the gut of the organism modify the chemistry sufficiently so that ingested sediment cannot be assumed to be in equilibrium with pore water (COPCs may be more bioavailable from ingestion of sediment than from pore water).

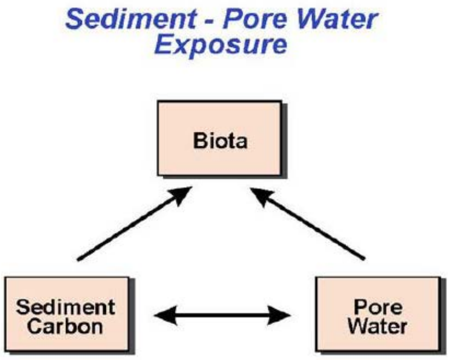


Figure 4-3. Schematic of the relationship of EqP in sediment, pore water, and biota. (Adapted from Di Toro 2008).

4.1.3.2 Target lipid narcosis model

Narcotic chemicals are those that exhibit nonspecific effects on organism behavior (i.e., no target organ or specific site of toxicity is observed), and therefore their effects upon an organism are additive (USEPA 2003d). The target lipid narcosis model assumes that mortality will occur at a threshold level of a chemical in the organism's lipid phase.

Narcosis theory is used to predict pore-water concentrations that cause acute toxicity to the organism from a particular chemical. While this is not a direct method for collecting pore-water data, it is a method used to evaluate pore water toxicity. The hydrocarbon narcosis model is one of the methods used to characterize sediment toxicity of nonionic organic compounds based on pore-water concentrations. The acute toxicity values are then converted to concentrations that are indicative of chronic toxicity, referred to as final chronic values. The FCVs are then compared to a particular site's pore-water chemical concentrations to indicate the potential for toxicity, where

- pore-water concentration < FCV indicates no toxicity
- pore-water concentration > FCV indicates potential for toxic effect

The ratio of pore-water concentration to the FCV is termed a "toxicity unit." Risk to the benthic community from narcotic chemicals can be evaluated using an additive TU approach (see Table 4-3 above). Narcotic chemicals often found in sediments include PAHs (USEPA 2003d) and 32 other nonionic organic compounds (USEPA 2008b).

4.1.3.3 ∑SEM – AVS

Bioavailability of some cationic metals in most anoxic sediments can be predicted by measuring the 1:1 relationship (in µmoles) between AVS and SEM (total SEM = sum of cadmium, copper, lead, nickel, silver and zinc). Both AVS and the sum of the SEMs (∑SEM) are liberated from wet sediment samples when treated with cold 1N HCl (hydrochloric) acid in the laboratory. The difference, termed "∑SEM – AVS," is a useful tool for predicting metals bioavailability and toxicity (or lack thereof) to benthic organisms in sediments (Di Toro et al. 1990, Hansen et al. 1996, USEPA 2005c, Di Toro 2008).

Earlier literature cites the ratio of ∑SEM to AVS (i.e., ∑SEM/AVS). More recent literature, however, expresses the difference between ∑SEM and AVS (i.e., ∑SEM – AVS). The advantages to using ∑SEM – AVS are that it does not get very large when AVS is very low and that it can be modified to develop partitioning relationships that include other phases such as TOC (Di Toro et al. 2005a, 2005b).

The ∑SEM – AVS model is predicated on the same premise as the EqP model, i.e., the toxicity of metals in the sediment is directly related to its equilibrium between activity in sediment and the pore water. For cationic metals, however, solubility is theoretically governed by the strong complexation of cationic metals by sediment sulfides. By comparing the molar quantity of ∑SEM and AVS in a sediment sample, a measure of the bioavailable metal fraction can be estimated (Di Toro et al. 1990), where

- ∑SEM – AVS <1 indicates the ∑SEM are bound to sulfide (sulfide is in excess) and are therefore not bioavailable.

- ∑SEM – AVS >1 indicates the ∑SEM exceed acid soluble sulfide concentrations and therefore may be bioavailable.

Under the reducing conditions often found in sediments (typically higher in sulfate-rich brackish or marine waters), metals bioavailability is reduced as a result of precipitation of metals as insoluble sulfides (Text Box 4-4) because the solubility product constants for most metal-sulfide associations are very high and exchange from metal sulfides to water is low (NRC 2003, USEPA 2005c).

Text Box 4-4. (∑SEM – AVS)/f_{oc} Example Calculation

The calculation of (∑SEM – AVS)/f_{oc} is performed to determine whether potentially toxic divalent metals (cadmium, copper, lead, nickel, zinc and silver) are tightly sequestered by naturally occurring sulfides in surface sediment. An excess of AVS will ensure that the bioavailability of metals (and the probability for toxicity) is low; an excess of SEM may indicate the potential for toxicity, unless the sediment fraction of TOC is enough to act as another binding phase to bind metals that are not bound by AVS. The following data is from actual sediment samples obtained from the laboratory analysis of upper (0–3 feet) core samples in the Lower Hudson River (salinity ~10 ppt).

	Laboratory Results[a]						Calculations			
Location	Cu	Ni	Pb	Zn	AVS	TOC (mg/kg)	∑SEM (µmol/g)	∑SEM – AVS (µmol/g)	fOC (g/g)	∑SEM – AVS/f_{oc} (µmol/g)
Station A	10.1	1.4	1.7	13.3	41.0	27100	26.5	-14.5	0.027	-535.1
Station B	0.8	0.3	0.3	2.0	5.8	29600	3.4	-2.4	0.030	-81.8
Station C	25.2	0.2	0.7	2.9	7.0	18000	29.0	22.0	0.018	1219.4

[a] Units: metals and AVS = µmoles/g; TOC = mg/kg.

The laboratory results for individual metals required to calculate SEM, as well as AVS, are always reported as µmol/g of sediment (cadmium and silver were below the reporting limits for SEM). The results for TOC are reported as mg/kg.

The first step is to add all of the SEM metals to obtain a sum of the SEM (∑SEM). The result obtained for AVS is then subtracted from the ∑SEM. The next step is to divide the TOC result (reported as mg/kg) by 1,000,000 (mg/kg) to obtain f_{oc} (g/g). The ∑SEM – AVS difference is then divided by f_{oc}.

Per the USEPA ESB metals mixtures guidance (2005c), if the result is <130 µmol/g_{oc}, then toxicity to benthic invertebrates is not anticipated (Samples A and B). If the result is >3000 µmol/g_{oc}, then toxicity is likely (no samples exceeded this criterion in the above example). If the result is between 130 and 3000 µmol/g_{oc}, then toxicity is uncertain (Sample C).

The ∑SEM – AVS model is most useful in identifying conditions in which sediment toxicity is unlikely to occur. The ∑SEM – AVS paradigm has therefore been shown to be accurate predictors of the *absence* of mortality in sediment toxicity tests (Di Toro et al. 1990, Hansen et al. 1996, USEPA 2005c). At the time of the development of the ∑SEM – AVS paradigm, predictions of the actual toxicity in laboratory-spiked or field sediments were less accurate.

This uncertainty was later addressed by the valuable insight that the fraction of sediment organic carbon (f_{oc}) also plays a major role in the binding of excess divalent metals (Mahoney et al. 1996, USEPA 2005c). It was determined that when the ∑SEM – AVS was normalized by dividing by the f_{oc}, toxicity is likely when the (∑SEM – AVS)/f_{oc} is >3000 µmol/g_{oc}, uncertain when the concentration is 130–3000 µmol/g_{oc}, and not likely when the concentration is <130 µmol/g_{oc} (Figure 4-4).

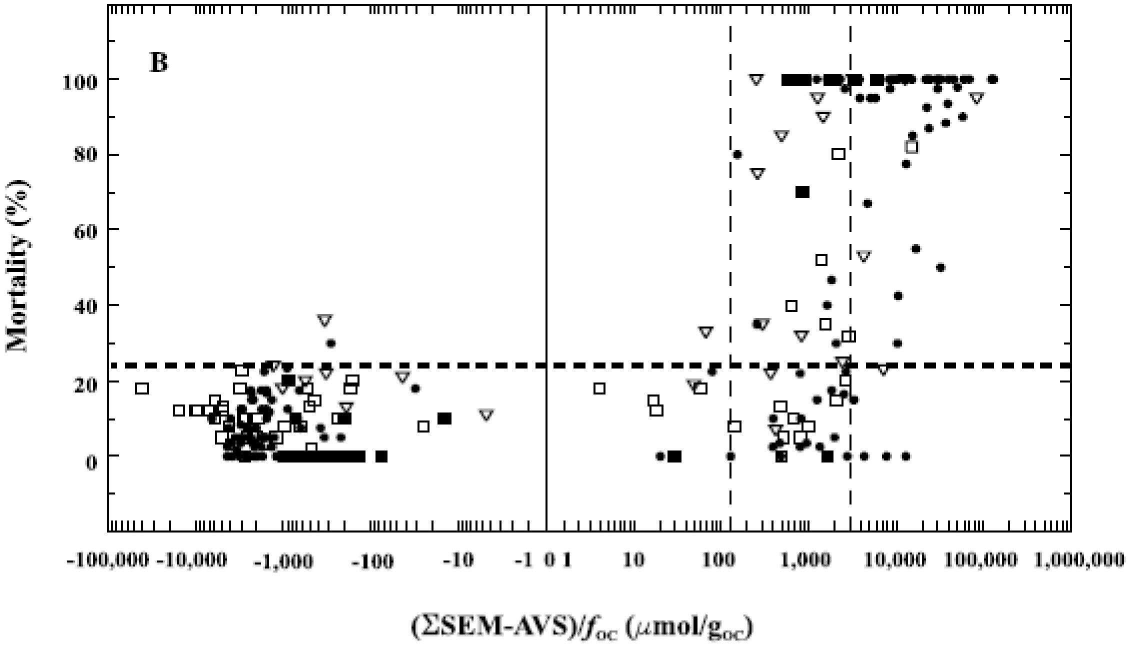


Figure 4-4. Relationship between (∑SEM – AVS)/f_{oc} and benthic immortality for both field and spiked sediments. (*Source:* USEPA 2005c)

A major uncertainty with ∑SEM – AVS is that even under reducing conditions, direct uptake of metal does occur in some infaunal species after ingestion of the various metal forms found in sediments, including metal sulfides (Luoma and Jenne 1977, Lee et al. 2000). The AVS method assumes no contribution to exposure from dietary metal uptake from either sediments or other food sources. Lee et al. (2000) showed that assimilation from diet was the best explanation for the poor correlation observed between measured cadmium, zinc, and nickel bioaccumulation by five different benthic species and the ∑SEM – AVS predictions (NRC 2003).

∑SEM – AVS also assumes that reducing conditions will be constant (i.e., reducing conditions at time of sampling must remain stable into the future). AVS, however, varies both spatially and seasonally. ∑SEM – AVS considerations are most applicable in sediment environments characterized by high levels of sulfate (e.g., estuarine or marine environs) and/or organic matter where bacterial activity can be expected to minimize oxygen penetration into the sediments, typically generating stable anoxic, reducing conditions (e.g., palustrine wetlands with seasonal die-off). The model does not account for potential dissociation during oxidation of the metal sulfide complexes (and thus increased bioavailability) that may occur with resuspension events nor the subsequent potential reformation of metal sulfides. An adequate modeling framework is needed that addresses the permanence issue, i.e., whether metals that are bound as metal sulfides can be considered to pose no reasonable risk even under changing conditions.

4.1.3.4 Biotic Ligand Model

The biotic ligand model (BLM, Figure 4-5) for cationic metals is also predicated on the same premise as the EqP and ∑SEM – AVS models for dissolved constituents (Di Toro et al. 2005b), in that the toxicity of a constituent in the sediment is directly related to the equilibrium concentration in the pore water. The BLM strictly addresses metals but involves an extensive set of equilibrium considerations to estimate the free metal (truly dissolved) concentration in pore water in relation to available biotic (and abiotic) ligands. Additionally, and this is an important distinction from other pore-water models, the model also incorporates biotic uptake as an equilibrium process and not a one-way exchange. Thus, ligand (absorbing) sites of an organism compete for the available free ion much as inorganic ligands (e.g., hydroxide or bicarbonate) and organic ligands (e.g., humic acids) do. Major and minor inorganic ligands may vary in importance from metal to metal. In other models, organic ligands in dissolved and sediment-bound forms are treated as a single organic matter ligand pool. Additionally, the model also deals with other (non-COPC) ions that compete for the biotic ligand sites (e.g., sodium and calcium), incorporating the parameter of hardness to compete with the uptake of the metal ion of concern.

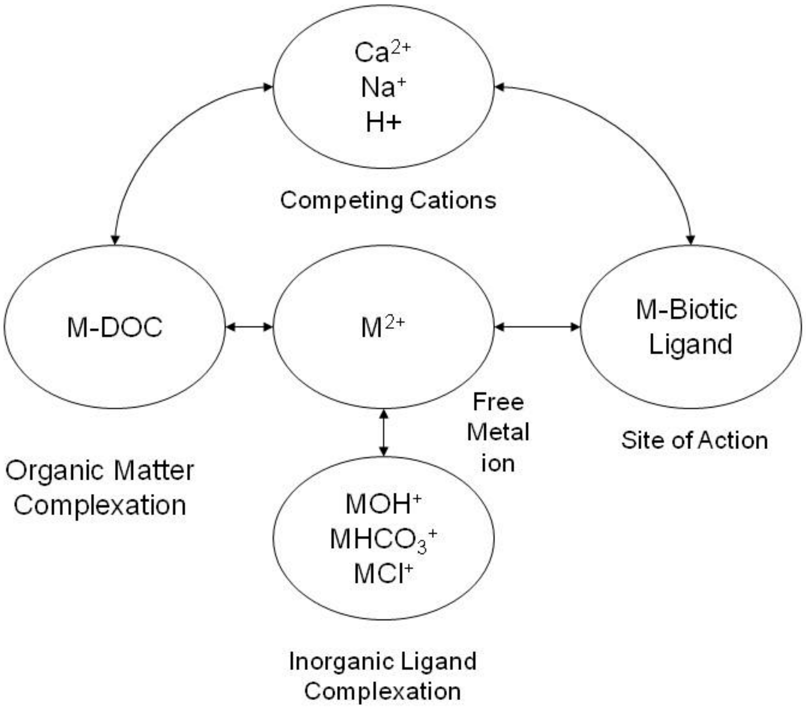


Figure 4-5. Schematic diagram of the biotic ligand model. (*Source:* USEPA 2003a)

These additions add a significant level of complexity to the model, as it is now necessary to approximate all dissolved forms of a metal as well as estimate the equilibrium "dissociation" constant for the biotic ligands. In some instances several ligand sites are suggested by the data, each with its own constant. Estimation of the biotic ligand equilibrium coefficient must also take into account the factors that affect inorganic and organic ligands, pH, ionic strength, temperature, and other solution-related parameters.

Recent work (Di Toro et al. 2005b, USEPA 2003a) suggests that a sediment-based BLM can be developed that will avoid some of the complexities in estimating the details of pore-water chemistry. Recent applications suggest that published results may be applied across multiple sites while biotic ligand equilibrium constants are developed for various species.

The development of the sediment BLM showed that the median lethal concentration on a sediment OC–normalized basis was essentially unchanged over a wide range of concentrations of pore-water hardness, salinity, DOC, and any other complexing or competing ligands. The sediment BLM showed that the most important factor affecting bioavailability of divalent cationic metals was the pore-water pH.

4.2 Application of Bioavailability Tools in Risk Assessment and Risk Management

This section is based on case study examples of how bioavailability tools and related measurements have been integrated into the sites' risk assessment and risk management phases protecting benthic organisms. Although COPCs may not be bioavailable to benthic organisms in toxic amounts, this condition does not imply that they are not bioavailable and potentially transferable through the food chain. The potential for biomagnification to higher trophic level organisms should be identified in the CSM and planned for in the risk assessment. Assessment of bioavailability to higher trophic level organisms is covered in subsequent sections of this guidance. The tools described in this chapter identify the concentrations of COPCs that have the potential to move into the base of the food chain. These data can then be used for subsequent modeling to assess risk to upper trophic level receptors.

At a minimum, bulk sediment chemistry analyses should be conducted at all sites. If sediment concentrations are above their respective screening values, then a second tier of sampling and analysis can be conducted, which can more specifically include bioavailability. These analyses may include site-specific chemistry endpoints (e.g., pore-water chemistry), sediment toxicity testing, and macroinvertebrate surveys. As mentioned previously, these three steps (chemistry, toxicity, and macroinvertebrate surveys) represent the Sediment Quality Triad (Long and Chapman 1985, Chapman 1996). It should be noted, however, that benthic macroinvertebrate surveys are highly dependent on the habitat conditions and may reflect differences in physical/chemical sediment properties that are not associated with the site-specific COPCs.

Source of Toxicity

Stressor identification is the process of identifying the cause of an apparent toxicity response. Toxic responses in benthic invertebrate bioassessments may be caused by the following:

- contaminants
- noncontaminant constituents (e.g., ammonia, sulfides)
- physical disturbances (e.g., low oxygen, hydraulic disturbance)

A process for identifying the source of toxicity could include the following:

- statistical correlations between chemical sources of toxicity and results
- gradient analysis between chemical sources of toxicity and toxicity results
- toxicity identification evaluation
- pore-water measures
- verification using spiked sediment bioassays and/or organism transplant

An example of a tiered approach is in the assessment of sediment PAH contamination. USEPA recently indicated that PAH effects to benthic organisms should be evaluated in the following tiered approach (Burgess 2009):

1. Assess PAH bioavailability based on bulk sediment analysis (including comparisons to SQGs and the use of EqP to estimate pore-water concentrations for comparison to FCVs).
2. Assess PAH bioavailability based on the analysis of interstitial water (i.e., direct measure of pore-water PAHs) and compare to FCVs).
3. Assess PAH bioavailability based on aquatic toxicity testing (i.e., amphipod acute and chronic tests).

Successive tiers are evaluated only if the previous tier indicates a potential impact to benthos. In this case, successive tiers provide a higher level of certainty in the bioavailability analysis.

As identified previously in this document, there are three principal areas where bioavailability data gathered during assessment activities can be used to make informed risk management decisions at a contaminated sediment site:

Assessing Bioavailability to Benthic Invertebrates

- Determine whether bulk sediment chemistry measures exceed SQGs or promulgated state standards.
- If these are exceeded, then compute COPC bioavailability using spreadsheet models of partitioning (EqP) or sequestration (SEM/AVS).
- If these are exceeded, then one or more of the following can be evaluated:
  - pore-water chemistry using active or passive pore-water samplers
  - laboratory sediment toxicity tests using site-appropriate organisms and conditions
  - benthic macroinvertebrate surveys
  - tissue analysis from field-collected organisms
  - infer bioavailability in laboratory bioaccumulation exposures

- risk assessment
- remedy selection
- remedial design/implementation/monitoring
  - environmental dredging and monitoring
  - monitored natural recovery
  - long-term monitoring of cap performance

This guidance focuses on only the risk assessment phase; however, some of the case studies include discussion of bioavailability in the context of remedy selection and remedial design and implementation. A follow-on ITRC project and guidance will address remedy selection/design/implementation and monitoring.

4.2.1 Bioavailability in Risk Management

Risks are identified in the risk assessment based on exposure and effects assumptions. It is in the risk management stage where the decision maker must determine whether the information presented is sufficient to warrant an immediate remedial action or the overall evidence suggests that conditions exist that ameliorate the immediate concerns about risks. A good risk characterization articulates major assumptions and uncertainties, identifies reasonable alternative interpretations, and reaches scientific conclusions (USEPA 1998c). Bioavailability data can reduce uncertainty by providing more relevant information on exposure concentrations. This leads to a more realistic exposure assessment as compared to the conservative assumptions derived from bulk sediment chemistry alone.

Bioassessments are useful for identifying biological impairments, but they cannot identify the underlying causes of impairments. Stressor identification is needed to ensure that an impacted site is being cleaned up for the appropriate stressor (COPC) to protective levels. Other factors can influence toxicity tests or benthic macroinvertebrate community surveys. Nonpollutant constituents such as excessive detritus or organic materials, ammonia, phosphorous, sulfides, or microbial pathogens can directly influence toxicity tests and benthic community surveys. Chemical and physical factors such as changing salinity, low oxygen, very fine or coarse grain size, or hydraulic conditions (e.g., flood scouring or deposition, propeller wash) can also influence bioassessments.

USEPA (2000c) developed a general guidance document for the identification of stressors and has been the leader of development and use of TIEs in water and sediments. California has developed guidance for achieving SQOs in bays and estuaries that includes a description of a sequential series of actions initiated when SQOs are not met (California EPA 2009). These include stressor identification and use many of the tools to assess bioavailability previously discussed in this section.

In the case studies that follow, some or all of the stressor identification processes discussed previously were used to evaluate benthic exposure.

4.2.1.1 Vandenberg Air Force Base Site 5 Cluster (Bear Creek and Pond), California

The simplest example of toxicity source identification is conducting toxicity tests where bulk sediment measurements exceed the SQGs. At the Vandenberg site, the sediment investigation focused on a small freshwater creek and terminal pond that were contaminated with metals from former rocket-launching activities. The only risk pathway of concern was toxicity to benthic organisms. Bulk sediment chemistry analysis detected metals concentrations in sediment that approached or exceeded the SQGs. The California state regulatory agencies and the Air Force elected to conduct sediment toxicity tests with the amphipod *Hyalella azteca* to determine whether these metals were bioavailable at toxic levels. Sediment toxicity testing demonstrated that site sediments were not toxic, and as a result the site received a no further action (NFA) determination from the regulatory agency.

4.2.1.2 Lower Fox River, Wisconsin

The Lower Fox River and Green Bay Superfund Site in Wisconsin is principally a PCB-contaminated site, although other contaminants (e.g., PAHs, mercury, dioxin) were identified in the sediments of the river and bay. While multiple receptors (ecological and human) were evaluated, a comprehensive assessment of bioavailability to benthic organisms was conducted during the sediment remedial investigation.

For benthic infauna, calculated hazard quotients (HQs) based on PCB SQOs were high. Benthic infaunal community analyses showed that the system was largely dominated by pollution-tolerant oligochaetes and chironomids but that the system was recovering in place. Bioassays on bulk sediment samples collected from the same locations as benthic infaunal samples showed toxicity using the amphipod *Hyalella azteca*, the oligochaete *Lumbriculus variegatus*, the chironomid *Chironomus riparius*, and the mayfly *Hexagenia limbata*. Pore-water toxicity was also observed in acute and chronic bioassays on algae (*Selenastrum capricornutum*), invertebrates (*Ceriodaphnia dubia*), bacteria (*Photobacterium phosphoreum*), and fish (fathead minnow, *Pimephales promelas*). Measured body burdens in native infauna showed uptake of PCBs but not dioxins or PAHs. The results of the above studies would suggest that PCBs were impacting benthic resources. However, a TIE conducted on sediments from Operable Unit (OU) 4 and Green Bay demonstrated that ammonia, not PCBs, was responsible for most of the observed effects (Ankley, Katko, and Arthur 1990). The use of TIE testing determined that ammonia was most responsible for the benthic toxicity observed and that the PCBs did not play a major role in benthic toxicity.

This case study highlights how bioavailability testing, specifically using TIE, was helpful in that PCBs were identified as being “unavailable” to benthic organisms and were not the primary cause of benthic toxicity. Ultimately, this information factored into the USEPA record of decision (ROD) as the remediation for sediments was not based on the protection of the benthic community but rather on the protection of human health and upper trophic level receptors.

4.2.1.3 Myrtle Street Embayment, Lower Duwamish Waterway, Washington

The Lower Duwamish Waterway Superfund Site investigation focused principally on bedded-sediment contamination, but the site is also considered to be impacted by continuing releases to the system from surface water and subsurface groundwater discharges. Groundwater releases were principally evaluated by sampling seeps during low-tide sequences and by placing piezometers and peepers in the sediment. These approaches were not effective at all locations due to the need for rapid characterization over tidal cycles at a finer spatial grade. Peepers placed subtidally were also not thought to adequately capture volatile organic compounds (VOCs) at one particular site, the Myrtle Street Embayment Study Area.

Two overlapping discharging solvent plumes were identified at the Myrtle Street Embayment, a shallow aerobic plume that was mostly tetrachloroethene (PCE) and trichloroethene (TCE) and a deeper anaerobic plume of daughter compounds such as dichloroethene (DCE) and vinyl chloride (VC). Wells located 50 feet inland indicated that the plumes ranged from the top of the aquifer (at about 10 feet below ground surface [bgs]) to more than 45 feet bgs. The groundwater well concentrations were up to 1000 times groundwater cleanup levels while in seep samples concentrations were up to 100 times cleanup levels. However, as the freshwater plume encountered the tidal salt water wedge, the groundwater discharge area narrowed and rose over the wedge. In the process, the discharge area where benthic infauna would be exposed narrowed to about 10 vertical feet from 35 vertical feet. USEPA and the Washington Department of Ecology were concerned that the “worst” groundwater was discharging deeper in the waterway and therefore polluting the sediments.

Diver-placed diffusion samplers, GORE Modules were used to characterize the discharge to the embayment through localized seeps and generalized upwelling beneath the embayment. GORE Modules consist of GORE-TEX membrane tubes housing hydrophobic adsorbents which capture and measure VOCs and semivolatile organic compounds (SVOCs). These groundwater samplers (ITRC 2007, USEPA 2000b) were deployed in a systematic close-grid fashion across the embayment, known seeps, and potential critical discharge areas (Figure 4-6). Sampled over multiple tide cycles, the samplers were able to identify an expanded seep discharge face near the top of the saltwater wedge but demonstrated lack of a subtidal embayment discharge.

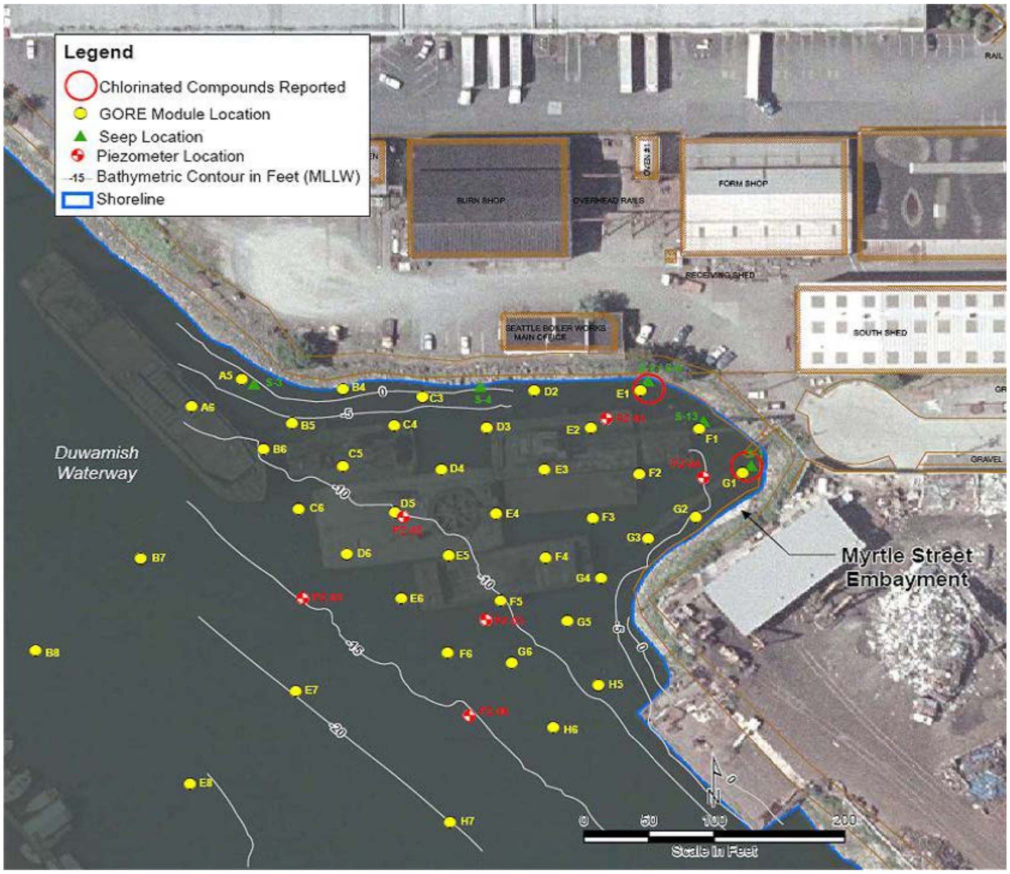


Figure 4-6. GORE Module and seep locations, Phase 1: Embayment-wide sampling event.

The results demonstrated there was no complete transition from groundwater to the bioactive layer of the sediment zone. Therefore, a complete exposure route did not exist between the contaminated groundwater seeping into the bay and the estuarian benthic community. The investigation showed an incomplete exposure pathway to subtidal organisms and, although a direct measure of bioavailability could not be discerned, the lack of detection of constituents of potential ecological concern (COPECs) by the GORE Modules did prove the null hypothesis, i.e., that potential receptors were not exposed and that there was therefore no risk to these receptors or their predators in the waterway. Without the investigation, the discharge area would have been assumed to be lower and more diffuse than it actually was, making it likely that additional biological sampling would have been placed in areas where exposure was limited.

4.2.1.4 Indian River Power Plant, Delaware

Cleanup levels based on the EqP-TU approach were calculated for intertidal sediments contaminated with NAPL and dissolved-phase diesel-range organics that resulted from a diesel fuel spill from a leaking underground pipeline into the Indian River sediments. The pipeline was taken out of service, and a sheet pile wall with sealed interlocks was installed to preclude the future migration of residual oil into the river sediments. Subsequent investigation work consisted of identifying the extent of impact, assessing risk to aquatic receptors, implementing a remedial action, and restoring the shoreline.

For each sample collected during the investigation of impact extent, bulk sediment chemical measures of PAH parent compounds and alkylated homologs were first normalized to the TOC concentrations at each corresponding sample point. Pore-water concentrations of these compounds were then predicted using EqP and were subsequently divided by analyte-specific acute and chronic values calculated from narcosis theory. For each sample, the TUs for individual compounds were summed to yield total acute and chronic TUs. TUs >1 indicated that pore-water exposure concentrations were potentially high enough to cause toxicity to benthic organisms. The state required excavation of all sediments with chronic TUs >1, which corresponded to a total PAH cleanup criterion of 2 mg/kg. In total, approximately 480 cubic yards of sediment was ultimately removed from the Indian River shoreline, and confirmatory samples indicated that the calculated cleanup criteria were met. Excavated sediments were replaced with clean material of similar grain size composition and were allowed to be naturally reworked and contoured over several tidal cycles prior to revegetation efforts.

A long-term monitoring program was subsequently established to ensure that the remedial efforts would remain protective of ecological receptors and included regular visual site inspections to monitor erosion and health of vegetation, photo-monitoring of vegetative growth and site development, vegetation sampling for various parameters, and sediment sampling for PAHs and TOC.

4.2.1.5 Onondaga Lake, New York

Site-specific remediation goals for the protection of benthic infauna were developed for the Onondaga Lake Superfund site. COPCs in lake sediments included benzene, toluene, ethylbenzene, xylenes, chlorinated benzenes, mercury, PAHs, PCBs, dioxin, and dibenzofurans. Separate preliminary remediation goals (PRGs) were developed for benthic, wildlife, and human health protection. Site-specific sediment effects concentrations (SECs) were developed for the protection of benthic infauna, as well as bioaccumulation-based sediment quality values (SQVs) for the protection of wildlife and preliminary remediation goals for fish. Tools employed to develop the SECs included bulk sediment chemistry, pore-water chemistry, toxicity testing, macroinvertebrate surveys, and tissue chemistry.

The sediment PRG was based on five site-specific SECs and one published PEC for the COPCs identified in the risk assessment. The SECs and PECs were calculated using data from paired sediment chemistry and acute sediment toxicity tests with *Chironomus tentans* and *Hyalella azteca*. Since the results for *C. tentans* were found to be the more sensitive test, these toxicity data were then used to develop the following five site-specific SECs: ER-L, TEL, ER-M, PEC, and AET. The geometric mean of these five Onondaga Lake SECs was calculated to provide a single consensus-based PEC for each COPC. For mercury, the PEC was calculated at 2.2 mg/kg.

4.2.1.6 Soda Lake, Wyoming

An NFA determination was reached for a former refinery evaporative pond at Soda Lake near Casper, Wyoming (see Text Box 4-5). From 1958 to 1990, Standard Oil built and operated a settling pond and evaporative basin to receive residuals from its oil refinery in Casper. After 1990, an estimated 1.7 million gallons per day (mgd) of water from the North Platte River were pumped to the lake to maintain the aquatic habitat for the over 300 species of birds, including 19 threatened and endangered (T&E) species that used the lake for migratory feeding and nesting. Other important species included red fox, wolverine, mink, prairie dog, and pronghorn antelope.

Subject to a Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) under the direction of the Wyoming Department of Environmental Quality (WDEQ), the levels of VOCs, PAHs, and metals in the retention pond sludge were sufficiently elevated to warrant removal and disposal at a Corrective Action Management Unit. The RFI included ecological metrics at CSM-identified trophic levels, all of which contributed to the NFA for the evaporative basin. For benthic-related effects, the following measures contributed to the decision.

Text Box 4-5. Case Study: Soda Lake, Wyoming

COCs at Soda Lake were principally PAHs, VOCs, metals, and selenium. After conduct of the RCRA facilities investigation and corrective measures study, the WDEQ-selected remedy included closure of the Inlet Basin by removal of all contaminated sediments to a Corrective Action Management Unit and an NFA for the Main Lake. The NFA was determined based on extensive measurements used to evaluate bioavailability:

- bulk sediment chemistry
- pore-water chemistry
- groundwater flow and chemistry
- surface-water chemistry
- bedded sediment toxicity testing
- EqP evaluations
- benthic and epibenthic surveys
- sediment profile imaging
- submerged or emergent aquatic vegetation
- benthic fish
- avifauna
- mammals

Triad Analysis. Triad sediment surveys suggested a potential impact from refinery residuals in the main lake. Sediment COPCs exceeded SQGs for PAHs, xylenes, phenol, and metals. Solid-phase bioassay testing was conducted to measure acute and subchronic toxicity of surface sediments. Low-level toxicity was observed for some stations, but toxicity was not correlated with chemical concentrations. In addition, when bioassays for some of the observed toxic stations were repeated, no toxicity was observed. Quantitative benthic surveys within the Main Lake showed low diversity but high abundance. An SPI survey confirmed the low diversity throughout the lake but also showed low dissolved oxygen levels. Qualitative assessments of epibenthic invertebrates showed a rich and diverse assemblage, including organisms that are important as prey for birds: insect larvae in the orders *Odonata*, *Ephemeroptera*, and *Plecoptera*, in addition to water fleas (*Daphnia pulex*), callenoid copepods, and amphipods (*Hyalella azteca*).

Bioavailability Assessment. COPCs measured in sediment pore water included acetone, phenol, carbon disulfide, and metals. Acetone was believed to be a laboratory artifact, and metals were shown to occur at background levels. Bulk sediment total PAHs were compared to total PAH threshold effect criteria (Swartz 1999), and no exceedances were observed. EqP was used to calculate maximum pore-water concentrations from observed bulk sediment concentrations. Even after applying a highly conservative 16-fold factor to account for unmeasured alkyl PAH compounds, predicted PAH TUs were <1.0. In surface water, organic COPCs were measured above their detection limits, but metals other than selenium were below NRWQC. Selenium levels were not an issue for benthic organisms but were addressed for higher trophic level receptors, including fish, birds, and mammals.

4.2.1.7 Tectronix Wetlands, Beaverton, Oregon

An NFA was determined for a reach of Beaverton Creek in Oregon based on results from bulk sediment chemistry, toxicity testing, and ∑SEM – AVS comparisons (see Appendix C). Historic operations at the Tektronix, Inc. site resulted in releases of metals that exceeded Oregon Department of Environmental Quality (ODEQ) Level II screening level values (SLVs) for freshwater sediments. Additional characterization of the sediments was conducted to assess the bioavailability of the sediment-associated metals and their toxicity to benthic organisms. Surface sediment samples were collected and analyzed for AVS, ∑SEM, total metals, grain size, total solids, and TOC. In addition, toxicity tests with *Hyalella azteca* and *Chironomus dilutus* were performed on a subset of surface sediment samples collected on site and at upstream reference locations. These locations were selected to provide good spatial coverage as well as a range of ∑SEM and AVS concentrations.

Toxicity testing showed that none of the sediment samples had an adverse effect on amphipods or midges based on the *H. azteca* mortality endpoint and *C. dilutus* growth endpoint. However, the results were somewhat confounded by the fact that increased *C. dilutus* mortality was observed in some samples when compared with one of the two upstream reference locations. The bioavailability of the sediment-associated metals and the likelihood that these chemicals would have caused the observed toxicity was assessed using ∑SEM – AVS. USEPA guidelines (USEPA 2005c) state that any sediment for which $(\sum SEM - AVS)/f_{oc}$ is < 3000 μmol/g OC poses an uncertain risk with regard to adverse biological effects resulting from metals toxicity. Sediment samples that showed an effect relative to the upstream station were less than half of that value. In addition, the USEPA guidelines state that the $(\sum SEM - AVS)/f_{oc}$ threshold above which adverse biological effects resulting from metals toxicity are expected is 3000 $\mu mol/g_{oc}$. The maximum $(\sum SEM - AVS)/f_{oc}$ result in any sediment sample was 360 $\mu mol/g_{oc}$, approximately ten-fold below the USEPA adverse effect threshold of 3000 $\mu mol/g_{oc}$. The assessment concluded that the surface sediment metals concentrations exceeding the ODEQ

Level II SLVs were unlikely to be responsible for the observed *C. dilutus* mortality and that metals concentrations did not pose potential risks to the benthic community.

4.2.1.8 Hackensack River, New Jersey

Bioavailability of chromium in sediments in the Hackensack River near its confluence with Newark Bay, New Jersey (Magar et al. 2008, Martello et al. 2007) was evaluated as part of an assessment of risks and remedial alternatives. Chromium at the site was partly attributable to historical waterfront disposal of chromium ore processing residue. The key measures of bioavailability were presence and conditions that would favor formation of the toxic species hexavalent chromium (Cr^{6+}) or the less toxic trivalent chromium (Cr^{3+}) that is the prevalent form in reducing conditions commonly found in sediments. Measures and findings included the following:

- SPI surveys indicated that principally reducing conditions that favored formation of Cr^{3+} were found throughout the site except in a thin (<2 cm) surface layer.
- AVS measures across the site also confirmed the overall reducing conditions in the sediments.
- Pore-water sampling and analyses from the reduced sediments and within the top oxygenated layer never detected Cr^{6+}; Cr^{3+} was found only at low concentrations in pore water despite bulk sediment concentrations as high as 2090 mg/kg.
- Cr^{6+} analyses in bulk sediment indicated detectable levels, but Cr^{6+} was not detected in a sediment resuspension and oxidation test 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 in exposed organisms were within the range of those found in laboratory control organisms.
- Toxicity tests showed adverse effects of site sediments on amphipods but not polychaetes, even though the polychaete test species is known to be particularly sensitive to Cr^{6+}. Effects on amphipods were determined to be associated with PAH, not Cr^{+6}, concentrations. These findings were confirmed by tests at an upstream site affected by chromium ore processing residue that demonstrated no toxicity to amphipods at total chromium concentrations up to 1490 mg/kg (Becker et al. 2006).

Taken together, these and other lines of evidence demonstrated very low bioavailability of chromium in study area sediments and supported a decision of MNR.

4.2.1.9 Buffalo River, New York

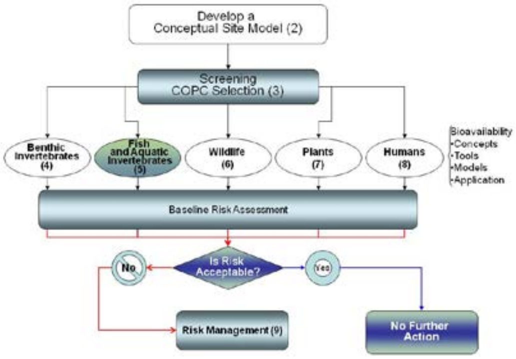
At the Buffalo River Great Lakes area of concern, multiple bioavailability tools were used to develop of a site-specific remedial goal for total PAHs. The development of the remedial goal was based on USEPA's *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures* (USEPA 2003d). Supporting lines of evidence included pore-water measurements of parent and alkylated PAHs, sediment toxicity tests using *Hyalella azteca* and *Chironomus tentans*, an evaluation of USEPA's target lipid model, and bioaccumulation tests with *Lumbriculus variegate*. This case study focuses primarily on the use of pore-water analyses to measure PAH bioavailability and to establish site-specific EqP coefficients.

Pore water was collected Buffalo River sediment samples and analyzed for concentrations of 34 parent and alkylated PAHs using SPME followed by GC/MS. The pore-water results were combined with parent and alkylated PAH concentrations in whole-sediment samples and sediment TOC concentrations to determine site-specific, sediment K_{oc} values for each measured parent and alkylated PAH. The Buffalo River K_{oc} values are typically higher than USEPA's default values (USEPA 2003d) and fall within the range of experimentally determined values from other contaminated sediment sites (Hawthorne et al. 2007). These results demonstrated that PAH bioavailability in Buffalo River sediments is less than predicted through models typically used to estimate chemical partitioning to sediments using default partition coefficients.

The site-specific partition coefficients calculated from the pore-water results were applied to the calculation of a site-specific PAH toxicity unit using USEPA's EqP method. These results, along with additional lines of evidence, including the toxicity test results, were used to determine site-specific remedial criteria protective of benthic organisms and fish. Using default partitioning values would have resulted in an overly conservative remedial goal for PAHs, had site-specific partitioning data not been available.

5. BIOAVAILABILITY TO FISH AND WATER-COLUMN INVERTEBRATES

This section presents the concepts and tools for assessing bioavailability to water-column invertebrates, amphibians, and fish that are exposed to contaminants originating from sediments. While the principal emphasis is on fish, water-column invertebrates are included as these are often prey items for fish and a pathway for contaminant uptake into fish. Amphibians are also included here as there are currently 23 amphibian species classified as endangered or threatened and 11 additional species being evaluated for listing (USFWS n.d.). Both amphibians and fish are considered to be sentinel organisms that can provide indications of contaminant effects that may otherwise go undetected.



Most of the tools and measures used in this evaluation (see Table 5-1, later in this chapter) are already well documented in federal and state documents (Tables 2-2 and 5-2, later in this chapter). These include water quality analyses, tissue residue measures, bioassays, macroinvertebrate and fish surveys, and both simple and complex models that take into account site-specific conditions that may influence contaminant bioavailability. An excellent resource for understanding the mechanisms of bioavailability and toxicology of fish is *The Toxicology of Fishes* (DiGuilio and Hinton 2008).

5.1 Conceptual Site Models for Water-Column Organisms

Section 4.1 discussed the principal exposure routes for sediment-bound contaminants into benthic invertebrates. These same exposure routes are also germane to water-column invertebrates, amphibians, and fish:

- ingestion of benthic or water-column organisms that have been exposed to contaminated sediments and subsequently consumed as prey
- release of contaminants (dissolved or particulate) from sediments into surface water where they can be ingested or absorbed across gills or skin
- bottom-foraging fish incidentally ingesting sediment as a component of their diet

Figure 2-3 illustrates physical transport and ecological receptor processes in a freshwater system.

CSMs, discussed in Chapter 2, are equally important to consider for assessing contaminant bioavailability to fish and aquatic invertebrates. Figures 2-1 and 2-2 illustrate the processes involved in contaminant movement from sediments into the water column and subsequently into the aquatic food web. Benthic organisms are prey for fish that forage into sediments for food. Additional sources of prey are infauna that move out of the sediment and/or into the water column (e.g., mayflies and freshwater and marine amphipods). Water-column food webs are also important because releases of contaminants can occur from sediments by simple diffusion, groundwater advection, or sediment resuspension events with subsequent uptake by water-column organisms. Therefore, resuspension of highly contaminated sediments into the water column can result in acute toxicity to both invertebrates and fish.

Figure 2-2 presents an example of an ecological conceptual model for a representative aquatic ecosystem. In these food webs, bioavailability and exposure depend on which trophic level the organism feeds within. Bottom-feeding fish (e.g., carp, bullhead) have a relatively short food chain. Exposure includes ingestion of not only contaminated prey, but also contaminated sediments, as well as absorption across the gills and dermal contact. Predatory fish (e.g., perch or walleye) living in the water column are exposed via consumption of prey such as benthic invertebrates, water-column invertebrates (i.e., zooplankton), and various other fish species that have acquired contaminants through other food sources.

5.2 Tools and Measures

Evaluating bioavailability to aquatic invertebrates and fish can range from relatively simple tools and measures to those that are complex and integrate bioavailability factors into fate and transport models. Figure 5-1 is a generalized flow diagram that could be used to assess bioavailability and effects to aquatic invertebrate and fish communities. Methods used in these evaluations include the following:

- chemical tests
  - sediment
  - surface- or pore-water quality chemistry
  - tissue residue analyses
- biological tests
  - toxicity testing

Tools for Assessing Bioavailability to Aquatic Invertebrates, Amphibians and Fish

- Determine whether water quality chemistry measures exceed alternate water quality criteria.
- Carry out laboratory aquatic toxicity tests using site-appropriate organisms and conditions.
- Estimate contaminant uptake using bioaccumulation factors (BAFs) or BSAFs.
- Perform tissue residue analyses.
- Analyze contaminant metabolites (e.g., PAHs) in fish bile.
- Conduct population surveys and compare to similar reference conditions.
- Determine in situ bioavailability by active or passive pore-water samplers.

  - population (community) surveys
- predictive
  - estimates of uptake from mathematical modeling

The major classes of these measures discussed in Chapter 4 are also germane here.

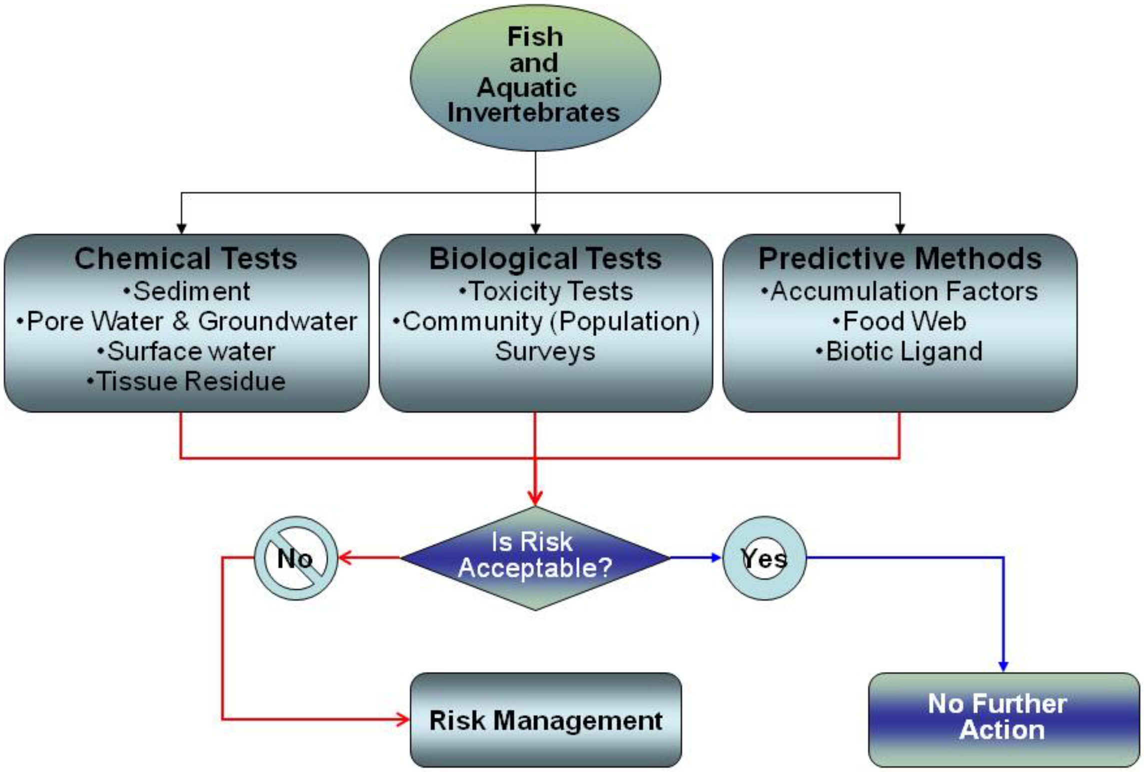


Figure 5-1. Water-column invertebrate exposure evaluation for bioavailability.

The tools discussed in this section have been classified as chemical, biological, or predictive. As a matter of convenience, these subdivisions help to classify these tools and their application as described in Table 5-1.

5.2.1 Chemical Approaches

Figure 5-2 illustrates the importance of chemical measures through the food chain to fish. This illustration presents concentrations of PCB congener #52 through a Great Lakes food web to trout and salmon to demonstrate the importance of evaluating bioaccumulation from sediments and water. In this example, PCB #52 was bioavailable, at some level, in the water column and sediment. It is unclear, however, how PCB #52 became bioavailable in the water column and what fraction was bioavailable in the sediments.

Table 5-1. Tools and measures for the fish and water-column invertebrate pathway

Measure	Approach	Description (see Appendix C for descriptions)
Chemical	Surface or pore water (direct, indirect)	• Surface-water samples (grab, composite) • Total and/or dissolved COPCs • Passive samplers (peepers, DGTs, PDBs, SPMEs, PE, POMs) • Geochemical parameters (TSS, TOC, DOC, humic acid, pH, salinity) • Compare to water quality criteria
	Sediment testing	Use literature BSAF to predict fish tissue concentrations
	Tissue residue analysis	• Direct collection and measure of tissue COPCs and percent lipid • Field bioaccumulation studies (e.g., caged fish) • Measure bile metabolites (PAHs) in fish • Calculation of BSAFs • Laboratory bioaccumulation studies (e.g., *Pimephales promelas, Cyprinodon variegatus, Salmo gardnerii*) • Comparison to screening values applicable to impacts on water-column organisms
Biological	Toxicity testing	• Test procedures can include the following: o Invertebrate acute/chronic (e.g., *Daphnia* or *Ceriodaphnia* life cycle) o Amphibian acute/chronic (*Rana pipiens* 10-day development) o Fish acute/chronic (*P. promelas* or *C. variegatus* growth) • Tests may be conducted with the following: o Bedded sediments o Resuspended sediments (USEPA/USACE dredged sediment testing protocols) • Analysis and inference of bioavailability based on the following: o Statistically significant response relative to controls o For larger species (fish, tadpoles), COPC body burden may also be measured
	Population analyses	• Population sampling methods include the following: o Water-column invertebrates, plankton: net sampling o Amphibians: trap sampling o Fish: beach seine or electrofishing • Analysis and inference of bioavailability based on the following: o Identification to lowest practicable taxon o Statistically compare populations to clean reference areas o Subsampling of fish and amphibians for tissue analyses
Predictive measures	Uptake models	• Biota-sediment accumulation, bioaccumulation, and/or bioconcentration factors • Fugacity models • Kinetic models

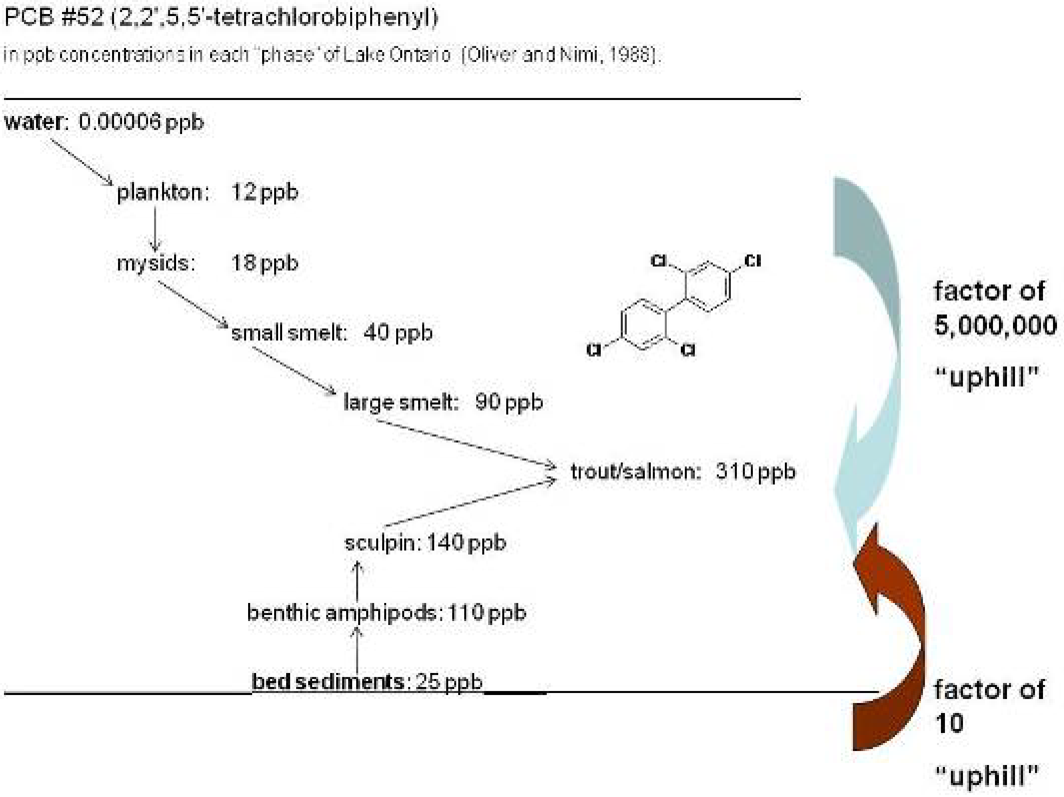


Figure 5-2. Representation of bioaccumulation pathways for PCB congener #52 in a Great Lakes food chain. (*Source:* Gschwend 2008)

5.2.1.1 Sediment quality

The measures of sediment quality discussed in Chapter 4 are equally applicable for amphibians and benthic-feeding fish. While bulk sediment chemical measures are not a measure of bioavailability when correlated with biological observations such as incidence of fish tumors or lesions (Bauman et al. 1991; Bauman, Smith, and Metcalfe 1996; Meador et al. 1995; Cormier et al. 2002) or abnormal development in amphibians (Burger and Snodgrass 2000), they can be used to infer bioavailability and exposure. Statistical correlations between contaminant levels measured in sediments to those measured in fish or to incidences of observed effects are often confounded by the fact that many fish species have large home ranges and are influenced by many types of stressors. Nevertheless, bulk measures of contaminants in sediments can form the foundation for exploring those relationships.

Broader analysis of individual PCBs and PAHs is increasingly being used to characterize exposure and risks. Many site characterizations have relied on measures of Aroclors (or the sum of Aroclors as total PCBs) to characterize exposure and risk to human and ecological receptors. Measurements on PAHs may also be differentially grouped (e.g., "parent" PAHs,[3] with sums of

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[3] Lists of parent PAHs vary across different federal and state programs. USEPA lists 18 parent PAHs, while many state programs list 16–18. A common set of PAHs includes naphthalene, 2-methylnaphthalene, acenaphthylene,

the low-molecular-weight PAHs [LPAHs], high-molecular-weight PAHs [HPAHs], and total PAHs) and have traditionally been used for characterization. Recent focus has been placed on using more complete bulk sediment (as well as water and tissue) analyses of the full suite of 209 PCB congeners (Cleverly 2005, California EPA 2003, DeGrandchamp and Barron 2005, NAVFAC 2001) and the parent plus 34 alkylated PAHs (Burgess 2007; Di Toro and McGrath 2000; Di Toro, McGrath, and Hansen 2000).

While these extended measures may be relevant to assessing risk at a site, there is a shortfall in the understanding of the bioavailability of each compound in the extended analyses to support risk management use. For example, there are 209 PCB congeners which do not necessarily track from sediments through a food web. While PAHs may be metabolized by fish and amphibians, they are not typically detected in tissue. Differential accumulation of PCB congeners for different species is well documented (Bright, Grundy, and Reimer 1995; Froese et al. 1998; Kay et al. 2005). Patterns of PCB congener tissue residues vary with species, trophic levels, and season. An issue paper for the Navy on PCB congeners in ecological risk assessment (NAVFAC 2001) noted that while congener-specific analyses generally offer lower detection limits and a higher information content than do Aroclor analyses, these improvements must be balanced against cost.

5.2.1.2 Water quality measures

Water quality measures have increased importance for water-column organisms. Phytoplankton and zooplankton both adsorb and absorb COPCs, which subsequently move through a food web. Amphibians absorb some chemicals across their skin. Fish can accumulate high body burdens of lipid-soluble contaminants during respiration across the gills. The physiological processes associated with chemical bioavailability across gills or skin tissue are beyond the scope of this document; however, an in-depth review is provided in a chapter by Erickson et al. (2008).

Similar to sediments, bioavailability to water-column organisms is based on the portion of a chemical that is freely dissolved. Nonionic organic compounds and some cationic metals complex with DOC and are thus not available for sorption across cell membranes in phytoplankton or across fish gills. For example, the presence of DOC binds metals such as silver, lead, copper, cadmium, and cobalt, thus reducing bioavailability to fish. Conversely, the presence of DOC may increase the bioavailability of mercury to both phytoplankton and fish. Equilibrium processes also occur in water, with contaminants partitioning between DOC, particulate OC, and the freely dissolved phases.

In addition to DOC, another factor affecting bioavailability of metals to water-column organisms is the formation of inorganic complexes, or ligands, in hard water. USEPA (2003a) defines a ligand as a “complexing chemical (ion, molecule, or molecular group) that interacts with a metal to form a larger complex.” Cationic metals such as cadmium, chromium, copper, lead, nickel, silver, and zinc are thought to form complexes with hydroxides and/or carbonates that are

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acenaphthene, fluorene, phenanthrene, anthracene (LPAHs), fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b+k)fluoranthenes, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene (HPAHs).

indicated by increased levels of calcium and magnesium (measured as "hardness"), pH, and total alkalinity. Increased hardness has been associated with decreased toxicity (and implicitly decreased bioavailability), and for these cationic metals, the associated alternate water quality criteria for freshwater may be adjusted based on measured hardness in the site water. Most states allow hardness adjustments in the calculation of water quality criteria for applicable metals. Recent research (Erickson et al. 2008), however, indicates that hardness alone cannot account for free metal ion activity, which has led to the development of the biotic ligand model (Di Toro et al. 2001, USEPA 2003a) (see Section 4.1.3.4).

Measuring the proportion of freely dissolved metals or nonionic organic compounds is still a developing science. Not all compounds are detectable in water at low levels, and it may not be possible to obtain the specificity needed for the distinction between chemical species required to assess the bioavailable fraction. Advanced analytical techniques to obtain this information may be prohibitively expensive. Traditionally, the method used to distinguish the total from the dissolved fraction of a chemical in water has been to pass the water through a 0.45 µm filter. However, a large body of evidence has demonstrated that filtration is not sufficient to separate the particulate OC or DOC from the dissolved phase, and thus the resulting filtrate may not be a suitable measure of the dissolved component in water (Nollet 2007, Boethlin and Mackay 2000).

Section 4.1.1.3 includes tools for assessing bioavailability in surface waters, and Table 2-1 provides links to information on water quality sampling and characterization. Passive samplers can provide some measure of freely dissolved compounds, but analytical detection limits and chemical speciation (e.g., metals) for some contaminants remain an issue. To minimize uncertainty with the water measures, it is important that (1) the appropriate sampler is being used, (2) the time to equilibrium is confirmed, and (3) materials have been adequately calibrated against known standards.

Luthy (2010) reports that the different polymer materials used for measurements of organic compounds by passive samplers dictate the individual properties of each sampler and thus differences in uptake rates as well as ease of application in the field. Luthy cites Adams et al. (2007) in reporting that PE is a practical material with faster time to equilibrium and less fouling than with SPMDs since only a single layer of plastic is exposed on both sides. Cornelissen et al. (2008) compared five passive samplers and concluded that the selection of a specific passive sampler depends on the objective of the study. If fast equilibrium and low detection limits are required, a thin (55 mm) POM is advantageous and has a greater chemical capacity compared to other thin samplers like SPME fibers. However, if low detection limits are not required and measurements need to be made quickly, either PE, SPME fibers, or thin POM can be used (Luthy 2010). For organic compounds, the use of performance reference compounds embedded on the sampler is needed to ascertain that the sampler is in equilibrium with the surrounding water or pore water (Fernandez, Harvey, and Gschwend 2009). Gschwend et al. (in press) compared measures made by PE, POM, and SPME of PCB congeners against direct (instrument) readings from pore water. The results in this controlled group was within a factor of 2.

5.2.1.3 Tissue residue

Measuring chemical concentrations in fish is the most common method for inferring that a specific contaminant is bioavailable. Tissue residue concentrations integrate chemical bioavailability, multiple routes of exposure, and assimilation into an organism. As discussed previously, tissue residues, coupled with bulk sediment measures, have been correlated to observed toxic effects in the field such as lesions, tumors, or subcellular effects.

Assessing bioavailability of contaminants from sediment using fish tissue residues must consider the site location, history, and size; contaminant transport processes; and the physiology, life history, size, sex, and trophic level of the target fish species. For example, for a small site with a limited area of contamination, one should consider evaluating a species with a limited home range. For larger sites, sampling could include longer trawls or multiple collections within the contaminated area. Strategies include analysis of individual whole fish, removing fillet and then separately analyzing both the fillet and offal, fish tissue plugs, compositing multiple small fish into a single analysis, or sampling from specific organs. A useful resource for considering methods of fish sampling is *Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis* (USEPA's (2000c). This guidance provides suggested species selection criteria for fish, turtles, and shellfish; field sampling procedures (sampling design, sample collection, and sample handling); laboratory processing procedures; and analytical guidance. Other useful information in this guidance includes statistical methods given various assumptions (e.g., how many individuals per composite sample, how many replicates per composite sample).

Care must be exercised to collect the right tissue type (whole body is typically most relevant for wildlife in ecological risk assessments) and size class for an avian receptor of interest. For example, the 10–30 cm long fish generally consumed by an osprey are larger than fish (generally <20 cm long) consumed by great blue herons (Sample and Suter 1999). Tissue residues for many bioaccumulative chemicals, particularly those that biomagnify in food chains, tend to be higher in larger fish relative to smaller fish, so collecting the proper size class is an important consideration. Species of fish (or at least a guild, such as bottom feeders) must also be considered, since there may be large differences in the rate of uptake and accumulation among the various components of the fish community. Target collection must be tailored to the receptor(s) being evaluated and to the composition (relative abundance) of the fish community at the site. If concurrent chemical concentrations in sediment are measured, site-specific BAF/BSAF values may be calculated and extrapolated to other portions of the site for which tissue samples were not collected, assuming sediment contamination is an issue in these areas.

Lipid content may vary seasonally and influence bioavailability and exposures. Some species may store contaminants in fat reserves when preparing for migration, hibernation, or reproduction. Adverse effects from these contaminants may not occur until the fat reserves are metabolized for energy requirements, at which point the organism and/or its offspring may no longer be exposed to site contaminants. Lipid normalization of contaminant levels in tissue is standard practice for many organic contaminants (i.e., a factor in derivation of BSAFs) and is intended to reduce observed variability in tissue contaminant concentrations. However, the analysis of lipid(s) is not an exact science. Seasonal variation in organism lipid content and/or method variability and a lack of precision in lipid concentrations reported in units of percent can have a large impact on lipid-normalized concentrations of bioaccumulative chemicals such as PCBs and polychlorinated dibenzodioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs). Typically, lipids cannot be detected in tissues below concentrations of 0.2%. Various methods (e.g., gravimetric, thin-layer chromatography [TLC]/flame ionization detector [FID]) used to determine lipid content include the use of extraction solvents (e.g., hexane, ether, chloroform) and extraction techniques (e.g., Soxhlet, accelerated solvent extraction [ASE], supercritical fluid extraction [SFE]). There is no accepted standard method (Duncan et al. 2007b). Sometimes lipid analytical methods are specified as part of a protocol for a specific contaminant such as PCBs and PCDDs/PCDFs (e.g., USEPA Methods 1668A and 1613B, respectively).

Normalization of nonionic organic contaminant sediment concentrations to the f_{oc} in the sediment is applied to the denominator of the BSAF equation. Like partitioning to lipids, partitioning to f_{oc} usually makes nonionic organic COPCs less bioavailable. While analytical methods for TOC are more established than those for lipids, analytical precision and variability in analysis of OC also can have a large impact on normalized concentrations of chemicals expressed in units of parts per trillion.

Measuring PAHs in fish tissues is not a useful measure of exposure as fish readily metabolize PAHs (Meador et al. 1995; Johnson, Collier, and Stein 2002; Johnson et al. 2008). Exposure to PAHs in fish requires measuring the metabolized PAHs in bile. Measures of biliary PAHs should be considered as estimates; the methods cannot provide a direct level of PAH concentrations in tissues. However, these measures have been correlated with other indicators of exposure and toxicity (Meador et al. 1995; Pickney et al. 2001, 2004), with one study demonstrating a positive correlation between measures of PAHs collected with a SPMD with biliary PAHs (Verweij et al. 2004). Once measured, a way of interpreting the data is via the application of the tissue residue toxicity approach (Beckvar, Dillon, and Read 2005; Dillon, Beckvar, and Kern 2010; Meador et al. 2008). Measured tissue residue values in the fish are compared to levels known to cause an acute or chronic response. One of the most commonly referenced databases in past investigations is USACE's Environmental Residue Effects Database (ERED) (http://el.erdc.usace.army.mil/ered). While initially focused on associating adverse effects with known tissue levels, ERED has incorporated bioaccumulation data. As stated by USACE and USEPA, ERED was developed to reduce the level of uncertainty associated with interpreting bioaccumulation data for the purpose of making regulatory decisions. ERED contains tissue effects data for a wide range of species, including benthic infauna, fish, shellfish, birds, and mammals.

5.2.2 Biological Methods

Biological methods for analyzing water-column organisms are similar to those discussed for sediments and include bioassays and population surveys. While bioassays and laboratory bioaccumulation studies for fish are commonly employed for assessing contaminated sites, population surveys for fish are less frequent, due in part to the logistics associated with collecting the organisms in a systematic and statistically meaningful way. Arguably, population surveys do not provide a measure of bioavailability, but when applied in conjunction with sediment and water chemistry, bioassays, and tissue residue studies, they can help provide the links between contaminant bioavailability and effects.

5.2.2.1 Toxicity testing

Section 4.1.2.1 discussed toxicity test procedures, organisms, and interpretation in depth. Appendix C-T3 lists the standard tests.

For freshwater systems, the more commonly used aqueous-phase toxicity tests evaluate pore water, elutriates, and water-column samples. Numerous aquatic invertebrate and fish species can be used for aqueous-phase testing; method documents typically list the test species appropriate for use in the method. Other methods or species/endpoints of potential use include in situ bioassays that evaluate fish embryo development (ODEQ 2000) and tests that use amphibians (see Appendix C-T3). Commonly employed marine and estuarine toxicity tests for water-column organisms include larval bivalve tests (e.g., *Mytilus, Crassostrea, Mya*), mummichog (*Fundulus* sp.), sheepshead minnow (*Cyprinidon variegates*), and silversides (*Menidia* sp.).

5.2.2.2 Population surveys

Population surveys of fish or amphibian communities can be an important component in a weight-of-evidence approach for assessing effects. While not a direct measure of bioavailability of a contaminant, changes in characteristics of a population exposed to a site COPC imply that the contaminant is bioavailable. When coupled with other measures such as sediment chemistry, tissue residues, bioassays with the contaminated sediments or site water, suborganismal bioindicators such as lesions or tumors, or single-chemical toxicity tests, population surveys can provide a clear link between in-place contaminants, uptake, and effects (Suter et al. 1999).

How to conduct population surveys of fish or amphibians is beyond the scope of this document. A limited set of references follows, but most states have their own programs for collecting fish species associated with monitoring biological integrity of state waters or collecting samples for fish consumption advisories. More instructive is how population surveys have been used in assessments of contaminant bioavailability and risk characterization.

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- USFWS (U.S. Fish and Wildlife Service). n.d. "Amphibian Declines and Deformities." www.fws.gov/contaminants/Issues/Amphibians.cfm.

5.2.3 Predictive Measures

Predictive measures for identifying contaminant uptake in fish are mathematical algorithms that link sediment contaminant concentrations to residues in fish tissue. These expressions range from relatively simple ratios of contaminant concentrations in sediment or water to those in fish tissues to complex models that include transfer between trophic levels incorporating feeding rates and prey preferences; area use; assimilation efficiency; and loss by metabolism, growth, or reproduction. Bioavailability (at least to fish) is assumed in these models; the simple transfer ratios are derived from either large databases or from site-specific sediment and tissue data. The fugacity and kinetic models that are discussed are rooted in direct measures of individual uptake and loss parameters.

These models have assumed increased importance not only in assessing risk, but also in setting cleanup criteria (Glaser and Bridges 2007). Many of these mathematical equations may be rearranged to solve for sediment concentrations that are safe for human or ecological receptors. An important caution when using models is articulated in the *Models in Environmental Regulatory Decision Making* (NRC 2007), which indicates that models may "best be viewed as tools to help inform decisions rather than as machines to generate truth or make decisions."

5.2.3.1 Accumulation factors

Accumulation factors for aquatic organisms are simple mathematical ratios that relate the measured concentration for a given compound in an organism (or organism compartment such as lipids) to the concentration in the medium from which the compound is taken up (Schwarzenbach, Gschwend, and Imboden 2003). Often application of accumulation factors assumes (1) all measured uptake exposure comes from a single medium (water, sediment, or prey), (2) 100% of the exposure related by the tissue measure occurs in the vicinity where that medium measure was taken, (3) the trophic level of the fish is not considered, and (d) the ratio reflects exposure to the bioavailable fraction of the contaminant in the medium.

Application of accumulation factors is widespread; they are used in the development of NRWQC (USEPA 1995a, 2000c), development of sediment protective standards in some state programs (e.g., ODEQ 2007), and prediction (internationally) of bioaccumulation into the food web (Environment Canada 1998). Despite the limits imposed by the assumptions listed above, accumulation factors for persistent and bioaccumulative organic compounds have been demonstrated to have a reasonable level of accuracy in predicting concentrations of these compounds in fish (Arnot and Gobas 2006; Burkhard, Cook, and Lukasewycz 2005; Wong, Capel, and Nowell 2001). Conversely, accumulation factors have been less reliable for metals and organo-metalloid complexes (Luoma and Rainbow 2005), which has led to the development of alternative predictive models such as the BLM (see Section 4.1.3.4, Di Toro et al. 2001). A good compilation of bioaccumulation databases is found in Weisbrod et al. (2007).

Accumulation Factors

- **Bioconcentration factor (BCF)** expresses the accumulation in organism tissue of contaminants from water-only exposures in the laboratory.
- **Bioaccumulation factor (BAF)** expresses the field accumulation in organisms from all routes of exposure; determination of the BAF is based on the concentration in the organism divided by the freely dissolved concentration in water from the site.
- **Biota-sediment accumulation factor (BSAF)** represents the lipid-normalized contaminant concentration in tissue relative to the organic carbon–normalized concentration in sediments for organic chemicals or wet wt./wet wt. or dry wt./dry wt. concentrations for metals.
- **Biomagnification factor (BMF)** is the ratio of the concentration of a contaminant in an organism relative to the concentration in its diet.

The most commonly applied accumulation factors are as follows:

- bioconcentration factor (BCF)
- bioaccumulation factor (BAF)
- biotic sediment accumulation factor (BSAF)
- biomagnification factor (BMF)

Section 5.3 discusses examples of the application of various bioaccumulation factors in remedial decision making.

BCF is the ratio of a contaminant retained in an aquatic organism following its absorption through respiratory and dermal surfaces from the surrounding water, but it does not does not include accumulation via dietary exposure (Weisbrod et al. 2007). BCFs are typically determined from laboratory bioconcentration studies. Mathematically, this is simply expressed as the concentration in tissue (mg/kg) divided by the concentration (mg/kg) in water as follows:

$$BCF = \frac{[tissue]}{[water]}$$

BAF is net uptake and retention of a chemical in an organism from all routes of exposure (diet, dermal, respiratory) and any source (water, sediment, food) as typically occurs in the natural environment (Spacie, Mccarty, and Rand 1995). Bioaccumulation typically is based on field measurements and may be expressed as either a BAF relative to freely dissolved contaminants concentrations in water or a BSAF relative to chemical concentrations in sediment (Spacie, Mccarty, and Rand 1995). Simply put, a BAF is expressed as the ratio of the concentration in tissue (mg/kg) to the concentration in sediment (mg/kg) as follows:

$$BAF = \frac{[tissue]}{[sediment]}$$

BSAF is used principally for estimating uptake from sediment. The estimate of the concentration on a lipid basis in fish is proportional to the concentration of a compound normalized to the sediment OC concentration. Mathematically, this relationship is expressed as follows:

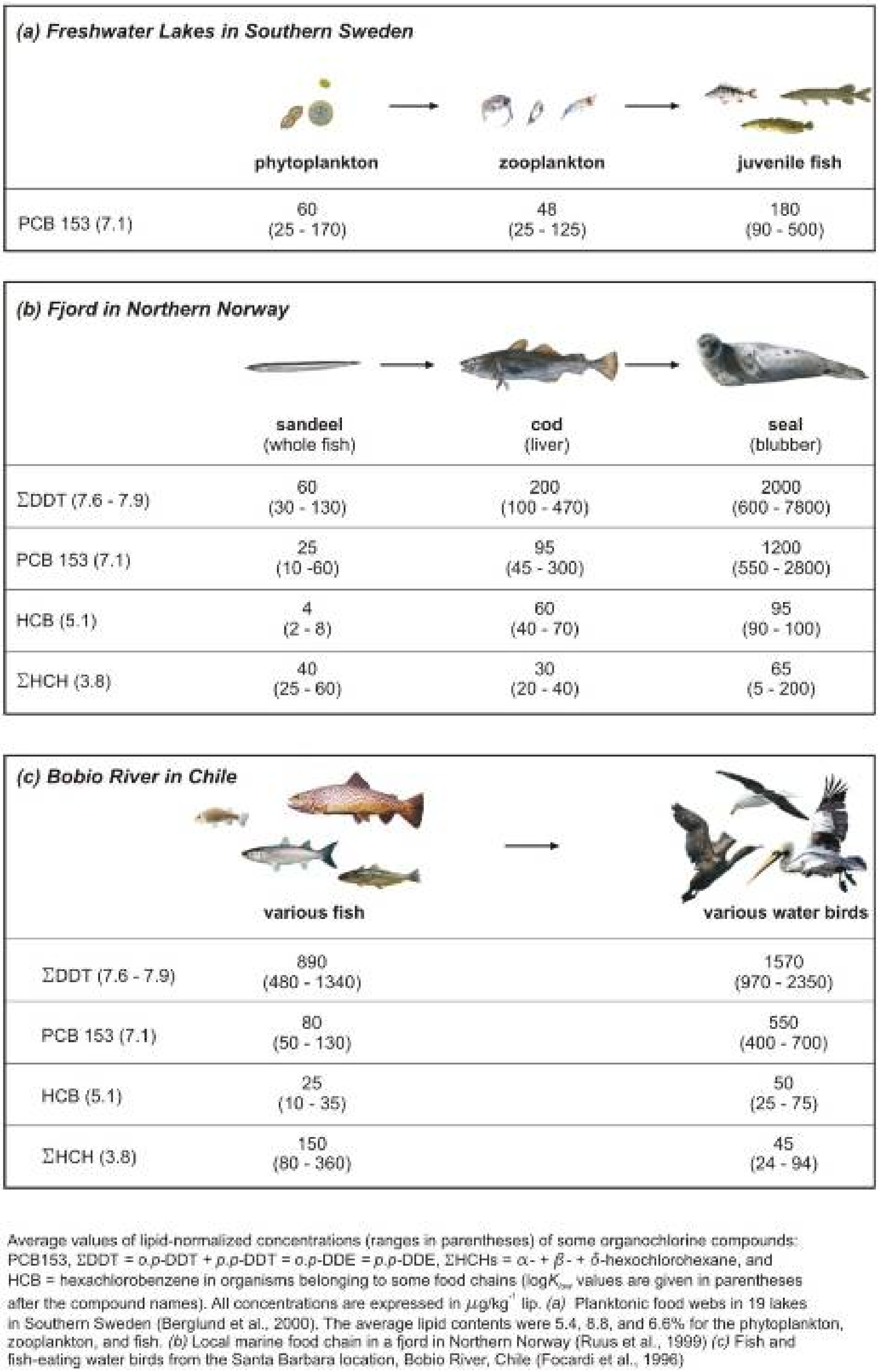
$$BSAF = (\frac{[tissue]}{flipid})/(\frac{[sediment]}{foc})$$

where the concentration in tissue is normalized to the fraction of tissue lipids (f_{lipid}) and the dry weight sediment concentration is normalized to the f_{oc} in sediment.

BMF is used to express how the concentration of a given compound in an organism increases as one examines successive trophic levels within a given food chain. Biomagnification is generally observed for recalcitrant lipophilic compounds with high K_{ow} but is generally not as great a concern for metals except those which can be biotransformed to organic forms (e.g., organotins, methylmercury and methyl selenide) (NRC 2003).

$$BMF = \frac{[organism]}{[diet]}$$

Figure 5-3 shows an example of the importance of biomagnification. Typically, within aquatic food webs BMFs are relatively small, a factor of 1–10 but generally in the range of 2–5. BMFs for higher trophic levels like birds or seals can be orders of magnitude higher. Section 5.3 discusses the application of these accumulation factors in remedial decision making. Chapter 6 covers contaminant uptake and food chain transfer to birds and mammals.



(a) Freshwater Lakes in Southern Sweden

	phytoplankton	zooplankton	juvenile fish
PCB 153 (7.1)	60 (25 - 170)	48 (25 - 125)	180 (90 - 500)

(b) Fjord in Northern Norway

	sandeel (whole fish)	cod (liver)	seal (blubber)
ΣDDT (7.6 - 7.9)	60 (30 - 130)	200 (100 - 470)	2000 (600 - 7800)
PCB 153 (7.1)	25 (10 -60)	95 (45 - 300)	1200 (550 - 2800)
HCB (5.1)	4 (2 - 8)	60 (40 - 70)	95 (90 - 100)
ΣHCH (3.8)	40 (25 - 60)	30 (20 - 40)	65 (5 - 200)

(c) Bobio River in Chile

	various fish	various water birds
ΣDDT (7.6 - 7.9)	890 (480 - 1340)	1570 (970 - 2350)
PCB 153 (7.1)	80 (50 - 130)	550 (400 - 700)
HCB (5.1)	25 (10 - 35)	50 (25 - 75)
ΣHCH (3.8)	150 (80 - 360)	45 (24 - 94)

Average values of lipid-normalized concentrations (ranges in parentheses) of some organochlorine compounds: PCB153, ΣDDT = *o,p*-DDT + *p,p*-DDT = *o,p*-DDE = *p,p*-DDE, ΣHCHs = α- + β- + δ-hexochlorohexane, and HCB = hexachlorobenzene in organisms belonging to some food chains ($\log K_{ow}$ values are given in parentheses after the compound names). All concentrations are expressed in $\mu g/kg^{-1}$ lip. *(a)* Planktonic food webs in 19 lakes in Southern Sweden (Berglund et al., 2000). The average lipid contents were 5.4, 8.8, and 6.6% for the phytoplankton, zooplankton, and fish. *(b)* Local marine food chain in a fjord in Northern Norway (Ruus et al., 1999) *(c)* Fish and fish-eating water birds from the Santa Barbara location, Bobio River, Chile (Focardi et al., 1996)

Figure 5-3. Examples of bioaccumulation and biomagnification for select organochlorines in fish-based food webs. (The legend should read µg/kg lipid or µg*kg^{-1} lipid. Adapted from Schwarzenbach, Gschwend, and Imboden 2003.)

5.2.3.2 Food-web models for persistent bioaccumulative compounds

Food-web models (Figure 5-4) are an important tool for estimating the concentrations of contaminants moving from sediment into fish via the food chain. These models are applied not only in environmental decision making at contaminated sediment sites but also in setting water quality criteria, developing waste-load allocations, and evaluating new chemical products. Food-web or food-chain models have been used at a variety of sites, including the Hudson River, N.Y.; the Housatonic River, Mass.; the Lower Fox River, Wisc.; the Lower Duwamish River, Wash.; the Willamette River, Ore., Soda Lake, Wy.; and the Southern California Bight. As pointed out in Section 5.2.3, "Bioavailability (at least to fish) is assumed in these models; the simple transfer ratios are derived from either large databases or from site-specific sediment and tissue data."

Figure 5-4. Representation of a food web used for bioaccumulation modeling.

Much of the initial work in developing food-web models has been in association with PCB uptake in the Great Lakes, but more recently food-web models have also been used to estimate bioaccumulation of other nonpolar organic compounds. There are two basic classes of models for bioaccumulative compounds: fugacity and mechanistic (see Appendix C-T7). Fugacity models are steady-state mass balance equations that partition compounds through the system based on chemical properties (Mackay 1979, 1982, 1991; Campfens and Mackay 1997; Sharpe and Mackay 2000, Morrison et al. 1996, 1997). Mechanistic models are based on a series of differential equations that incorporate an array of physical and biologically based parameters, including chemical partitioning and release; uptake with consideration of feeding rates and prey preferences; area use; assimilation efficiency; and loss by metabolism, growth, or reproduction (Thoman and Connolly 1984; Thoman 1989; Thoman, Connolly, and Parkerton 1992; Gobas and Mackay 1987; Gobas 1993; Arnot and Gobas 2006, Morrison et al. 1996, 1997).

Appendix C-T5 lists several of the more commonly used bioaccumulation models. It is recommended that these models be used only with the aid of a team of modelers, statisticians, and biologists who can contribute to the parameterization and validation of the model for the specific aquatic system under consideration.

5.2.3.3 Biotic ligand model

The BLM (Appendix C-T4), discussed in Section 4.1.3.4, is especially important to the understanding of metals bioavailability to water-column organisms. A "biotic ligand" is a complexing chemical that is a component of an organism (e.g., chemical site on a fish gill) (USEPA 2007a).

Figure 5-5 shows that the model evaluates the formation of metal complexes, as well as the competitive binding at the gill interface, to determine metal toxicity. The BLM is constructed so that metal toxicity can be predicted based on the inputs of total metal concentration, temperature, pH, DOC, major cations (Ca, Mg, Na, and K), major anions (SO_4 and Cl), alkalinity, and sulfide. Figure 5-6 shows that measured and BLM-predicted silver LC_{50} concentrations (the concentration of a chemical the kills 50% of the test species) for two species of fish and three species of *Daphnia* show a high degree of correlation.

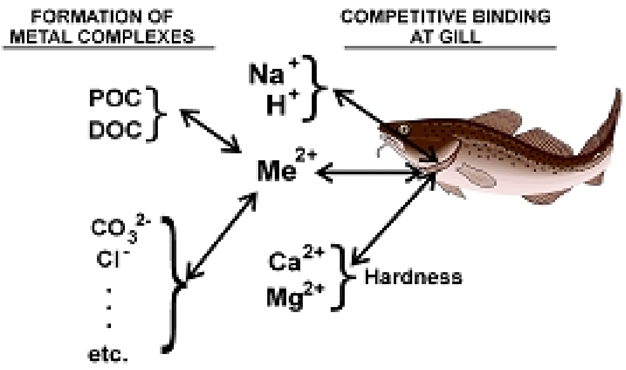


Figure 5-5. Schematic of the biotic ligand model. (Courtesy HydroQual.)

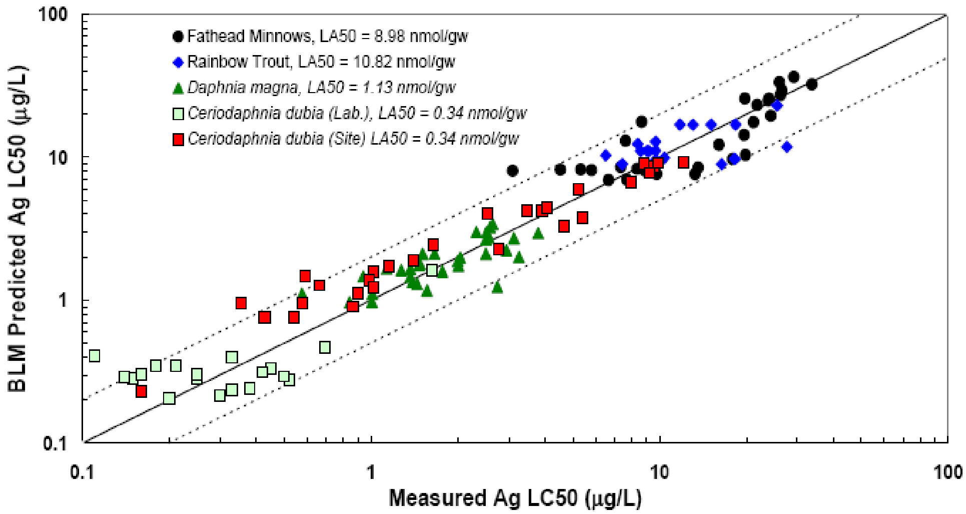


Figure 5-6. Comparison of measured vs. BLM-predicted LC_{50} values for silver. (*Source:* USEPA 2007a)

A Windows version of the BLM in a simple-to-use spreadsheet format can be downloaded at www.hydroqual.com/wr_blm.html. The current version allows for calculating cadmium, copper, silver. and zinc toxicity to fathead minnows, rainbow trout, and three species of *Daphnia sp*.

5.3 Application of Bioavailability Tools in Risk Assessment and Risk Management

Contaminant levels in fish tissue are often the determining factor in setting remediation management and cleanup goals for sediment sites and most often for human health–related risks. For risk characterization specific to fish, the measured or model-estimated tissue concentrations may be compared to chemical-specific, tissue residue toxicity concentrations to determine whether the fish or amphibians are at risk from contaminant exposure. Bioassays or population surveys can provide an additional line of evidence to the assessment of potential risks to the fish or amphibian communities. However, as the case studies below illustrate, a commonly observed condition is that site chemical data stands in direct contrast to population surveys or bioassays.

Best professional judgment is required to sort through the data to determine the risk management action.

Remedial action levels in sediments can be set by determining an acceptable level of risk based on tissue residues and using the mathematical factors or models discussed in Section 5.2. in reverse to solve for the “safe” sediment concentrations. An example of this process is the Oregon SQGs derived for fish consumption discussed in Chapter 2, where the safe tissue residue values for human consumption are determined and BSAFs are used to back-calculate the presumed safe sediment value. This practice, however, typically results in very conservative sediment concentrations (often below naturally occurring background levels).

The same four principal areas discussed in Section 4.2, where bioavailability data may be applied to inform decisions and remedies, risk assessment, risk management, remedial selection, and remedial design/implementation, are equally applicable here. Appendix D contains details of each of the case studies cited below.

5.3.1 Bioavailability in Risk Management

For water-column organisms, assessment of bioavailability can have a critical role in the following three risk management objectives:

- identification of appropriate stressor(s)
- identification of exposure route(s)
- development of sediment cleanup levels

USEPA’s general guidance document for the identification of stressors (USEPA 2000c), in conjunction with the TIE procedures of USEPA (Burgess et al. 1996; USEPA 1989b, 1989c) and/or states (e.g., California EPA 2008), are applicable to water-column invertebrates and fish.

Stressor Identification

Identifying stressors for water-column organisms can follow the same general principles previously outlined in Section 4.2.1. Efroymson et al. (1996) provided a series of questions that should be considered to determine where contaminants are bioavailable:

- Is the fish community less species rich or abundant than would be expected?
- Do individual fish display injuries that are indicative of significant toxic effects?
- Is the water toxic to aquatic organisms?
- Does the water contain chemicals in toxic amounts?
- Do the fish contain chemicals in toxic amounts?
- What factors account for apparent discrepancies in the results?
- What is the likelihood that the fish community is at least 20% less species rich or abundant than it would be in the absence of contamination?

It should be noted that investigations of aquatic community stressors may not always yield a clear conclusion. For example, Suter et al. (1999) noted that, for the Clinch River OU in Tennessee, only one of the subareas offered a clear relationship upon which remedy decisions could be made. For the Spring River in Kansas, a clear correlation could be demonstrated between metal concentrations and aquatic community impacts. Conversely, at a former wood-treating facility in Oregon, there were no connections to site contaminants, which suggested that the contaminants were not bioavailable or that measured endpoints were not sensitive enough to detect the effects.

Tri-State Mining District, Spring River and Tributaries, Kansas, Missouri, and Oklahoma
The Tri-State Mining District (TSMD) study site provides an example of using studies that demonstrate a clear relationship between stressors in the water and effects to water-column organisms. The TSMD encompasses a large area in southeastern Kansas and adjoining portions of Missouri and Oklahoma. Commercial extraction of Pb- and Zn-bearing ores from more than 4,000 subsurface mines over 120 years left a legacy of health and environmental problems, including elevated contaminant levels in fish and probable declines in some native fish and macroinvertebrate populations. To determine whether elevated levels of selected metals in surface water and fluvial sediment were possible factors limiting the distribution and abundance of freshwater mussels in the Spring River Basin, population surveys and supporting physical habitat assessments were performed throughout the basin and above and below former mining sites. Concentrations of 16 trace elements in surface waters and tissues of mussels and Asian clams (*Corbicula fluminea*) were determined at most survey sites. Overall, streams draining heavily mined areas exhibited depauperate (or fully extirpated) mussel assemblages and correspondingly elevated concentrations of Cd, Pb, and Zn in water, sediment, and bivalve tissue. Other evaluated environmental chemistry parameters and physical habitat conditions assessed at the stream reach scale demonstrated little general relationship to the degraded status of these assemblages. Taken together, these results suggested that pollution attributable to former mining operations is bioavailable and continues to adversely influence environmental quality and impede the recovery of mussel communities in a large portion of the Spring River Basin.

McCormick and Baxter Superfund Site, Oregon
Fish and crayfish surveys were conducted at this former wood-treating facility on the shores of the Willamette River in Portland (Pastorok et al. 1994). To assess the effects of the residual creosote-derived contaminants including PAHs and dioxins, the assessment included sediment chemistry, bioassays, tissue residues in fish and crayfish, and fish histopathology. Sediment chemistry and toxicity testing indicated that a substantial area of the Willamette River sediments proximal to the site was likely to be toxic (USEPA 1996n). By contrast, tissue residue values for PAHs in crayfish (*Pacifastacus leniusculus*) and large-scale sucker (*Catastomus macrocheilus*) were low (PAH metabolites were not measured), and there were no statistical differences between the site and upstream in the histopathology of the 249 fish livers examined. Based principally on the sediment chemistry and bioassay data, as well as continuing NAPL discharges from sediments to the Willamette River, the ROD required the placement of an impermeable cap (USEPA 1996n).

5.3.2 Bioavailability in Remedy Selection

Bioavailability considerations in remedy selection are highlighted below. In one case, NFA was indicated. In the second, a removal will occur, with post-removal risk verification confirmed by using bioaccumulation modeling for fish. While other exposure pathways were considered for these sites, only the fish receptor pathways figured into the remedy selection.

Fifteen Mile Creek, Oregon

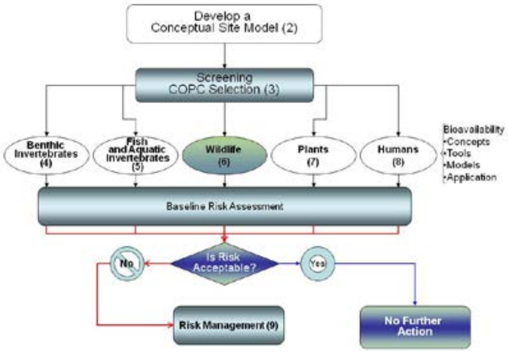
Approximately 2600 gallons of the pesticide oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene) spilled into Fifteen Mile Creek, located proximal to the Columbia River. Approximately 1200 feet of the creek from the accident site to the confluence with the Columbia River was affected. While not especially toxic to mammals or birds, the pesticide is toxic to fish. The Oregon Department of Fish and Wildlife estimated that about 5500 fish died as a result of the spill. Post-spill monitoring over a three-year period evaluated the persistence and bioavailability of oxyfluorfen. Chemical-specific measurements were performed in sediment, upland soil, surface water, pore water, and crayfish and trout. Site-specific sediment/water and biota-sediment accumulation factors were determined. Bioaccumulation in fish tissue was evaluated based on the chemical concentrations in caged trout, juvenile and adult, and crayfish. Other data included laboratory bioassays, benthic invertebrate studies, fish histopathology, and chemical concentrations in the diet of lamprey, trout, crayfish, and piscivorous mammals. Caged trout were placed in the creek for 30 days in June 2001 to evaluate their survival rate and tissue residues. These data were used to evaluate ecological risks, as well as human exposure pathways for subsistence and sport fishermen and recreational swimmers. After three years of sampling, risk assessment indicated that residual contamination did not exceed acceptable levels. Therefore, no further action was required.

Bradford Island Removal Project, Oregon

Bradford Island is part of the Bonneville Dam complex on the Columbia River approximately 40 miles east of Portland. The site is located adjacent to the former Bradford Island landfill, and the contaminants of interest (COIs) include PCBs, PAHs, and metals. An in-water removal of sediment was conducted in 2007. Following the removal action, the data indicate unacceptable levels of PCBs in crayfish and fish tissue; however, the report emphasizes that this may not be an accurate reflection of site risk because the organisms sampled were likely exposed to contamination in sediment that has since been removed. The current recommendation by USACE is to monitor tissue levels in the future when a true picture of current exposures can be obtained.

6. BIOAVAILABILITY TO WILDLIFE

The focus of this section is how the bioavailability of contaminants in freshwater and marine sediments can be incorporated into ecological risk assessments (ERAs) of avian and mammalian wildlife receptors. Figure 6-1 shows a general flow diagram for this consideration.



Since the focus is on aquatic systems (sediments), the key avian groups of potential concern are as follows:

- omnivores (e.g., ducks, geese, swans, gulls)
- piscivores (e.g., herons, egrets, bald eagles, ospreys, kingfishers, loons, cormorants, pelicans)
- invertivores (e.g., stilts, sandpipers, rails)
- aerial insectivores that forage over/near open-water areas (e.g., swallows, terns) or wetland insectivores (e.g., marsh wrens)

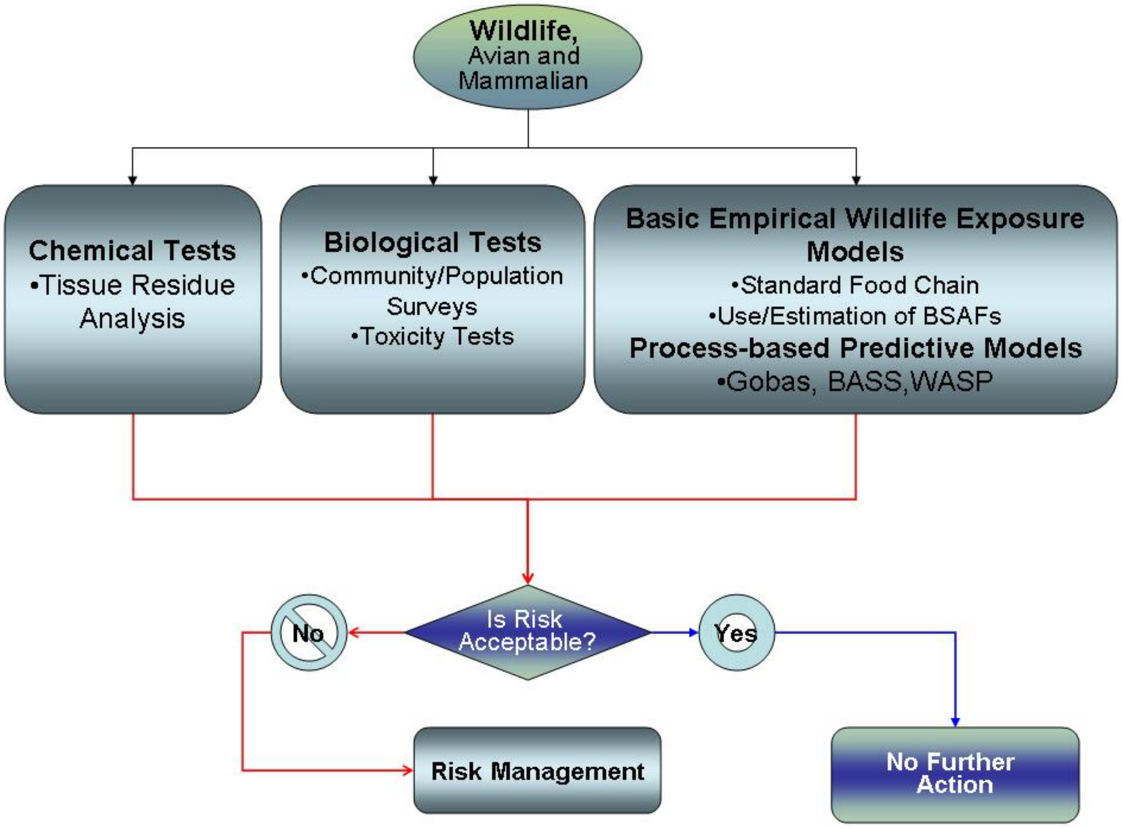


Figure 6-1. Evaluating avian and mammalian wildlife for bioavailability.

Key mammalian groups are as follows:

- aquatic and semiaquatic herbivores (e.g., beavers, muskrats)
- semiaquatic omnivores (e.g., raccoons)
- piscivores (e.g., otters, minks)
- insectivorous mammals (e.g., bats)
- marine mammals (e.g., harbor seals, sea otters)

6.1 Conceptual Site Model for Wildlife Receptors

Most wildlife exposure to environmental contaminants is from dietary intake, particularly for chemicals that bioaccumulate. Exceptions are fish and species with incidental sediment ingestion (e.g., dabbling ducks, sandpipers). Exposure from inhalation, dermal contact, and drinking water are generally insignificant relative to dietary intake and sediment ingestion.

Exposure is, thus, heavily influenced by bioaccumulation/bioavailability of contaminants in sediment/pore water to lower trophic level species (mainly fish and water-column invertebrates—Chapter 5 and plants—Chapter 7). These are prey for aquatic or semiaquatic wildlife and avian species. While there are some receptors that prey on adult birds, eggs, or young or semiaquatic mammals (such as muskrats), these receptors are the exception, and consumption of these prey species may be seasonal and/or opportunistic.

USEPA (2000a) has developed a list of chemicals that are persistent, bioaccumulative, and toxic (PBT) compounds in sediments. Table 6-1 lists suspected bioaccumulating chemicals for ecological pathways. It is not intended to be an extensive review of the literature for these target chemicals. States may have additional chemicals that expand on this list, for example Oregon (ODEQ 2007).

Table 6-1. Chemicals of concern (*Source:* USEPA 2000a)

List 1 (required for analysis)		**List 2 (strong concern and priority for study)**	
Chemical	**Analytical method**	**Chemical**	**Analytical method**
Metals (mg/kg)		***Metals (mg/kg)***	
Arsenic	6020	Chromium VI	7196A or 7199
Cadmium	6020	***Polycyclic aromatic hydrocarbons (μg/kg)***	
Chromium	6020	Benzo(a)pyrene	8270C
Copper	6020	Biphenyl	8270C
Lead	6020	Perylene	8270C
Mercury	7471A	***Halogenated extractable compounds (μg/kg)***	
Nickel	6020	1,2,4,5-Tetrachlorobenzene	8270C
Selenium	7740	Heptachoronaphthalene	8270C
Silver	6020	Hexachloronaphthalene	8270C
Zinc	6020	Octachloronaphthalene	8270C
Polycyclic aromatic hydrocarbons (μg/kg)		Pentabromodiphenyl ether	8270C
Fluoranthene	8270	Pentachloronaphthalene	8270C
Pyrene	8270	Tetrachloronaphthalene	8270C
Chlorinated aromatics (μg/kg)		Tetraethyltin	Michelsen, Shaw, and Stirling 1996
Hexachlorobenzene	8081A	Trichloronaphthalene	8270C
Phenols (μg/kg)		***Miscellaneous extractables (μg/kg)***	
Pentachlorophenol	8270	4-Nonylphenol, branched	8270C
Pesticides and PCBs (μg/kg)		***Pesticides (μg/kg)***	
Chlordane	081A	Chlorpyrifos	8141
Alpha-benzene hexachloride		Dacthal	8081A
Total Aroclor PCBs	8082	Diazinon	8141
Total DDT	8081A	Endosulfan	8081A
		Ethion	8141
		Kelthane	8081A
		Mirex	8081A
		Oxadiazon	8141
		Parathion	8141
		Trifluralin	8081A

6.2 Chemical Approaches

Wildlife soil screening levels (SSLs), if available (for example, ODEQ 2007), can be used as a first-cut tool to determine whether contaminant concentrations in sediment are not expected to result in a risk to wildlife. These SSL concentrations are derived from empirical dietary studies with representative species in which chemical concentrations in the diet were observed to cause toxicity. The degree of bioavailability observed is specific to the study conditions and test species and may not represent site-specific conditions or species at other locations where the screening levels are applied. There are two parts to the development of wildlife SSLs:

- Determine the most appropriate endpoint and associated safety factor(s) for risk assessment. Endpoints used may include the lowest dose or concentration resulting in a NOAEL or a "lowest observable adverse effects level" (LOAEL) in a receptor.
- Relate the results for the test organism to the site conditions and target species of interest and the sediment concentrations of the COI.

Unless assuming a direct (incidental) ingestion of sediment in the diet (e.g., sandpipers), relating chemical concentrations in sediments to an anticipated exposure scenario for a receptor can be difficult since the association often depends on an indirect relationship between the diet and the site-specific sediment concentrations. Some regional and state approaches for these evaluations are listed below. Some of the approaches provide useful information for deriving wildlife SSLs but may require additional modeling, conservative assumptions, or other information to create SSLs that are relevant to wildlife inhabiting or foraging at the site.

USEPA

USEPA (U.S. Environmental Protection Agency). 1993. *Wildlife Exposure Factors Handbook*, 2 vols. EPA/600/R-93/187. Washington, D.C.: Office of Research and Development. http://cfpub.epa.gov/ncea/cfm/wefh.cfm?ActType=default.

State Guidance

- NJDEP (New Jersey Department of Environmental Protection). 1998. *Guidance for Sediment Quality Evaluations*. http://www.nj.gov/dep/srp/guidance/srra/ecological_evaluation.pdf.
- ODEQ (Oregon Division of Environmental Quality). 2007. *Guidance for Assessing Bioaccumulative Chemicals of Concern in Sediment*. Environmental Cleanup Program. www.deq.state.or.us/lq/pubs/docs/cu/GuidanceAssessingBioaccumulative.pdf.
- OEHHA (Office of Environmental Health Hazard Assessment). n.d. "Cal/Ecotox (California Wildlife Biology, Exposure Factor, and Toxicity) Database." California Environmental Protection Agency in collaboration with University of California at Davis. http://oehha.ca.gov/cal_ecotox/default.htm.
- RSET (Regional Sediment Evaluation Team). 2006. *Northwest Regional Sediment Evaluation Framework*, Interim Final. Prepared by U.S. Army Corps of Engineers—Seattle District, Portland District, Walla Walla District, and Northwestern Division; Environmental Protection Agency Region 10; Washington Department of Ecology; Washington Department

of Natural Resources; Oregon Department of Environmental Quality; Idaho Department of Environmental Quality; National Marine Fisheries Service; and U.S. Fish and Wildlife Service.

- WDOE (Washington Department of Ecology). 2001. "Site-Specific Terrestrial Ecological Evaluation Procedures." Washington Administrative Code (WAC) 173-340-7493. www.ecy.wa.gov/programs/tcp/policies/terrestrial/wac_1733407493.htm.

Departments of Defense and Energy

- NFESC (Navy Facility Engineering Service Center). 2003b. *Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments at U.S. Navy and Marine Corps Facilities, Part 1: Overview of Metals Bioavailability.* http://www.itrcweb.org/contseds-bioavailability/References/bioavailability01.pdf.
- Sample, B. E., and G. W. Suter II. 1994. *Estimating Exposure of Terrestrial Wildlife to Contaminants*. ES/ER/TM-125. Ridge, Tenn.: Oak Ridge National Laboratory. www.esd.ornl.gov/programs/ecorisk/documents/tm125.pdf.
- U.S. Army Public Health Command. n.d. "Army Risk Assessment Modeling System (ARAMS)." http://phc.amedd.army.mil/topics/labsciences/tox/Pages/ARAMS.aspx.

Tissue Residue Analysis

Depending on the receptor tissues evaluated, analysis of chemical concentrations can provide a direct measurement of biological uptake. Many investigators have attempted to relate adverse toxicological effects in birds to the concentrations of individual COPCs in specific avian tissues (Beyer, Heinz, Redmon-Norwood 1996). The tissues most commonly investigated in birds and mammals and the associated COPCs include the following:

- eggs (metals, metalloids such as selenium, PCBs, organochlorine pesticides, PCDDs, and PCDFs)
- feathers, fur (e.g., mercury)
- blood (e.g., lead)
- organs, such as brain, kidney, and liver (metals, metalloids, PCBs, organochlorine pesticides, PCDDs, and PCDFs)
- fat/blubber (in marine mammals, lipophilic contaminants such as PCBs and polybrominated diphenyl ethers)

Tissue Residue Analysis

Advantages

- Directly assesses bioaccumulation
- Can be nondestructive
- May not be expensive (e.g., feather collection)
- Can be used for multiple COCs

Disadvantages

- Can be complicated and require a high skill level (e.g., blood collection)
- Addresses only a single receptor at a time
- Direct extrapolation to effects may not be possible

An advantage of testing feathers, fur, blood, body fat, or muscle is that it can be done nondestructively and the organism does not need to be sacrificed. Measures in tissues such as feathers or fur, however, are not well suited for evaluating bioaccumulation of most contaminants. Feathers and fur are typically routes for excretion and detoxification; therefore, concentrations in these tissues may not be indicative of anything except relative exposure.

Field tissue residue measurements can be compared to laboratory-derived tissue residue thresholds. These threshold values can be found in the various databases, including USACE ERED (USACE n.d. "The Environmental"); Jarvinen and Ankley (1999); Beyer, Heinz, Redmon-Norwood (1996); and the Contaminant Hazard Review series published by the U.S. Geological Survey (USGS) at www.pwrc.usgs.gov/infobase/eisler. These databases are relevant to wildlife species as they include tissue residue values and thresholds for many bird and mammal species. Receptors contained in the above references may not be applicable to a given site. In these cases surrogate species are often used.

Unfortunately, for most chemicals, the advantage the tissue-based toxicity approach provides in reducing uncertainty in the assumptions of chemical bioavailability is offset by the additional uncertainty introduced by the development of the tissue-based toxicity reference values. Our level of understanding regarding the critical body burden and/or toxic mode of action and the amount of data which we have for chemicals like selenium, lead, and cadmium is atypical. For most chemicals, more data are available for dose-response or concentration-response relationships than for tissue residue toxicity relationships. Thus, the estimation of impacts associated with specific tissue residues remains limited by the state of the science.

6.3 Biological Approaches

An additional set of options involves collecting information on actual (direct) measures (Appendix C-T9) of impairment. These tools can be used as an adjunct or replacement for modeling and can indicate whether contaminants are bioavailable at a site. The following are some of the commonly available tools.

6.3.1 Population Surveys

Population surveys are methods of evaluating abundance and reproductive success of receptors and may be used to infer the effects of exposure to COPCs. Population sampling may include measurement endpoints such as population counts and age structure, bird clutch size and fledging success, mammal pup/kit counts, and weight gains. See Section 4.1.2.2 for a description of how community structure and function can provide evidence of COPC-related effects.

6.3.2 Toxicity Testing

Toxicity tests typically measure toxic effects of contaminants on organisms under controlled conditions. While a study of this type does not directly relate the fish tissue concentration to the sediment concentration, it can account for the bioavailability and toxicity of the COPCs as they occur in the prey diet (e.g., fish) of the wildlife species used for testing. Laboratory toxicity studies can be conducted with a contaminated diet collected in the field (see below) or spiked in the laboratory or using other dosing mechanisms (e.g., oral gavage).

Laboratory Tests for Direct Measurements

Advantages
- Controlled environment
- Direct relationship between tissue and sediment

Disadvantage
- Not as representative of site conditions

For an example of laboratory toxicity testing in mammals, ecological risk assessments of PCBs in the Housatonic and Saginaw rivers were conducted by collecting carp directly from these rivers, analyzing PCB concentrations in the carp, and formulating feed to obtain different dose levels for two-generation caged mink studies (Bursian and Aulerich 2003, Bursian et al. 2006, Heaton et al. 1995, Tillet et al. 1996). The mink were monitored for several effects endpoints (i.e., body weight, organ weight, behavior, reproductive success, offspring weight, offspring weight gain) that could be associated with the specific concentration of PCBs in the carp. Dose-response curves were successfully generated for both studies for several endpoints, accounting for the potential contribution of other contaminants in the fish to the observed toxicity.

6.4 Basic Empirical Wildlife Exposure Models

A variety of models and tools be applied to estimate bioavailability from sediments to biota (Appendix C-T9). These tools range from the incorporation of site-specific information into simple equations (ODEQ 2007, USEPA 1993) relating sediment concentrations to effects on wildlife species to more complicated models that incorporate an increasing number of site-specific variables into the dynamics of contaminant movement in the food chain. These tools predict tissue concentrations or adverse biological effects. At the most comprehensive level, models that include consideration of seasonal changes (e.g., diet and home range) and digestive processes (kinetic-, energetic- and fugacity-based trophic models) can be applied for assessing potential bioaccumulation and/or effects.

6.4.1 Basic Modeling Inputs

Basic Modeling

Advantages
- Inexpensive
- Can be performed using assumptions with a limited number of site-specific inputs
- Unlikely to underestimate exposure
- Generally accepted by regulators

Disadvantages
- Determining data representativeness
- Requires field measurements to calibrate and obtain site-specific results
- Likely to overestimate exposure

At the most basic level (i.e., screening level assessments), the only site-specific inputs (other than selecting specific wildlife receptors that are relevant to a site based on habitat and other factors) to a food-web model are the measured concentrations of chemicals in water and/or sediment. Receptor-specific model inputs (food and water ingestion rates, dietary composition [including incidental sediment ingestion], and body weight) are based on available literature values (e.g., USEPA 1993). This screening-level assessment typically uses conservative estimates for these parameters and assumes 100% contaminant bioavailability. While useful for screening assessments, this assumption is often incorrect, particularly for metals in sediment that are known to have relatively low bioavailability factors (e.g., arsenic, barium, lead and chromium). If subsequent quantitative risk assessment is necessary, assumptions such as this should be refined to better reflect likely site and receptor parameters values. As previously described in Section 5.2.1.2, lower trophic level organism (prey) tissue concentrations are typically modeled from sediment (or water) using literature-based BSAFs or BAF/BSAF models (which allow for some adjustment for site-specific conditions (e.g., using measured site TOC or percent tissue lipid into the BSAF formula). Section 5.2.3.1 described accumulation factors for fish and aquatic invertebrates in more detail. Table 6-2 provides some key sources of BAF/BSAF values. ODEQ (2007), RSET (2009), and USEPA (1993) provide additional information on exposure factors relevant to wildlife tissue residue modeling based on chemical concentrations in sediment.

Sediment Ingestion Rates

Animals that consume fish typically have the lowest sediment ingestion rates; species that consume bivalves, benthic invertebrates, and rooted vegetation have much higher rates—up to 22% for the canvasback (Beyer, Perry, and Osenton 2008). Benthic-feeding shorebirds may have incidental sediment ingestion rates of up to 30% (Beyer, Conner, and Gerould 1994).

6.4.2 Exposure Considerations

There are differences in chemical bioavailability from ingested tissue versus ingested sediment since the disposition and form of the COPC may differ. For example, mercury and arsenic in sediment are typically present as inorganic forms, but fish tissue contains almost entirely methylated organic forms of these metals. Living organisms metabolize many organic chemicals, so prey tissue may contain metabolites as well as the parent compounds. Some of these metabolites may be more toxic than the parent compound (e.g., PAHs, dichlorodiphenyldichloroethene [DDE]). DDE, a metabolite of dichlorodiphenyltrichloroethene (DDT), is generally considered more toxic for reproductive effects than the parent compound. Metabolites may not be present in sediment unless physical, microbial, or other biological processes change the chemical form of the parent compound. In addition, for chemicals like PCBs, PCDDs, and PCDFs, certain congeners tend to be degraded or metabolized at slower rates than others, leading to a relative enrichment of particular congeners in both sediment and the associated food web over time. Thus, the congener distribution in a sediment sample will likely differ from that in a plant sample, which will differ from that in a fish or bird tissue sample. This variability complicates modeling of bioaccumulation through the food web.

Some site assessments have made simplifying assumptions based on the availability of the contaminants as a result of the physical characteristics of the habitat (e.g., depth of water, depth of bioturbation zone). In general, avian and mammalian species limit their foraging to water depths of 25 feet or less. For example, double-crested cormorants dive from the water surface to an average depth of 15 feet and a maximum depth of 26 feet (Johnsgard 1993). Eelgrass, which is a principal dietary component for many bird species, occurs at depths only up to 25 feet in Puget Sound (Washington Department of Natural Resources 2001). While mammals such as harbor seals and river otters may dive to deeper depths, most of their foraging activity is likely to be in the upper meters of the water column where prey species are most abundant and their visual-based ambush strategy is more effective (USEPA 1993).

As discussed previously, most ERAs use “standard” food-web models to estimate exposure to wildlife from dietary pathways. Bioavailability should be accounted for in the estimate or measurement of the dietary sources, as well as the fraction of the contaminant present in the food source that is assimilated by the receptor. Thus, the next step in making the model more representative of site conditions is the incorporation of site-specific concentrations.

6.4.3 Site-Specific Measurements

Given the uncertainties with non-site-specific BSAFs (see Section 4.1.3.3), direct sampling of prey tissues is the most robust quantitative measure of bioaccumulation and bioavailability. Direct tissue measurements integrate bioavailability directly into the methodology and allow calculation of site-specific BSAFs (Meador et al. 2008). These BSAFs can then be extrapolated to the universe of dietary sources and receptors.

BSAF determinations have implicit sources of uncertainty and variability built in, including the following, each of which is clarified below:

- lipid analysis
- OC analyses and sediment f_{oc}
- chemical analysis of contaminant concentrations in organism tissues
- identification of appropriate site-specific factors linking the organism to the sediment

Lipid content, in both prey and the wildlife receptors, may vary seasonally and influence bioavailability and exposures. Some species may store contaminants in fat reserves when preparing for migration, hibernation, or reproduction. Adverse effects from these contaminants may not occur until the fat reserves are metabolized for energy requirements, at which point the organism and/or their offspring may no longer be exposed to site contaminants. Lipid normalization of contaminant levels in tissue is standard practice for many organic contaminants (i.e., a factor in derivation of BSAFs) and is intended to reduce observed variability in tissue contaminant concentrations. However, the analysis of lipid(s) is not an exact science. Seasonal variation in organism lipid content and/or method variability and a lack of precision in lipid concentrations reported in units of percent can have a large impact on lipid-normalized concentrations of bioaccumulative chemicals such as PCBs and PCDDs/PCDFs. Typically, lipids cannot be detected in tissues below concentrations of 0.2%. Various methods (e.g., gravimetric, TLC/FID) used to determine lipid content include the use of extraction solvents (e.g., hexane, ether, chloroform) and extraction techniques (e.g., Soxhlet, ASE, SFE). There is no accepted standard method (Duncan et al. 2007b). Sometimes lipid analytical methods are specified as part of a protocol for a specific contaminant such as PCBs and PCDDs/PCDFs (e.g., USEPA Methods 1668A and 1613B, respectively).

Normalization of nonionic organic contaminant sediment concentrations to f_{oc} in the sediment is applied to the denominator of the BSAF equation. Like partitioning to lipids, partitioning to f_{oc} usually makes nonionic organic COPCs less bioavailable. While analytical methods for TOC are more established than those for lipids, analytical precision and variability in analysis of OC also can have a large impact on normalized concentrations of chemicals expressed in units of parts per trillion.

Laboratory Tests for Direct Measurements

Advantages

- Controlled environment
- Direct relationship between tissue and sediment

Disadvantage

- Not as representative of site conditions

Another factor influencing variability in observed BSAF concentrations is the fact that even with sessile organisms, the ability to co-locate biota and the sediment to which the biota are exposed may be challenging. In practice, the top 10–15 cm of sediment is considered to be the biological active (or bioturbation) zone (Oliver et al. 1980, Weston 1990, Aller and Dodge 1974) and is the sediment interval that is sampled for the determination of site-specific BSAFs. However, the animals that live in or below this zone (e.g., burrowing clams, worms, shrimp), principally in marine habitats, may feed or draw in water at the sediment surface or may have feeding strategies that are selective to particle size or to suspended particulates. Therefore, the sediment contaminant concentrations to which these organisms are exposed may differ substantially from bulk sediment concentrations in the top 10–15 cm that are typically used to normalize f_{oc}.

Prey items for the vast majority of wetland and aquatic avian receptors are plants, invertebrates (including shellfish, like mollusks), and/or fish. Other prey items may include amphibians, reptiles, other birds, and small mammals, but these prey items do not typically compose a significant proportion of the diet for most wetland and aquatic avian receptors. For some site-specific baseline investigations, tissue concentrations may be measured in some prey species but not in others; therefore, modeling methods are used for those prey items that are not measured but are considered in the diet of the receptor.

Additional guidance for the direct sampling of chemical concentrations in tissue can be found in the following:

- *Biomonitoring of Environmental Status and Trends (BEST) Program: Selected Methods for Monitoring Chemical Contaminants and Their Effects in Aquatic Ecosystems* (Schmitt and Dethloff 2000)
- *Biomonitoring of Environmental Status and Trends (BEST) Program: Field Procedures for Assessing the Exposure of Fish to Environmental Contaminants* (Schmitt et al. 1999)
- *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments* (USEPA 1997b)
- “Field Studies for Ecological Risk Assessment” (USEPA 1994b)

Bioaccumulation into prey species, which are consumed by wildlife species, can be evaluated using laboratory testing techniques. Laboratory bioaccumulation test methods are available on invertebrate test species (polychaetes, oligochaetes, insect larvae, bivalves, and crustaceans) (USEPA 1991, 1998b, 2002e; ASTM 2010) in both freshwater and marine environments. Other parameters required for a wildlife exposure model (e.g., site-specific receptor body weights, ingestion rates, and dietary composition) are rarely quantified on a site-specific basis. Bioaccumulation (and bioavailability) can also be evaluated by placing caged organisms (e.g., mussels) or units that mimic bioaccumulation (such as SPMDs) at the site for a predetermined time period and then analyzing the tissue or device for contaminant accumulation.

6.5 Process-Based Predictive Models

Predictive models (Appendix C-T9) based on kinetic, mass balance, and steady-state relationships have been developed to describe the bioaccumulation of HOCs in aquatic food webs (e.g., Thoman, Connolly, and Parkerton 1992; Gobas 1993; Arnot and Gobas 2004). The bioaccumulation portion of these models rely on the contaminants' K_{ow} to estimate uptake and elimination constants through respiration and diet of aquatic organisms in different trophic levels. Contaminant tissue concentrations in aquatic organisms are calculated (i.e., modeled) for different trophic levels of a food web through diet and respiration. The modeled tissues concentrations can then be used to estimate dose- and dietary-based exposure and risk quotients for upper trophic level mammals and birds consuming aquatic organisms (USEPA 2009).

Predictive Modeling

Advantages

- Can be less expensive than effects measurements
- Does not require direct evaluation of target receptors and is less intrusive than tissue sampling
- Can potentially incorporate multiple exposure mechanisms

Disadvantages

- Requires a high skill level and input from multiple disciplines to complete
- Potential for error without sufficient field validation of key model parameters
- May not be acceptable by regulators as a final result, especially if it indicates no unacceptable exposure

K_{ow} can influence exposure as follows:

- For chemicals with a log K_{ow} <4, direct uptake from water is a more important exposure pathway.
- For chemicals with a log K_{ow} >4, dietary uptake is the more important means of chemical exposure and there may be potential for food-chain transfer.

In general, these models are sensitive to chemical K_{ow}, lipid content, and the ratio between the chemical concentration in the water column and in the sediment. These factors can be difficult to quantify since literature-based K_{ow}s vary depending on the source used, tissue lipid analytical methods are generally not precise, and even with low limits of detection it is difficult to measure HOC concentrations in surface water. Notwithstanding the above, these models are generally accepted by the scientific community as a reasonable approach for estimating the bioaccumulation of persistent HOCs in aquatic systems (Burkhard 1998). A few of the more well-known predictive models, some of which have been applied to a variety of sites, are briefly discussed below.

The Gobas (1993) model has been used to successfully estimate concentrations in fish and wildlife, primarily for lake food webs. The Gobas (1993) model for fish is currently available in electronic format from Simon Frasier University (see Appendix C-T5 and C-T7). The model is also available embedded in a forwardly predictive, risk-based program: TrophicTrace (http://el.erdc.usace.army.mil/trophictrace). Each of these forms of the model is restricted to fish as prey species for birds and mammals. Arnot and Gobas (2004) published a broader model that includes other aquatic species that could be prey for wildlife and mammals. Although originally developed and applied to the Great Lakes ecosystem for modeling PCBs and selected pesticides, the Arnot and Gobas (2004) model has been applied and validated for other ecosystems, including the Hudson River, Fox River/Green Bay, and Bayou D'Indie in Louisiana.

In the 1980s, USEPA initiated the Gill Exchange and Transport System (GETS) model for calculating chemical uptake into aquatic organisms. This model was amended with a food component to form the Food and Gill Exchange Transport System (FGETS) while the successor model to FGETS is the Bioaccumulation and Aquatic System Simulator (BASS) model (USEPA n.d. "Bioaccumulation"). The BASS model simulates the population and bioaccumulation dynamics of age-structured fish communities. Further information on these models can be found at www.epa.gov/ceampubl/fchain/bass/index.html.

WASP7 (Water Quality Analysis Simulation Program) (USEPA n.d. "Water") helps users interpret and predict water quality responses to natural phenomena and man-made pollution. This revised and updated version of the WASP model is currently available in the public domain at www.epa.gov/athens/wwqtsc/html/wasp.html. This version incorporates fish age structure and population dynamics into the simulation of the bioaccumulation of hydrophobic COPCs.

Research to validate these legacy models in aquatic ecosystems has resulted in the general conclusion that the models are accurate within an order of magnitude (Burkhard 1998). Thus, many risk assessors have chosen to calibrate the models with subsequent field sampling programs or to skip the modeling activities and empirically evaluate the bioavailability of contaminants by directly sampling aquatic organisms.

6.6 Application of Bioavailability Measures in Risk Assessment and Risk Management

As discussed previously, the methods for evaluating contaminated sediment impacts on wildlife run the gamut from simple literature-based evaluations to detailed modeling and site-specific toxicity studies. As the level of complexity increases, the opportunities for accounting for the bioavailability of contaminants also increase. In many cases, several lines of evidence are evaluated to determine whether the contaminant is (1) not bioavailable to the wildlife, (2) bioavailable at levels that are unlikely to cause an adverse impact, or (3) bioavailable at levels that require remedial action. The following examples of receptor evaluations identify how the bioavailability assessment was used to quantify risk at a site.

Population Survey: Tree Swallow Example

The tree swallow is a species frequently used for site nesting evaluations, particularly for PCB- or dioxin-contaminated sites, because it nests in artificial structures and thus can be attracted to a site through the erection of such structures. Nest boxes also lower predation rates (a potential confounding factor) and allow easy access for monitoring egg laying, nestling growth, and nest success or for collecting eggs or young for tissue residue analysis. Tree swallows are aerial insectivores that forage over wetland and aquatic habitats and thus are exposed via the diet to insects that emerge from contaminated sediments.

Avian Receptors (Tree Swallow)

Tree swallows are aerial insectivores that forage over wetland and aquatic habitats and are thus exposed via the diet of insects that emerge from contaminated sediments. This species is a very useful avian receptor for evaluating contaminated sediments because of the following:

- They readily use nest boxes, so study areas can be established at specific locations of interest where suitable habitat is present.
- Individual swallows generally feed within 400 m of their nest sites on emergent aquatic insects, so residues in their tissues reflect local sediment contamination for chemicals that readily accumulate in such tissues.

- Tree swallows nest within close proximity to one another, allowing adequate sample sizes to be obtained.

Accordingly, this species has been widely used to evaluate the bioavailability of sediment contaminants and their effects on avian receptors at a variety of sites, including the Great Lakes (Bishop et al. 1999, Froese et al. 1998), the Fox River and Green Bay, Wisconsin (Custer et al. 1998); the Woonasquatucket River, Rhode Island (Custer et al. 2005); the Housatonic River, Massachusetts (Custer et al. 2003); and the Hudson River, New York (McCarty and Secord 1999, Secord et al. 1999).

Such studies typically involve placing nest boxes in areas that reflect a spatial gradient of sediment concentrations for contaminants such as PCBs, dioxins/furans, and/or organochlorine pesticides, including placement in uncontaminated reference areas. Nests are monitored and direct measures of various population-level metrics are collected. Typical metrics include clutch size, hatching success, nestling growth rate, and fledging success.

A statistical comparison of metric values between contaminated areas and reference areas allows for a direct evaluation of potential population-level effects, especially when coupled with direct measures of exposure (biomarkers and/or tissue residue data). Tissue residues are typically measured in eggs, newly hatched young, and/or nestlings near the fledging stage. If measured over time, these data also allow for direct measurement of the rate, in addition to the extent, of bioaccumulation. When coupled with the corresponding measurement of chemical concentrations in sediment, benthic invertebrates, and emergent insects (the latter is typically through the analysis of the gut contents of older nestlings), site-specific BSAFs can be calculated that relate sediment concentrations directly to the tissue residues in eggs or nestlings, which can in turn be related to measures of reproductive effects.

Custer et al. (1998) used tree swallows to evaluate the bioaccumulation and effects of PCBs on avian reproduction from exposure to PCBs in the sediments of the Lower Fox River and Green Bay. PCBs were measured in eggs, newly hatched young, and 12-day-old nestlings collected from nest boxes placed in contaminated reaches (site) and from upstream (uncontaminated) reference areas. Measures of reproductive success (e.g., clutch size and hatching success) were also collected. While total concentrations and rates of accumulation for PCBs (and DDE) were elevated in site samples relative to reference samples, clutch size was not adversely impacted, and hatching success was not significantly correlated with PCB concentrations in eggs. These data were used to conclude that population-level effects to reproducing tree swallows were not occurring in the Lower Fox River and Green Bay from exposure to PCB-contaminated sediments.

Other Sources of Information

Some cleanup sites in the country have required larger-scale investigations than other sites. These “mega” sites typically compile the “state of knowledge” related to many of the scientific and engineering variables needed for decision making. Significant compilations of both reviewed literature and site-specific bioaccumulation information exist within the remedial investigation reports for these studies. Such sites include Portland Harbor, Fox River, Hudson River, Puget Sound Naval Shipyard, Passaic River, Great Lakes reports, Commencement Bay, Chesapeake Bay, and the Everglades.

Froese et al. (1998) collected and analyzed sediments, benthic invertebrates, tree swallow eggs, and nestlings to evaluate linkages between PCBs in sediments and at various trophic levels in the Saginaw River, Michigan. An SQC for PCBs (based on toxic equivalents [TEQs]) protective of sensitive avian species at the same trophic level as tree swallows (0.15 ng/g TOC) was calculated using the site-specific data (concentrations of sediments, benthic invertebrates, tree swallow eggs, and nestlings), a food-web model, and an acceptable HQ of 1.0. Using this value and the BSAF calculated for tree swallow nestlings, the HQ for sediments in Saginaw Bay, Michigan was determined to be 0.7. This HQ was interpreted to indicate that the dioxin-like PCB congeners present in the sediments of the bay should not cause adverse effects to tree swallows at the locations studied.

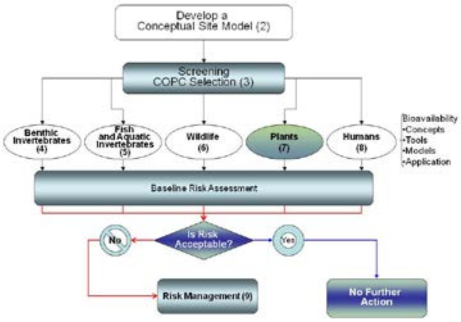
7. BIOAVAILABILITY IN PLANTS

Determination of direct plant toxicity from plant tissue concentration measurements is generally not a factor in ecological risk assessment and management. More often, measured plant tissue concentrations are intended to be used in the food chain exposure assessment for humans and wildlife.

Plants serve as primary producers in ecosystems. At its most extreme, plant toxicity can result in loss of this function (e.g., unvegetated areas). Secondary effects may include erosion, habitat loss, or food loss for other trophic levels. However, because of their sessile nature (with the exception of aquatic algae), plants have evolved unique chemical exclusion (e.g., at the root zone) and compensatory (e.g., metals chelation) mechanisms that allow them to control chemical bioavailability and to survive in environments that could be toxic to other types of life. For example, miners historically used observations of specific metal-tolerant or hyperaccumulating plants (i.e., metallophytes) to determine locations of mineral-rich soils (Baker, Brooks, and Reeves 1988).

There is also a wide array of plant sensitivities to chemicals. Lewis (1995) has shown that some freshwater plants, such as periphyton (aquatic algae that grow on rocks), are more sensitive to many chemicals than are fish and invertebrates. Other plants are less sensitive and may help remediate contaminated areas (i.e., phytoremediation) (Seidel et al. 2004). Plants can, for example, create and sustain oxygenated root-zone habitat suitable for communities of chemical-degrading bacteria, or they may uptake and sequester chemicals in specific parts of the plant that may then be harvested. Less-sensitive plants are frequently an important part of reclamation and restoration projects.

This chapter describes how bioavailability of contaminants in freshwater and marine sediments to plants can be incorporated into ERAs. Figure 7-1 shows a general flow diagram for the bioavailability tests for the plant pathway. Two methods of measuring bioavailability in plants are discussed in the following sections:



- chemical measurement of bioavailability in the specific plant tissues
- plant uptake BAFs used to estimate plant tissue concentrations

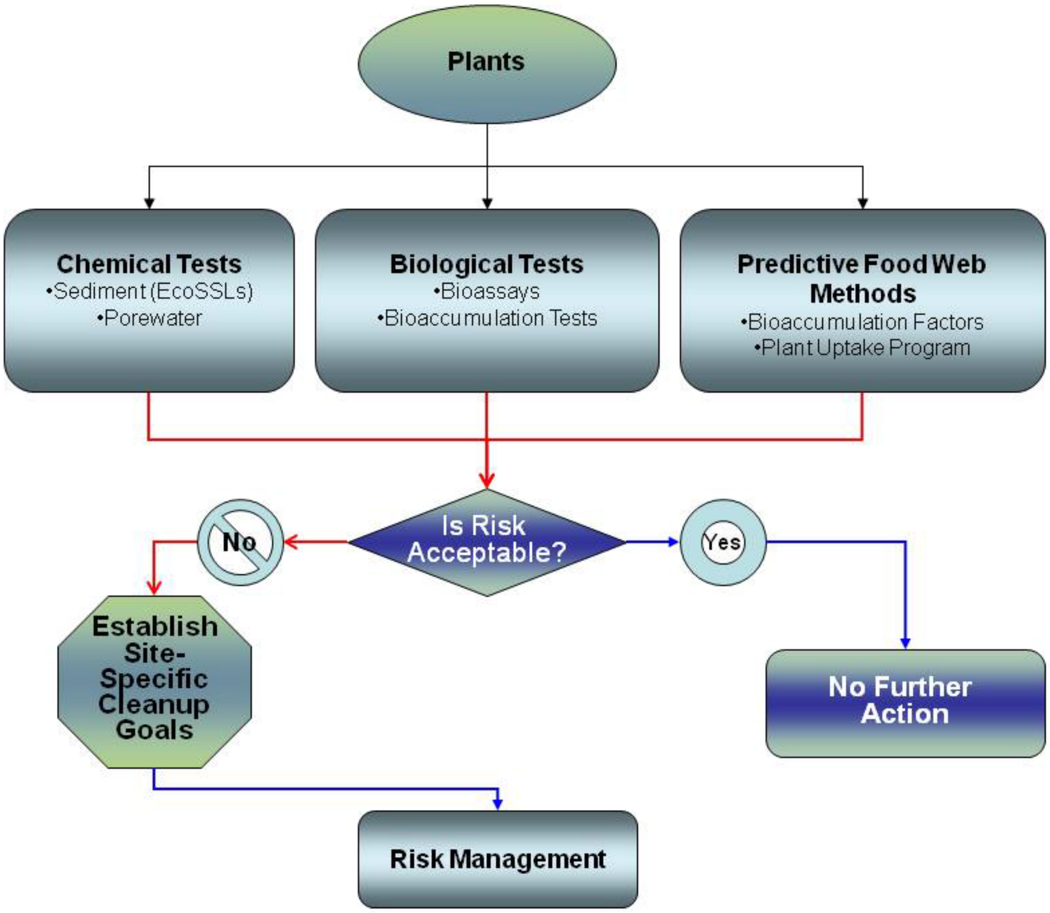


Figure 7-1. **Plant community decision diagram.**

7.1 Chemical Approaches to Plant Exposure Assessment

No sediment chemical screening levels have been developed for the protection of aquatic plants. Therefore, this section reviews SSLs (as a surrogate for sediment) and water screening levels (as a surrogate for sediment pore water) that are intended to be protective of plants, while acknowledging that sediment properties are distinct from soil (e.g., percent moisture and OC content). It is recognized that these thresholds for terrestrial plants may be significantly different than those for aquatic systems but may be an indicator of magnitude of potential harm.

USEPA has two sources of screening levels that address the potential for plant toxicity at hazardous waste sites. The first are ecological soil screening levels (EcoSSLs, www.epa.gov/oswer/riskassessment/ecorisk/ecossl.htm) compiled for the most common COPCs reported in recent RODs at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites (derived by workgroups with participants representing state, federal, consulting, industry, and academic stakeholders). The second contains chemical stressor concentration limits (CSCLs) published as part of the data collected for USEPA's Hazardous Waste Identification Rule (USEPA 1999a). The Department of Energy's ORNL has also developed *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants* (Efroymson et al. 1997, www.esd.ornl.gov/programs/ecorisk/documents/tm85r3.pdf). These screening levels are intended to be concentrations that cause de minimis effects on plant receptors and can be used to identify COPCs in soils requiring further evaluation in a baseline ERA. Most soil screening values are derived using conservative assumptions, and the resulting benchmarks are therefore also conservative (some may be less than site background levels).

7.2 Biological Approaches

7.2.1 Bioassays

Plant bioassays have been designed to determine phytotoxicity using a wide variety of aquatic plant species (Gorsuch et al. 1991). These tests have predominantly used terrestrial crop plants (e.g., lettuce) or freshwater aquatic algae and plants (e.g., duckweed).

USEPA (1994a) examined the utility of using a freshwater rooted vascular plant (*Hydrilla verticillata*, or water thyme) toxicity test. Out of 43 combinations of test species and endpoints, the *Hydrilla* endpoint of root length ranked third in terms of sensitivity, but other endpoints in this species were found to be less sensitive: shoot length (22nd), dehydrogenase activity (26th), chlorophyll a (28th), and peroxidase (43rd). Despite promising results with the root length endpoint, no standard regulatory test methods have been developed for *Hydrilla*.

Plant Bioassay Tests

Advantages
- Controlled conditions so the effects of the site sediment on chemical bioaccumulation in a specific plant species can be more directly assessed.
- Reduced variability in bioaccumulation, which has relevance to comparisons to available plant tissue screening levels.

Disadvantage
- Species tested and/or the concentrations measured may not be relevant to site-specific plants or the diet of wildlife/ humans.

Reviews of available toxicity tests and estuarine specific field and laboratory studies using plants are contained in Gorsuch et al. (1991) and Lytle and Lytle (2001), respectively. Currently, research is being conducted to develop aquatic plant species test methods including procedures for water milfoil (*Myriophyllum*—a draft method exists and has been evaluated by USACE), eelgrass (*Vallisnaria*), water weed (*Elodea*), and other species.

Most evaluations of plant toxicity involve the comparison of soil (or sediment) COPC concentrations to chemical parameters of concern concentration believed to cause toxicity in plants. The plant screening levels discussed in Section 7.1 have limited ability to predict plant toxicity, since the chemical bioavailability associated with specific site conditions is not known. However, a few sources of plant tissue thresholds of toxicity do exist for specific crops, as shown in Table 7-1.

7.2.2 Bioaccumulation

Plant bioaccumulation tests are less frequently implemented than toxicity test, and the only standard test methods use upland species, either human food crop test species (USEPA 1996a–m) or preferred confined disposal facility test species (USACE 2002). Appendix C lists plant toxicity and bioaccumulation test procedures and plant bioaccumulation field studies.

Table 7-1. Plant tissue toxicity reference values (ppm dry weight)

Analyte	Mature leaf toxic level[a]	Threshold for yield reduction			50% Yield reduction[e]
		Plant specific[b]	General[c,d]		
Arsenic	5–20	NA[f]	20	NA	NA
Cadmium	5–30	8 (barley)	15	5	NA
Chromium	5–30	NA	10	NA	5.9 (com)
Cobalt	15–50	NA	20	NA	NA
Copper	20–100	19 (barley) 21 (lettuce) 6 (rape) 11 (ryegrass) 11 (wheat)	20	10	40 (com) 60 (bush bean)
Lead	30–300	NA	35	NA	NA

[a] Kabata-Pendias and Pendias 1984.
[b] Beckett and Davis 1977.
[c] Davis, Beckett, and Wollan 1978.
[d] Macinoll and Beckett 1985.
[e] Chang, Granato, and Page 1992.
[f] Data not available.

7.3 Modeling Plant Bioavailability and Bioaccumulation

Plant bioaccumulation models based on empirical data have been extensively reviewed by ORNL (Bechtel Jacobs 1998a) as well as USEPA for the protection of human health and wildlife as part of the development of SSLs and EcoSSLs, respectively (USEPA 1996a–m, 2005a). These models represent the potential transfer of chemicals from soil to plants and, in the absence of sufficient data specific to aquatic plant chemical accumulations from sediment, they are the only viable surrogate for estimating chemical bioavailability and uptake in aquatic plants. Additionally, in the screening level ecological risk assessment (SLERA) protocol guidance, USEPA published summaries of soil-to-plant BAFs and considers these applicable as sediment-to-plant BAFs (USEPA 1999b). Despite the recommendation, we recognize that the physicochemical characteristics of sediment differ markedly from soil and may influence the bioavailability of chemicals in sediments to aquatic vegetation in ways that cannot be predicted. The primary difference is clearly the presence of continuous overlying water, which affects sediment redox potential, chemical bioavailability, and the types of biological communities that are present. The soil bioaccumulation models are intended to be used in environments where the organic matter content is less than 10% and pH is in the range 4.0–8.5.

BAFs and regression equations have been used to predict soil-to–terrestrial plant bioaccumulation. For the earlier evaluation performed by USEPA (1996m), only BAF estimates were available from the literature for the crops of interest. At the time

Bioaccumulation Model

Advantage
- Potentially less costly than direct measurement.

Disadvantages
- Estimates are uncertain and not site or tissue specific (e.g., roots, shoots, leaves, and berries) with most plant BAFs developed for specific soil conditions.
- Sediment conditions, particularly sediment redox potential, are known to affect chemical bioavailability to plants.

of a later evaluation (USEPA 2005b), some regression equations were available and were preferred over BAFs as long as the equation was significant (i.e., the slope differed significantly from 0 @ $p = 0.05$) and the coefficient of determination (R^2) was ≥0.2. Bechtel Jacobs (1998b) found that uptake factors did not lead to the best estimates of plant tissue concentrations.

Appendix C summarizes BAFs and bioaccumulation equations for inorganics available from USEPA SSL (USEPA 1996m), USEPA SLERA protocol (USEPA 1999b), and USEPA EcoSSL (USEPA 2005b) guidance. There are no specific sediment conditions (e.g., grain size and TOC) that can be used as modifying factors for a BAF. BAFs are applied to bulk sediment concentrations. Where a BAF is not available, USEPA EcoSSL guidance suggests using a default BAF of 1.

Equations for individual organic compounds were not available at the time of the SSL guidance (USEPA 1996m) but were reported in the USEPA SLERA protocols (USEPA 1999b) and EcoSSL guidance (USEPA 2005b) for select organic analytes (see Appendix C).

USACE has also developed a Plant Uptake Program (PUP version 1.0 EEDP-04-12, available at http://el.erdc.usace.army.mil/products.cfm?Topic=model&Type=drgmat) that can be used to estimate the bioaccumulation of inorganic chemicals from freshwater dredged material (sediment or soil media, Folsom and Houck 1990). This program was developed through the collaboration of the U.S. Army Engineer Waterways Experiment Station (WES, renamed Engineering Research and Development Center) Environmental Laboratory and Purdue University to evaluate wetland or upland dredged material disposal as a beneficial use option. The plant species used for this estimation was *Cyperus esculentus* (yellow nut grass), and uptake estimates were based on data collected 1977–1989 by WES and its contractors. These data showed that heavy metals extracted from sediment using diethylenetriaminepentaacetic acid (DTPA) correlated well with plant uptake. The program uses regression techniques (ordinary least squares) to estimate the upper 90% confidence interval of the concentrations taken up by plants.

The use of DTPA and other sediment extraction methods to determine the bioavailable fraction of contaminants to plants has been reviewed by the NRC (2003). Other chemical extracts used to estimate bioavailability to plants include ammonium bicarbonate-DTPA, dilute hydrochloric acid, the Mehlich-3 mixture (composed of acetic acid, ammonium nitrate, nitric acid, ammonium fluoride, and EDTA), and the Mehlich-1 mixture (composed of dilute solution of hydrochloric and sulfuric acids, NRC 2003). A limitation on the use of specific extract procedures is that correlations with actual plant concentrations may be poor if the plants evaluated are different than the species used in the development of the extraction procedures or if the matrix conditions are different than the conditions of those evaluated during the development of the extraction procedure (e.g., pH).

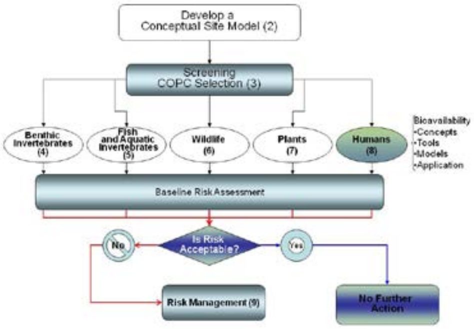
Chemical bioavailability to plants is challenging to predict given the wide array of plant species and their varying chemical accumulation potential, varying chemical conditions that can affect chemical bioavailability (e.g., pH and redox conditions), and the general lack of bioaccumulation models with specificity to plant tissue types (e.g., roots, seeds, or leaves). In practice, plant tissue concentrations are not frequently evaluated on contaminated sediment sites since generally other pathways (e.g., fish consumption by wildlife or humans) dominate the transfer of chemical contaminants in food chains. Site-specific measurements of plant tissue concentrations can quantitatively determine the degree to which chemicals are accumulating in plants and the degree to which this exposure pathway may contribute to overall sediment-related exposures. In the event that site-specific plant tissue measures are proposed, the refinement of target species and tissues needs to occur based on an understanding of the exposure pathway of concern. The plant tissues collected and processing methods used define the use of these data. For example, it may be appropriate to evaluate whole plant concentrations (e.g., algae), or it may be appropriate to evaluate plant parts separately (e.g., roots and shoots), depending on which plant parts are anticipated to be consumed by a particular receptor species. If human use of the plant product (i.e., fruit consumption) is a concern, the sample needs to be prepared in a manner that is consistent with how the product is consumed, which may include washing, peeling, and/or cooking. Other sample preparation steps may be appropriate if exposures to wildlife are being evaluated.

7.4 Application of Bioavailability Tools in Risk Assessment and Risk Management

Direct assessment of plant bioaccumulation potential can provide valuable information to a risk assessment that may otherwise be highly uncertain if based on the application of simple bioaccumulation models such as BAFs. Determination of direct plant toxicity from plant tissue concentration measurements is generally not a factor in ecological risk assessment and management. More often, measured plant tissue concentrations are intended to be used in the food chain exposure assessment for humans and wildlife. The St. Regis Paper Co. site in Minnesota provides an example of how select plant parts and processing methods were used in a human and ecological exposure assessment.

The **St. Regis Paper Company Superfund site**, located in the city of Cass Lake, Minnesota, is the former location of a wood-preserving facility that operated 1957–1985 (USEPA n.d. “St. Regis”). Creosote and pentachlorophenol (PCP) are the two wood preservatives used throughout the operational history. The principal COPCs at this site are PCDDs and PCDFs, unintended by-products associated with pentachlorophenol, that include the identified carcinogen 2,3,7,8-tetrachlorodibenzo-p-dioxin. Additional COPCs evaluated at this site include PCP, PAHs, PCBs, pesticides, and metals. The site occupies 125 acres within the exterior boundaries of the Leech Lake Band of the Ojibwe Indian Reservation adjacent to Pike Bay and Cass Lake (both freshwater bodies). Wild rice production is very important to the economy and culture of the Leech Lake Ojibwe people, and their reservation produces more wild rice than any other reservation in the state. Accordingly, it was important at this site to evaluate the potential human health risk posed by the consumption of wild rice. Human health risk was evaluated on processed rice samples, which involved finishing (i.e., parching, removing hulls, and winnowing) the rice. Unprocessed rice samples were used in the evaluation of ecological (avian and mammalian receptor) risk and to understand the effect processing had on rice sample concentrations. USEPA has not made these risk assessments available on the Internet, so the degree to which chemical concentrations were accumulated by rice (processed or unprocessed) cannot be reported. A cleanup decision has not been reached for this site, but a ROD is anticipated.

8. BIOAVAILABILITY TO HUMAN POPULATIONS



Consideration of bioavailability in human health exposure can significantly impact cleanup objectives and, consequently, the feasibility of particular remedial options. Bioavailability as it pertains to human exposure involves estimating the potential exposure to humans via food consumption using biouptake methods, most of which have been discussed in previous chapters, and can also include estimating the level of contaminant absorption by humans once exposure occurs.

As indicated in the generic CSM presented in Section 2.1, humans can be exposed to contaminated sediment both directly via wading or swimming in impacted areas and indirectly via consumption of organisms or plants that have accumulated contaminants from sediment. Because of the potential for biomagnification, low contaminant concentrations in sediment may result in unacceptable risks to humans consuming fish or shellfish. Compared with other human exposure pathways, fish consumption tends to be a common risk driver scenario for sediment sites. Human exposure to COPCs may also occur via ingestion of piscivorous wildlife, primarily game birds that may have some level of COPCs in their tissue as a result of their dietary consumption of impacted fish or shellfish. Ingestion of affected plants such as wild rice that are cultivated or grow wild in contaminated areas (see St. Regis case study in Section 7.4) can also be a complete exposure pathway.

The focus of this section is how the bioavailability of contaminants in freshwater and marine sediments affects human exposures. Other variables associated with evaluating human exposure, such as the extent or frequency of exposure, are topics for the risk assessment and are not considered here. Figure 8-1 shows a general flow diagram for this consideration.

8.1 Direct Contact

Human exposures risks may arise from dermal contact with sediment or incidental ingestion of sediment during activities such as swimming, beach use, dockyard work, boat and marine equipment operation/repair, diving, etc. A first-cut screening for this pathway can be completed by comparing bulk sediment concentrations to published federal or state SSLs (e.g., USEPA's "Regional Screening Levels for Chemical Contaminants at Superfund Sites," USEPA n.d. "Regional"). Since sediment direct contact exposures are generally so much lower than those for soil, if sediment concentrations are found to be below these criteria, no further assessment is required. If these preliminary screening criteria are exceeded, site-specific screening values may be developed by modifying exposure variables to reflect the differences between soil and sediment exposures.

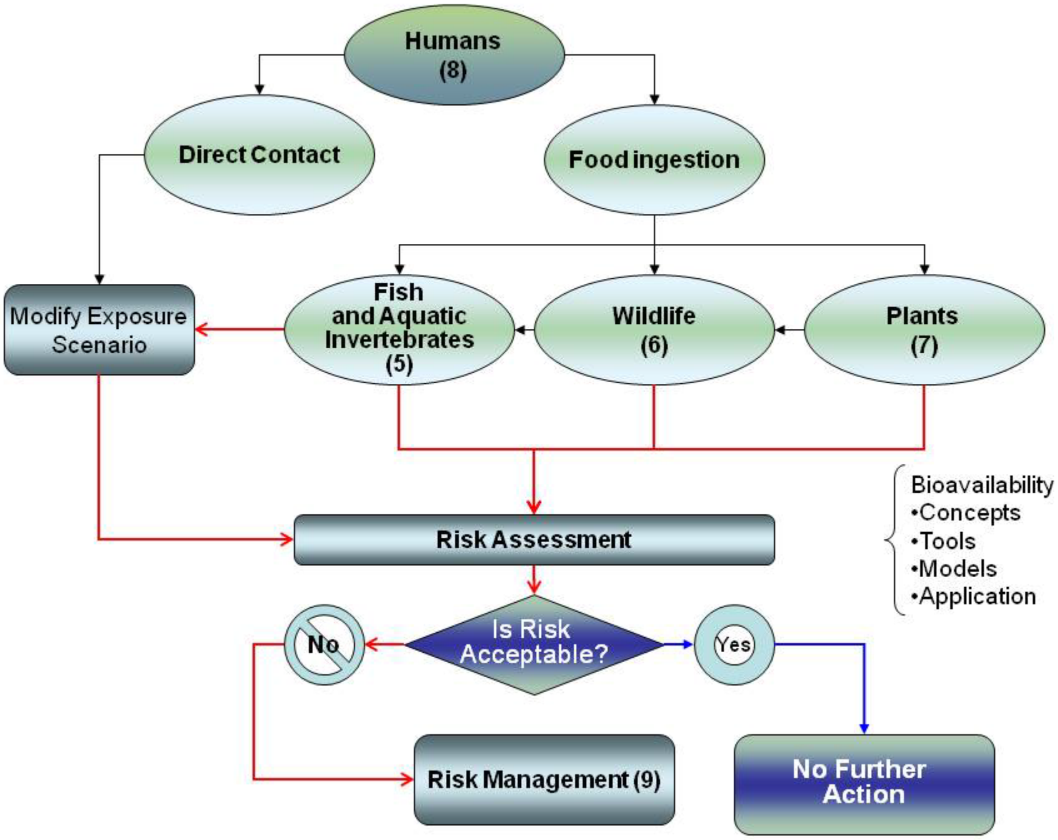


Figure 8-1. Human health decision diagram.

Human exposure to sediment differs from exposures to soil due to potential differences in the physicochemical properties of the two media, as well as the unique scenarios under which these exposures to sediments occur. However, because studies addressing human exposure to sediment are limited, assessments for sediment often default to scenarios and uptake values published for soil in either state or federal guidance. Bioavailability factors addressing various COPCs in soil (the adherence of sediments to skin, dermal absorption efficiency, and gastrointestinal absorption efficiency) have been empirically derived for some classes of COPCs and are available in USEPA's RAGS (USEPA 2004c). The Agency for Toxic Substances and Disease Registry toxicological profiles (www.atsdr.cdc.gov/toxprofiles/index.asp) also provide contaminant-specific absorption information. USEPA (2004c) also addresses bioavailability considerations for dermal contact with contaminated sediment. Factors that decrease bioavailability include water content, complexation in the water column, and the degree of sediment presence above water (submerged sediments typically wash off and do not pose an exposure concern). Several of the categories for skin adherence (e.g., wet soil) could apply to exposed sediment.

USEPA allows a rapid, inexpensive in vitro gastric simulation test to generate site-specific bioavailability factors following the ingestion of lead in soils (http://epa.gov/superfund/bioavailability/guidance.htm). Although sediment is a different medium, it is close enough to soil to justify that the mechanism of uptake in the gastrointestinal tract would be comparable. In cases where one or more COPCs drive an unacceptable risk outcome after using a default bioavailability factor and assuming sediment uptake is similar to soil, the user may want to conduct additional literature research or testing and/or engage in discussions addressing the bioavailability of the COPCs in sediments with the project team.

Individual USEPA regions may also have guidance on how to derive site-specific bioavailability factors. For example, Region 8 conducted several studies on the bioavailability of arsenic in a variety of soils found in Colorado (USEPA n.d. "Bioavailability"). Based on these studies, it recommends a conservative relative bioavailability factor of 0.5 for arsenic from contaminated soil (i.e., 50% of the soil arsenic, relative to sodium arsenate, will be absorbed from the gastrointestinal tract). An example of an animal study confirming this factor using site-specific sediment, which could be applied to any jurisdiction, is described at the end of this chapter.

8.2 Fish and Shellfish (Aquatic Invertebrate) Ingestion

In evaluating whether dietary exposure to humans is an important pathway, the type of contaminant should be considered. USEPA (n.d. "Persistent," www.epa.gov/pbt/pubs/aboutpbt.htm) has identified 12 PBT constituents. Some states and regions, such as Texas and the Pacific Northwest (RSET 2009), have established lists of contaminants for which the bioaccumulative pathway must be considered. In general, however, bioaccumulation concerns should be limited to selected classes of organics (pesticides, PCBs, dioxins) and mercury.

Evaluation of sediment-associated contaminant accumulation by fish and shellfish has been described in Chapters 4–6. This section describes how the accumulation evaluation is incorporated into human health exposure estimation.

8.2.1 Development of Screening Values

Generic screening levels for sediment for the fish ingestion pathway can be back-calculated from acceptable tissue levels (ATLs) that are estimated assuming a particular fish ingestion rate and human toxicity factors. In some cases, an established reference, such as a fish tissue advisory, may also be used. As previously defined (Section 5.2.3.1), BSAF or BAF values are often used to back-calculate a bulk sediment concentration associated with achieving an ATL for each individual COPC:

$$\text{screening level value} = f_{oc}(\text{ATL}/(\text{BSAF})(f_L))$$

where f_{oc} is the fraction of total organic carbon in the sediment and f_L is the fraction of lipid content in the edible tissue. For development of generic screening levels, default assumptions for f_{oc} and f_L are used. However, organic carbon and lipid fractions can be used to adjust screening levels based on site-specific bioavailability. Where site-specific data are unavailable for these two parameters, they may still be adjusted to better represent site-specific conditions by using published data for similar conditions (e.g., sediment type, edible fish species present, etc). Two sources of published BSAFs are USACE (n.d. "BASF") and USEPA (n.d. "BASF").

In some cases the site-specific SLVs are higher to the extent that exposure via a certain pathway is determined to be below a level of concern (see Text Box 8-1).

Text Box 8-1. Example of Site-Specific Screening Level Modification

ODEQ has established a recreational human fisherman generic sediment SLV of 0.019 mg/kg for hexachlorobenzene. The ATL in fish tissue is 0.0058 mg/kg, the estimated BSAF is 0.105 kg OC/kg lipid, and the default values for fish lipid fraction and sediment TOC fraction are 0.03 and 0.01, respectively. However, game fish at the site have a lipid fraction of 0.02, and sediment sampling indicates an average TOC of 0.10. Using the site-specific values in the SLV equation:

$$\text{site-specific SLV} = (0.10 \times 0.0058 \text{ mg/kg}) / (0.105 \text{ kg OC/kg lipid}) \times 0.02) = 0.28 \text{ mg/kg}$$

Thus, applying site-specific information raises the screening value 15-fold.

In cases where SLVs are being used to estimate food source concentrations, they might also be modified based on the contaminant concentration that is available in the sediment pore water, which in some cases may reflect the bioavailable contaminant fraction. It may be determined that the pathway for bioaccumulation involves the step of dissolution (bioaccessibility) into adjacent pore water before uptake into an organism's tissue can occur. There is significant uncertainty in this assumption as it is not clear what processes occur during digestion that may make sorbed contaminants bioavailable.[4]

Pore-water concentrations can be measured directly by several tools described in Appendix C. Pore-water concentrations can also be estimated using assumptions about EqP to sediment OC (organic compounds) or AVS (divalent inorganic metals) in the sediment. A variety of models have been presented in Chapter 4 that could be used to apply pore-water results to adjust the fraction of contaminant concentration that is bioavailable in the human health exposure pathway. Direct measurement of pore water has also been detailed in Chapter 4.

8.2.2 Direct Tissue Analysis of Fish/Shellfish

In many cases, human exposures to COPCs from consumption of fish and shellfish are estimated using actual measured concentrations of COPCs in tissue. Direct measurement of COPC concentrations in tissue reduces the uncertainty regarding bioavailability in sediments. Depending on the size of the impacted zone relative to the home range of the receptor species analyzed, it may be difficult to directly correlate concentrations of COPCs in sediment with fish tissue COPC concentrations. Impacts from contaminant sources upstream or downstream from the site may also complicate the relationship between site impacted sediment and fish concentrations. However, field measurements generally provide more accurate estimates of bioaccumulation than do published BSAFs, which tend to be generic and overly conservative.

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[4] One way to evaluate whether this is an important step for biouptake is to estimate or directly measure pore-water concentrations of COPCs and then develop a regression between pore-water concentrations and measured food-source concentrations. If there is a stronger correlation with estimated or measured pore-water concentrations than with bulk sediment concentrations, then dissolution into pore water is likely an important step in biouptake.

Collection and measurement of fish and shellfish (invertebrates) are discussed in Chapter 5; however, several additional factors are pertinent to determining the representativeness of these data when collected for use in human health evaluations:

- Site fidelity—Sampling should occur from areas where fishing/collection is known or predicted to occur.
- Species—Species should be sampled that serve as food sources for human populations. Size and/or age restrictions on fish that can be caught may apply to certain species.
- Tissue—Edible portions should be analyzed. Often only fish fillets are consumed, which tend to accumulate lower concentrations of contaminants than other portions (e.g., organs, bones, fatty deposits, etc.) of the fish. It is important to understand the local population and their potential practices since some populations consume or use entire fish.
- Preparation method—Different levels of contaminant loss are associated with different fish-preparation methods. For example, frying fish in a pan may retain more contaminants than grilling, in which fat is allowed to drip.

Depending on the size of the impacted zone relative to the home range of the receptor species analyzed and/or impacts from contaminant sources upstream and downstream from the site, it may be difficult to directly correlate concentrations of COPCs in sediment with fish tissue COPC concentrations. However, field measurements generally provide more accurate estimates of bioaccumulation than do published BSAFs, which tend to be generic and overly conservative. As has also been discussed in previous sections, fish tissue values can be estimated or obtained through laboratory bioaccumulation tests or use of caged species placed at the site.

8.3 Wildlife Ingestion

Fish are typically the primary species of concern when assessing human health risks for bioaccumulative contaminants in sediment. However, consideration should also be given to potential exposures that may occur via ingestion of other wildlife. Ducks, for instance, can be exposed to contaminated sediment via incidental ingestion of sediment and through dietary ingestion of aquatic vegetation and benthic and/or pelagic organisms. The primary method for assessing this pathway is to obtain information on the dietary habits of the species of concern and use data collected as described in Chapter 6 to estimate concentrations that may accumulate in the target wildlife species. Exposures are then estimated based on these dietary components.

8.4 Plant Ingestion

Similarly, humans may be exposed to sediment-associated contamination via ingestion of plants that have been grown in the contaminated area (e.g., seaweed, wild rice) or crops in which dredged spoil was used as a soil amendment. Chemical bioavailability to plants is challenging to predict given the wide array of plant species and their varying chemical accumulation potential, the varying chemical conditions that can affect chemical bioavailability (e.g., pH and redox conditions), and the general lack of bioaccumulation models with specificity to plant tissue types (e.g., roots, seeds, or leaves). In practice, plant tissue concentrations are not frequently evaluated on contaminated sediment sites since generally other pathways (e.g., fish consumption) dominate the exposure to COPCs. Site-specific measurements of plant tissue concentrations can quantitatively determine the degree to which chemicals are accumulating in plants and the degree to which this exposure pathway may contribute to overall sediment-related exposures. In the event that site-specific plant tissue measures are proposed, the refinement of target species and tissues needs to occur based on an understanding of the exposure pathway of concern. The plant tissues collected and processing methods used define the use of these data. For example, it may be appropriate to evaluate whole plant concentrations (e.g., algae), or it may be appropriate to evaluate plant parts separately (e.g., roots and shoots), depending on which plant parts are anticipated to be consumed by a particular receptor species. If human consumption of the plant product is a concern, the sample needs to be prepared in a manner that is consistent with how the product is consumed, which may include washing, peeling, and/or cooking. Other sample preparation steps may be appropriate if exposures to wildlife are being evaluated.

8.5 Application of Bioavailability Tools in the Human Health Pathway

8.5.1 Industri-plex Superfund Site, Woburn, Massachusetts

The Industri-plex case study illustrates the use of both in vitro and in vivo testing to assess the relative bioavailability (RBA) of arsenic in sediment to humans who could potentially be exposed through recreational contact. The Industri-plex site was once occupied by the former Merrimac Chemical Co., once the nation's leading producer of lead arsenate, the main insecticide used in apple orchards in the 19th century. Prior to completion of the human risk assessment, an arsenic bioavailability study was performed to increase the level of site-specificity being incorporated into the quantification of sediment risks. The bioavailability study consisted of two phases: an in vitro screening phase followed by an in vivo bioavailability assessment. The in vitro extraction test was performed on a total of 12 fine-sieved sediment samples obtained from four locations along the Aberjona River (www.epa.gov/region1/superfund/sites/industriplex/213091Appendix6part10.pdf). The in vitro test served as a screening tool to identify specific selection criteria for use in identifying a smaller number of samples to carry through to the in vivo assessment. The in vitro test measured the amount of arsenic that dissolves in a reactor that simulates the stomach fluid of humans, and the amount of arsenic that solubilized after one hour was used as a preliminary indicator of the in vivo RBA.

Using the results of the in vitro test to identify two appropriate sediment test materials, an in vivo bioavailability assessment was conducted wherein immature swine were fed dough balls containing sediment test materials at weights set to equal target doses of 300, 600, and 900 µg/day. Control animals were fed equivalent doses of sodium arsenate. Samples of urine were collected from each animal for three consecutive 48-hour periods on days 6/7, 8/9, and 10/11 of the study. Laboratory analyses were submitted in a blind fashion, and measurements accounted for all forms of arsenic (i.e., As[III], As[V], and methylated species). The RBA of arsenic in the sediment samples was calculated by dividing the absolute bioavailability (ABA, which is the amount absorbed/amount ingested) of the test sediments by the ABA of the sodium arsenate. The RBAs of the site sediments were 37% and 51%, respectively. The risk assessment toxicity factors were adjusted accordingly using the more conservative relative bioavailability factor of 0.51 (i.e., USEPA Integrated Risk Information System (IRIS) reference dose was divided by 0.51 and the cancer slope factor multiplied by 0.51). Thus, the study results reduced the estimated human health risks by half.

8.5.2 Johnson Lake

Johnson Lake covers an area over 18 acres and is directly connected to the Whitaker Slough, which in turn flows to the Columbia Slough, a quiescent waterway located south of the Columbia River. A number of environmental investigations conducted at the site have indicated elevated levels of PCBs, metals, and PAHs in lake sediment resulting from runoff from surrounding properties. Sediment samples collected throughout the lake indicated that PCBs were present at concentrations (57–1040 ppb) that exceeded screening levels (0.39 ppb) for protection of human health based on fish consumption. To assess the level at which PCBs were being accumulated in fish, a fish tissue sampling effort was undertaken. Tissue concentrations (90% upper confidence level of 870 ppb whole body fish) exceeded the ATL for human health (4.7 ppb). Whole body tissue samples were appropriate in this case as there was evidence that local populations were using whole fish in stews. Bioavailability was indirectly measured in this assessment through the calculation of a site-specific BSAF. The site-specific BSAF was then used to calculate a protective sediment concentration of PCBs.

ODEQ concluded that sediment contamination in Johnson Lake poses an unacceptable risk to human health based on the risk associated with ingestion of PCB-contaminated fish. Human health-based RAOs for this site were as follows:

- eliminate potential hot spots in Johnson Lake sediments by managing sediment to the extent practicable to reduce the average PCB concentration in sediment by approximately 72%
- prevent human consumption of fish with tissue concentrations greater than 0.003 µg/kg PCB congener 126

The areas with highest PCB concentrations were proposed for removal, reducing average sediment concentrations by 72%. This reduction in average PCB concentrations in the lake is expected to result in close to an order of magnitude reduction in potential cancer risk associated with fish ingestion. Once this initial reduction is achieved through active remediation efforts, such as the removal of sediments in the southern portions of the lake, natural recovery mechanisms along with upland source control measures are expected to further reduce concentrations to protective levels. The ROD for the Johnson Lake site can be viewed at http://www.deq.state.or.us/Webdocs/Forms/Output/FPController.ashx?SourceId=1311&SourceIdType=11.

9. INCORPORATION OF BIOAVAILABILITY INTO RISK ASSESSMENT AND RISK MANAGEMENT

Bioavailability information can augment traditional site characterization and human/ecological risk assessments to help refine the CSM for a contaminated sediment site and to better understand a receptor’s likely exposure to site contaminants. The following sections summarize the use of bioavailability in assessing the risk associated with contaminated sediment sites and provide an overview of the use of the bioavailability assessment data in risk management. Risk management integrates the results of the risk assessment with other technical, political, legal, social, and economic objectives to develop and implement risk reduction and exposure prevention strategies (SERDP and ESTCP 2008). This section provides insight on how bioavailability information can be used to understand, mitigate, and/or manage risk at a contaminated sediment site within the areas of risk assessment and risk management.

The ITRC Contaminated Sediments Team is developing follow-up guidance on strategic selection of remedial alternatives and best management practices for mitigating exposure and risk from contaminated sediment sites. Assessing bioavailability as a monitoring parameter will be important in this next guidance as well.

9.1 Risk Assessment

To truly understand sources of risk[5] at a site, an investigator or regulator should strive to gain the best possible understanding of the physical, chemical, and biological processes that "drive" the risk (i.e., the means of COPC transfer, uptake, and concentrations at which adverse effects to receptors occur). Tools selected to determine toxicity depend on site specific habitat and receptor groups (Figure 9-1). The tools and measures identified in Chapters 4–8 aid in the assessment of site-specific contaminant bioavailability. Bioavailability assessments provide a more accurate measure of site specific risk than comparing analytical results to generic screening values. For example, it has been shown through extensive laboratory and field research that the presence of carbon (naturally occurring or anthropogenic) in sediments has a large influence on pore-water concentrations of HOCs (see Section 4.1.1.2). Since impacts to benthic organisms depend to a large extent on the dissolved pore-water concentrations of these compounds, applying methods to determine pore-water concentrations enhances the ability to predict current and potential effects.

The decision-making process to determine the cause of toxicity within a risk assessment (Figure 9-1) likely involves using a weight-of-evidence approach. This approach is necessary because there is generally no definitive measurement tool that adequately demonstrates all bioavailability processes at the site. Decisions based on bioavailability measurements are influenced by the fact that bioavailability is often highly site specific and depends on soil/sediment type, aging/weathering of contaminants, fate and transport of the contaminant or the media in which the contaminant is present, exposure pathways, and potential receptors. Therefore, a single measurement, such as the indirect or direct analysis of pore-water concentrations, often requires supporting information to determine whether the bioavailability measurement is truly representative of site conditions (NRC 2003).

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[5] As discussed in Chapter 2, a detailed discussion of risk assessment is beyond the scope of this document; however, Table 2-2 provides references for conducting ecological/human health risk assessments.

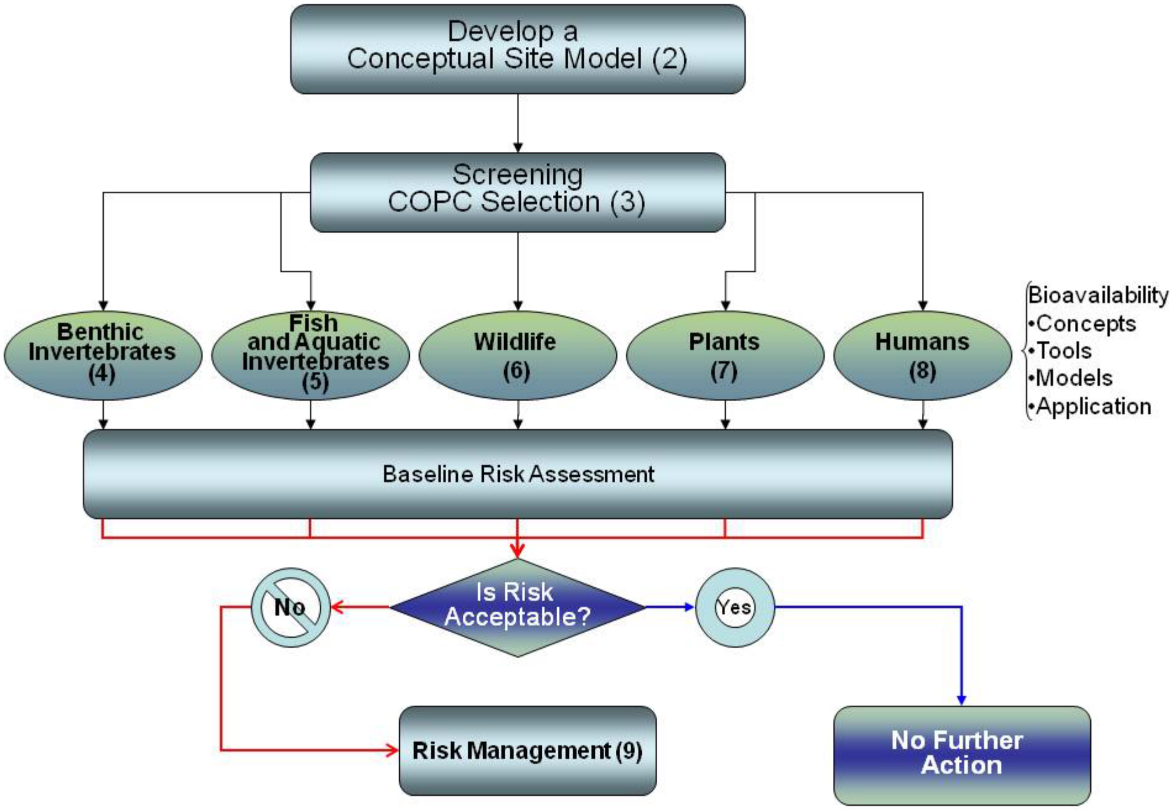

Figure 9-1. Sediment assessment process followed in this guidance.

An example of a weight-of-evidence approach for contaminated sediments is the three-tiered evaluation called the Sediment Quality Triad, which is often used to evaluate the benthic pathway (see Section 1.1). The SQT approach consists of three distinct measurements: sediment chemistry, toxicity testing, and macroinvertebrate surveys. Impact is evaluated based on consistent indications from at least two of the measurements. The complexity of a site and the number of exposure pathways evaluated determine the nature and number of lines of evidence needed to understand risk, including the selection of the appropriate bioavailability measurements.

The assessment of bioavailability can be a valuable tool in the site characterization and exposure assessment process. Advantages and challenges of using bioavailability information within the risk assessment process while contemplating risk management decisions are listed below:

Advantages

- Contaminants that are not bioavailable are not included in the calculation of risk.
- Protective cleanup plans can be optimized, and remedial costs may be reduced.
- Limited resources are more efficiently used.
- Risk of cleanup can be balanced with the risk posed by the contaminants in sediments.
- More technically defensible cleanup goals can be achieved and more accurate cleanup priorities established while still ensuring protection of human health and the environment.

Challenges

- Acceptance by the regulatory agency, stakeholders, and public is uncertain.
- Site-specific bioavailability results may be difficult to compare across sites.
- Higher initial cost during site characterization phase may be required.
- Time may be added to the schedule, which may be inconsistent with short timelines for remediation.

In general, bioavailability considerations should be incorporated into the risk assessment process to obtain a clearer understanding of contaminant toxicity and exposure pathways, such that remedy selection decisions can be optimized. The ITRC Contaminated Sediments Team has summarized the pathways, contaminants, and bioavailability tools that were used at various sediment sites in Table 9-1. Information in Table 9-1 was submitted to the ITRC during the course of this project. More information about each site is provided in Appendix D and may be useful in determining whether bioavailability considerations contributed to remedy decision making at a particular site and how the bioavailability data were used in the process.

Table 9-1. Summary table of exposure pathways, contaminants, and bioavailability tools at sediment sites

Site name	Exposure pathway	Contaminants	Bioavailability tools
1. Bremerton Naval Complex, OU B Marine, WA	Human health	Mercury	• Bioaccumulation (fish tissue)
2. Bradford Island Disposal Site, OR	• Human health • Benthic • Pelagic	• PCBs • Metals	• Tissue chemistry • Surface water chemistry • Trophic modeling
3. Buffalo River, NY	• Benthic • Pelagic	Parent and alkylated PAHs	• Pore-water EqP normalized to TOC
4. Camp Lejeune IR Site 89, NC	• Benthic • Pelagic	PAHs	• Trophic modeling • Macro invertebrate chemistry
5. Cass Lake, MN	• Human health • Benthic • Plants	• Dioxins • PCP	• Bioaccumulation
6. Centre County Kepone, PA	• Human health • Benthic • Pelagic	• Mirex • Kepone • Photomirex	• BAF
7. Diamond Alkali–Passaic River Study Area, NJ	• Human health • Benthic • Pelagic	• PCBs • Dioxin • Dieldrin • Chlordane • DDT • Tetrachlorodibenzo-p-dioxin (TCDD) • Mercury • Copper • Lead	• Tissue chemistry • Toxicity testing • BSAFs
8. Fifteenmile Creek, OR	• Benthic • Wildlife	Oxyflourfen	• Tissue chemistry • Toxicity testing (in situ and caged fish)

Site name	Exposure pathway	Contaminants	Bioavailability tools
9. Fox River, WI	• Human health • Pelagic	• PCBs • Mercury	• Benthic community survey • Bioassay of bulk sediment • Toxicity tests
10. Glenbrook Nickel–Coos Bay, OR	Benthic	Nickel	• Metal concentration relative to fine-grained material
11. Hackensack River, NJ	• Human health • Benthic • Pelagic	Chromium	• Pore-water chemistry • SEM/AVS • Benthic tissue analysis • Laboratory toxicity and bioaccumulation testing • Benthic community survey
12. HoltraChem, ME	• Benthic • Water-column vertebrates and invertebrates • Human health	Mercury	• Toxicity tests • Benthic community surveys • Bioaccumulation/bioassay
13. Horseshoe Road and Atlantic Highlands Superfund Site, NJ	• Benthic • Pelagic • Wildlife	Arsenic	• Tissue chemistry • Toxicity testing • Benthic community survey • Bioaccumulation
14 Imperial Refinery, OK	Benthic	PAHs	• Tissue chemistry • BSAFs • Toxicity testing
15. Industri-plex, MA	Human health	Arsenic	• In vivo relative bioavailability
16. Indian River Power Plant, DE	Benthic	PAHs	• Pore-water estimates using (EqP)
17. Johnson Lake, OR	• Human health • Benthic • Wildlife	• PCBs • Metals • PAHs • Petroleum hydrocarbons (PHCs)	• Tissue chemistry • Toxicity testing
18. Lake Hartwell PCB Superfund Site, SC	• Human health fish consumption • Benthic	• PCBs	• Sediment deposition and bioaccumulation modeling • Fish tissue analysis • Benthic tissue analysis
19. McCormick & Baxter Superfund Site, OR	• Human health • Benthic • Pelagic	• PAHs • Hydrocarbons • PCP • Metals	• Surface-water chemistry • Fish tissue analysis • Toxicity tests
20. Mocks Pond, IN	• Benthic • Human health	• PCE, TCE, DCE, VC	• Diffusion samplers in pore water
21. Myrtle Street Embayment, WA	• Benthic • Human health	• PCE, TCE, DCE, VC	• Diffusion-bed samplers in pore water
22. Moffett Field, CA	Benthic	• PCBs • Arochlor 1268 • Asbestos • Lead	• Tissue chemistry • Bioaccumulation (BAF) • Food-chain modeling

Site name	Exposure pathway	Contaminants	Bioavailability tools
23. Onondaga Lake, NY	• Human health • Benthic	• Metals • PAHs • PCBs	• Pore-water chemistry • Toxicity testing • Benthic community surveys • Tissue chemistry • Bioaccumulation/bioassay
24. OU 1, Marine Corps Air Station, NC	Benthic	• Organics • Metals	• Toxicity testing
25. Pearl Harbor Sediment, HI	• Benthic • Human health • Fish and water-column invertebrates • Birds	• Metals • PCBs • Dioxin • PAHs • Pesticides • Herbicides • Ordnance	• Tissue chemistry • Pore water • Toxicity tests • Benthic community surveys • Bioaccumulation/bioassay
26. Philadelphia Reserve Basin, PA	• Human health • Benthic • Pelagic • Wildlife	• PCBs • Metals	• Pore-water chemistry • Fish tissue chemistry • SEM/AVS • Benthic community survey • Bioaccumulation tests • Toxicity test
27. Portland Harbor, OR	• Human health • Benthic • Pelagic • Wildlife	• PCBs • Metals • PAHs • Pesticides • Tributyltin • Total petroleum hydrocarbons • SVOCs	• Surface water chemistry • Pore water • Benthic/pelagic tissue chemistry • Toxicity testing
28. Private Residence, PA	Benthic	• VOCs • PAHs	• Benthic community survey
29. Soda Lake, WY	• Benthic • Pelagic • Wildlife	Selenium	• Bioassays • Pore water (EqP) • Tissue chemistry • Trophic modeling
30. Former Springfield Gas Works, MA	Benthic	PAHs	• Pore-water chemistry (SPME) • Toxicity testing
31. Former Tarrytown General Motors Assembly Plant, NY	Benthic	• Chromium • Copper • Lead • Mercury • Zinc	• AVS/SEM • Pore-water chemistry • Benthic community survey • Tissue chemistry • Toxicity testing • Bioaccumulation

Site name	Exposure pathway	Contaminants	Bioavailability tools
32. Tectronix Wetlands, Beaverton, OR	Benthic	• Cadmium • Copper • Chromium • Lead • Mercury • Nickel • Silver • Zinc	• Bulk sediment chemistry • SEM/AVS • Bulk sediment toxicity bioassay
33. Tri-State Mining District, KS	Benthic	• Cadmium • Lead • Zinc	• Pore-water chemistry • Toxicity testing
34. Vandenberg AFB Site 5 Cluster	Benthic	Metals	• Bulk sediment chemistry • Toxicity testing
35. Washington Navy Yard, DC	Benthic	PAHs	• Pore-water chemistry (SPME) • Toxicity testing

9.2 Risk Management

USEPA recognizes the need to improve the scientific foundation for contaminated sediment remedy selection by improving site and risk characterization, understanding how different remedial options can effectively reduce risks to humans and the environment, and optimizing the cost-effectiveness of remedial actions. Furthermore, USEPA recognizes the important role that bioavailability plays in this scientific foundation (USEPA 2005a). Assessing bioavailability by using the tools described in this document can increase the understanding of the cause and sources of toxicity and lay the foundation for the most appropriate remedy and monitoring requirements at a site. As a result, RAOs can be established that more specifically address the risk pathways and sources.

Bioavailability can also be important in determining the appropriate methods for managing identified risk. Assessing bioavailability will not only help to focus action on chemicals that are available for uptake by receptors (with the potential to cause adverse effects), but also provide information pertinent to effective remedy design and implementation. By incorporating bioavailability considerations into the early stages of site characterization through the risk assessment process and up through the point of remedy selection, a more effective remediation may be accomplished, which will optimize overall cost. This approach can be particularly important at sediment sites where contamination has been spread across large areas and, in some cases, through multiple watersheds.

Sediment remedies typically involve capping, dredging, and/or natural recovery. Table 9-2 presents bioavailability considerations that may influence the remedial design, implementation, and monitoring associated with each of these cleanup options. These considerations apply as well to managing contaminant release and transport during implementation of capping and dredging, as well as monitoring residual contamination from both undisturbed sediments and sediments redeposited from suspended sediments resulting from cap placement or dredging operations.

Table 9-2. Reasons to consider bioavailability in the remedy selection, design, implementation, and monitoring phases

Remedy	Remedy selection	Remedy design	Remedy implementation	Remedy monitoring
No further action (NFA)	Provides a more accurate site exposure evaluation, which leads to a decision that there is no adverse impact to the environment as opposed to using standard (i.e., conservative, non-site-specific) risk assessment inputs (i.e., SQGs).	NA	NA	Can verify the lack of COC bioavailability over time.
Monitored natural recovery (MNR)/ enhanced monitored natural recovery (EMNR)	Provides a more accurate site exposure evaluation, which indicates that COC bioavailability will either remain constant or decrease with time.	Can provide a more accurate prediction of changes in COC concentrations and associated bioavailability with time based on site-specific data. EMNR cap design can be based on modeled reduction in bioavailability.	Thin layer caps may require similar bioavailability considerations as those included in Capping (see below).	Provides a measure of biota recovery (i.e., sediment toxicity, benthic community size and/or diversity). Can quantify either a decrease in bioavailability through sequestration/burial or an increases in bioavailability due to resuspension, groundwater flow, bioturbation, scouring, etc.
Capping	Provides a more accurate site exposure evaluation as opposed to using standard (i.e., conservative, non-site-specific) risk assessment inputs (i.e., SQGs) to establish RAOs. This evaluation may lead to a determination that capping can effectively isolate contaminants and adequately reduce bioavailability.	Can help provide a more accurate determination of cap thickness requirement based on estimated breakthrough (i.e., from pore-water measurement), or to isolate biota from direct contact with COCs (bioactive depth). Can help to determine cap materials that will limit contaminant mobility (e.g., OC content).	Provides verification of adequate cap thickness to isolate contaminated sediments from overlying water and biota. Can identify an increase in contaminant bioavailability during implementation: contaminant release and transport downstream. Provides a measurement of residual bioavailable contamination in sediments redeposited from particulates resuspended during cap placement.	Offers a measurement of cap effectiveness (i.e., cap integrity or pore-water COC concentrations migrating into and through the cap).

Remedy	Remedy selection	Remedy design	Remedy implementation	Remedy monitoring
Removal	Provides a more accurate site exposure evaluation as opposed to using standard (i.e., conservative, non-site-specific) risk assessment inputs (i.e., SQGs) to establish RAOs, enabling dredging to be focused on areas which are true source of bioavailability concern. Consideration of bioavailability should also be included in an assessment of impacts from dredging alternatives (e.g., resuspension impacts, residual sediment following removal, etc.).	Can assist in the development of site-specific cleanup goals and more accurately identify the associated limits of sediment in need of removal. Aids in the design of resuspension controls, should they be necessary.	Can identify an increase in contaminant bioavailability during implementation: contaminant release and transport downstream. Provides a measurement of residual bioavailable contamination in both undisturbed sediments and sediments redeposited from suspended sediments resulting from dredging operations.	Monitoring residual contamination focuses on concentrations that are actually bioavailable and pertinent media of concern (e.g., water column fish, benthic diversity, etc.).

The selected remedy should be designed to take into account where bioavailability measurements indicate adverse impact to receptors and the relationship to a particular media, concentration, or exposure pathway. For example, the thickness of and material used in a capping system could be adjusted to account for contaminant concentrations in sediment pore water rather than in bulk sediment. Likewise, the quality and quantity of components in active capping systems could be designed to take into account the fate and transport of contaminants in the exposure media of concern (i.e., advection/diffusion of pore water vs. static bulk sediment chemistry).

Since the objective of a remedial approach is to mitigate potentially unacceptable risks, bioavailability measurement tools can be useful in monitoring the effectiveness of a remedy as they can focus efforts on the particular pathway/media of concern. For example, pore-water monitoring within a cap might indicate whether groundwater discharge or upwelling is mobilizing contaminants into a clean cap or whether bioturbation is mixing clean sediment with the underlying contaminated sediment to a degree that receptors are being exposed again at harmful levels.

The future ITRC contaminated sediments guidance document will discuss the selection and implementation of a remedy at a contaminated sediment site; however, the following provides a brief overview on how bioavailability considerations have been incorporated into remedial decisions at a contaminated sediment sites.

The team has identified the following remedies and used case studies to highlight how bioavailability information influenced the decision at the site:

- no further action (NFA)
- monitored natural recovery (MNR) or enhanced MNR (EMNR)
- in situ capping
- removal

9.2.1 No Further Action

This decision is typically based on the evaluation that there is no adverse impact to human health or the environment from bioavailable levels of COPCs in the sediment. USEPA (2005a) states "No-action or no-further-action alternatives normally do not include any treatment, engineering controls, or institutional controls but may include monitoring. For example, at a site where risk is acceptable (e.g., because contaminant levels in surface sediment and biota are low and the site is stable), but the site contains higher levels of contamination at depth, it may be advisable to periodically evaluate the continued stability of buried contaminants." An NFA decision could be affected by considering site-specific bioavailability measurements which indicate contaminant concentrations that are actually available for receptor uptake and result in a risk-based evaluation of no adverse effect upon ecological or human receptors. As an example, at IR Site 89, Marine Corps Base (MCB) Camp Lejeune, sediment and surface water data indicated exceedances of benchmarks; however, an evaluation of bioavailability parameters indicated that conditions associated with the site were not different than reference conditions. Accordingly, it was concluded that there was no risk associated with the site, and no cleanup was performed. As an example, at Tektronix in Oregon, metals concentrations exceeded conservative screening levels, but evaluation of AVS/SEM indicated metals were not bioavailable at concentrations of concern. As a result, no remedial action for Beaverton Creek was determined to be necessary.

9.2.2 Monitored Natural Recovery

MNR is a remedy that typically uses known, ongoing, naturally occurring processes to contain, destroy, or otherwise reduce the bioavailability or toxicity of contaminants in sediment (ESTCP 2009). The decision to use MNR at a site is generally derived from a risk-based process that indicates that bioavailability of COPCs will either remain constant or decrease over time. MNR was the selected remedy at Lake Hartwell Site in South Carolina. At this site, even though there was a significant volume of sediment containing PCBs above the 1 ppm cleanup level established in the ROD, the higher PCB levels were buried at depth below sediments with lower PCB levels. Predictive modeling was used to estimate PCB levels in surface sediment and bioaccumulation in fish tissue over time. The results of this modeling showed that PCB concentrations were expected to decrease over time in both surface sediment and fish, and combined with the impracticability of dredging the large volume of impacted sediments (and anticipated limited effectiveness of dredging to reduce PCBs), MNR was selected. In addition, the ROD specified that sediment transport be enhanced in Twelvemile Creek by flushing sediments through dammed impoundments to accelerate MNR. EMNR is MNR combined with some other intrusive remedy (e.g., thin-layer placement of clean sediment at sites where the natural rate of sedimentation is insufficient to bury contaminants in a reasonable timeframe) to accelerate reductions in surface sediment concentrations (USEPA 2005a).

9.2.3 Capping

In situ capping refers to the placement of a subaqueous covering or cap of clean material over contaminated sediment that remains in place (USEPA 2005a). The design of appropriate capping systems depends on many physical, chemical, and biological variables. For instance, cap thickness depends on the rate of transfer of COPCs from underlying sediment pore water to the surface water above the cap, and therefore a more accurate determination of pore-water COPC concentrations and their effects on biota is essential. Additionally the cap thickness is often determined by considering the site-specific thickness needed to isolate biota from contaminated sediment (i.e., providing a clean bioavailable layer). A modification to this is an active cap. In the case of active caps, the physical, chemical, and biological processes that affect bioavailability, as outlined in this document, would be used to design a cover system to reduce bioavailability of COPCs (e.g., the use of activated carbon to sequester hydrophobic organics within the active cap). Capping of contaminated sediment has been employed at numerous sites throughout the United States. One example of where bioavailability played a role in delineating the areas to be capped is Onondaga Lake in New York. At this site there are numerous contaminants for which cleanup levels were established using multiple lines of bioavailability evidence. The remedy includes dredging in near-shore littoral areas to make room for an engineered cap, thin-layer capping in the main body of the lake, and MNR for the remainder of the site.

9.2.4 Removal

Dredging and excavation are means of removing contaminated sediment either while it is submerged (dredging) or after water has been diverted or drained (excavation) (USEPA 2005a). Dredging volumes are generally based on remedial goals that have been established during the site characterization process. Incorporating bioavailability measurements into a risk-based decision process can aid in the development of a site-specific remedial goal, thus targeting sediment removal only to areas that are known to cause toxicity. For instance, cleanup levels based on the EqP-TU approach were calculated for intertidal sediments contaminated with NAPL and dissolved-phase, diesel-range organics at the Indian River Power Plant site in Delaware. An underground pipeline leaked diesel fuel into sediments in the Indian River.

Bulk sediment chemical measures of PAH parent compounds and alkylated homologs were normalized to the TOC concentrations. Pore-water concentrations of these compounds were predicted using EqP and were subsequently divided by the analyte-specific acute and chronic values calculated from narcosis theory. For each sample, the individual quotients were summed to yield acute and chronic TUs. TUs >1 indicated that pore-water exposure concentrations were potentially high enough to cause toxicity to benthic organisms. The state required excavation of all sediments with chronic TUs >1, which corresponded to a total PAH cleanup criterion of 2 mg/kg. The PAH cleanup criterion determined the volume of sediments removed from Indian River. In total, approximately 480 cubic yards of sediment was ultimately removed from the Indian River shoreline, and confirmatory samples indicated that the calculated cleanup criteria were met.

9.3 Summary

This Web-based technical and regulatory guidance describes the mechanisms affecting contaminant bioavailability, the tools used to assess bioavailability, proper application of those tools relative to a specific endpoint (ecological or human), and how bioavailability information can be incorporated into risk management decisions at contaminated sediment sites. The tools described in this document aid in conducting a successful assessment with increased acceptance by regulators, practitioners, and public interests in your state or region. The ITRC Contaminated Sediments Team has developed this document to assist state regulators and practitioners in understanding and incorporating fundamental concepts of bioavailability into contaminated sediment management.

The bioavailability concepts, tools, and measures identified in this document are grouped based on receptor group, such as ecological (i.e., benthic, fish and aquatic organisms, wildlife, and plants) and human. The tools and measures identified in Chapters 4–8 aid in the assessment of site-specific contaminant bioavailability. Case studies are used to provide examples of how the identified tools and measures were used in decision making within each receptor group. The team has seen that these tools and models have been used to set scientifically and technically defensible cleanup goals at contaminated sediment sites and also have helped to select appropriate remedial strategies to mitigate exposure. The application of the tools described in this document may depend upon a variety of project constraints, such as schedule, number of COPCs, investigation resources, and acceptance by the regulatory agency and regulated community. The team has found that bioavailability processes are often not addressed when setting risk-based cleanup levels due to lack of scientific or technical understanding. Thus, the use of bioavailability in the sediment management process varies by state, although many use consistent risk assessment processes, i.e., USEPA's ERA guidance for Superfund (USEPA 1998c, 1997b, 1992b) and for human health (USEPA 1989a, 1989d).

Assessing bioavailability increases the understanding of the sources and causes of toxicity, and lays the foundation for the most appropriate remedy or monitoring requirements at a site. As NRC (2003) stated, "Explicit consideration of bioavailability processes and modeling in risk assessment would help to adjust cleanup goals by more accurately identifying that fraction of contaminant total mass that has the potential to enter receptor." In general, an investigator or regulator should strive to gain the best possible understanding of the physical, chemical, and biological processes that "drive" the risk (i.e., bioavailability by the means of COPC transfer, uptake, and concentrations at which adverse effects to receptors occur). Ultimately, if contaminants are present but not bioavailable, they should not be included in the calculation of risk. The decision-making process will most likely involve using a weight-of-evidence approach. Decisions based on bioavailability measurements are often highly site specific and influenced by soil/sediment type, contaminant aging/weathering, contaminant fate and transport, the media in which is the contaminant is present, exposure pathways, and potential receptors. Bioavailability should be incorporated in the risk assessment process to obtain a clearer understanding of contaminant toxicity and exposure pathways, such that remedy selection decisions can be optimized and resources efficiently focused. By incorporating bioavailability considerations into the early stages of site characterization through the risk assessment process and up through the point of remedy selection, a more effective remediation may be accomplished, which will optimize overall cost. Numerous case studies are provided throughout the document to illustrate the application of bioavailability adjustments or considerations in the establishment of remedial goals/decisions.

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Appendix A

Selected References on Bioavailability in Aquatic Systems

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SELECTED REFERENCES ON BIOAVAILABILITY IN AQUATIC SYSTEMS

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Appendix B

Categories of Contaminants

CATEGORIES OF CONTAMINANTS

Polycyclic Aromatic Hydrocarbons

PAH assessment requires initial evaluation of study objectives, specifically whether the focus is on the 16 priority pollutant PAHs vs. the suite of 34 PAHs (including 18 parent and 16 alkyl homologs (USEPA 2003d). NOAA expanded scan protocol can also be considered if additional alklyated PAHs are sought as well as site-specific requirements for lower analytical detection limits (Lauenstein and Cantillo 1998). The decision regarding which suite of PAHs to analyze has implications for the risk assessment, as well as consideration of PAH bioavailability. PAH bioavailability has been reviewed by Burgess et al. (2003); Schwarzenbach, Gschwend, and Imboden (2003); and Meador et al. (1995).

When evaluating benthic community response to PAHs in sediment, evidence has suggested that toxicity testing and community analyses data correlate better with PAH concentrations in pore water than with concentrations in bulk sediment (USEPA 2003d). This weaker correlation between bulk chemical data and both toxicity and community structure results is likely due to the strong partitioning of PAHs on sediment OC, including recalcitrant “black carbon” (Lohman, Macfarlane, and Gschwend 2005; Ghosh et al. 2003; Accardi-Dey and Gschwend 2002). The association of PAHs with sediment organic matter may result in bulk sediment PAH concentrations that demonstrate little or no chemical bioavailability in the aqueous phase. Following EqP theory, observed variations in sediment toxicity may be ascribed to the variations in pore-water PAH concentration that are due, in turn, to factors such as sediment OC content or quality that influence PAH partitioning between pore-water and sediment solid phases (Hawthorne et al. 2007, Burgess et al. 2003, USEPA 2003d, Di Toro et al. 1991). USEPA currently recommends that EqP be employed for prediction of PAH exposure concentrations, with narcosis theory recommended for determination of whether measured PAH concentrations are sufficient for causing adverse physiological effects (USEPA 2003d, Burgess 2007).

Although PAHs can accumulate within the tissue of benthic organisms, they do not generally bioaccumulate in higher trophic organisms (Eisler 1987, Erickson et al. 2008). This lack of higher trophic level bioaccumulation is due to the rapid biotransformation of PAHs in such organisms. For example, lack of PAH bioaccumulation in finfish has been attributed to the presence of mixed-function oxidases that allows for metabolism and excretion of PAHs through transformation of these lipid-soluble compounds into more-water soluble forms (Eisler 1987). In general, invertebrates lack a similarly effective system, and invertebrates, including bivalve mollusks, are therefore more apt to accumulate higher concentrations of PAHs (Law et al. 2002).

Polychlorinated Biphenyls

PCB assessment requires initial evaluation of whether the research focus includes commercial PCB mixtures (Aroclors), total PCBs, PCB homologues, or PCB congeners. Determination of the total PCB exposure is a central component of risk assessment for sites impacted by PCB contamination because the majority of available ecotoxicity benchmarks and bioaccumulation factors for PCBs are based on a total PCB concentration. Determination of total PCB concentration from the sum of PCB Aroclors includes the sum of Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260. Aroclors 1262 and 1268 are not typically included in a total PCB summation. Data on toxicity associated with the total PCB concentrations is mostly derived from dosing studies employing commercial Aroclor mixtures or from determination of field effects due to Aroclor-based total PCB measurements.

Recognizing that toxicity varies between congeners, a growing body of literature has documented effects on a congener-specific basis. In particular, heightened toxicity has been ascribed to dioxin-like coplanar PCBs (Van den Berg et al. 1998, Ahlborg et al. 1994). Dioxin-like coplanar PCBs are PCB congeners characterized by either zero or one chlorine atom in the substituent position closest to the biphenyl double bond. Concentrations of these dioxin-like coplanar PCB congeners are commonly expressed as the equivalent concentration of 2,3,7,8-TCDD, the dioxin congener with the greatest apparent toxicity (Van den Berg et al. 1998). An assessment of dioxin-like coplanar PCB risks should be considered as part of the weight of evidence in a risk assessment but should not be used as the sole measure of PCB toxicity (USEPA 2002e). The total PCB concentration calculated from the sum of PCB congeners is not directly comparable to the total PCB concentration calculated as the sum of Aroclor mixtures. This difference in summed PCB concentration is due to differences in analytical and quantitation methods between these strategies (Sather et al. 2001).

The EqP theorem is directly applicable to questions regarding PCB chemical partitioning and bioavailability. For PCBs, application of EqP theory to distinct Aroclor mixtures has demonstrated, for example, that EqP-based sediment quality benchmarks increase with increasing chlorination of PCBs, due to decreasing Aroclor bioavailability (Fuchsman et al. 2006). Likewise, as for PAHs, the OC content of the sediment impacts the bioavailability of PCBs to invertebrates species (Sun and Ghosh 2007; Moermond, Zwolsman, and Koelmans 2005; Pickard et al. 2001). For higher trophic level organisms, PCBs are not readily metabolized, and the residual tissue burden of PCBs for any higher trophic level organism is a function of the organism’s diet; PCB partitioning in the water column, pore water, and sediment; and the relative balance of the organism’s ingestion and egestion rates, as well as rates of growth, respiration, and metabolism (Campfens and Mackay 1997).

Normalization of sediment PCB concentrations to sediment OC content provides a site-specific strategy for refined assessment of PCB bioavailability (USEPA 2003d). Whereas there may be little or no relationship between the concentration of chemicals in sediment and observed biological effects, correlations between chemical concentration, bioaccumulation, and/or biological effects may be observed if chemical concentrations are presented on an OC-normalized basis (for hydrophobic chemicals) or defined in terms of a pore-water concentration (for chemicals that are only moderately hydrophobic) (USEPA 2003d). This normalization of sediment data in terms of sediment carbon content is consistent with one of the principal objectives of EqP theory (i.e., the selection of appropriate biological effects concentrations) and allows assessment of the varying bioavailability of PCBs in the sedimentary environment.

Pesticides

In general, it appears that TOC is the predominant factor influencing bioavailability of nonionic pesticides in the sediment environment. Lee and Jones-Lee (2005) state that some pesticides, such as the pyrethroid-based pesticides, tend to sorb strongly to sediments. Thus, the toxicity of pyrethroid-based pesticides depends on the TOC, with sediments with higher TOC being less toxic at a given pyrethroid concentration on a dry weight basis. Gan et al. (2005) present a summary of studies on the bioavailability of pyrethroid-based pesticides associated with aquatic sediments. These studies also support TOC playing a large role in the bioavailability of some pesticides. They also find that the amount of DOC in a water sample affects the water-column toxicity of pyrethroid-based pesticides. Lee and Jones-Lee (2005) note that the results of Gan et al. (2005) for the pyrethroid-based pesticides are similar to the results of Ankley and Collyard (1994) for the organophosphate pesticides diazinon and chlorpyrifos. As with many neutral organic chemicals, particulate TOC in sediments sorbs these pesticides, resulting in reductions in bioavailability and toxicity.

Other factors, like OC quality and quantity, and water properties, like pH and temperature, are also important in governing pesticide bioavailability. Additionally, sediment-contaminant contact time (i.e., aging) is an important determinant affecting chemical bioavailability in sediments for many organic compounds (Åkerblom 2007).

Routine chemical analyses determining bulk pesticide contaminant concentrations may not reliably predict toxicity to aquatic/sediment receptors. Standardized toxicity tests have been used to more accurately measure pesticide bioavailability/toxicity. USEPA (2008b) has recently published guidance using the EqP approach to derive site-specific sediment benchmark values for many nonionic pesticides. Advancements in determining pesticide pore-water concentrations using Tenax extraction and matrix-SPME fibers are also evolving (You, Landrum, and Lydy 2006).

Volatile Organic Compounds

VOCs tend to be weakly hydrophobic chemicals, which do not to persist in sediments due to their volatility and solubility. However, VOCs may occur in some sediments because of recent or ongoing releases. The method for assessing bioavailability of more strongly hydrophobic organic chemicals is typically the EqP approach. However, the EqP approach is ineffective for assessing VOCs in sediment because the standard EqP equation does not account for the contribution of dissolved chemical to the total chemical concentration in sediment. For chemicals with low organic K_{oc} values, such as VOCs, a modified EqP equation is available, which accounts for the dissolved fraction of total chemical concentrations in sediment (Fuchsman 2003). Results of the standard and modified EqP equations converge with increasing K_{oc} and are essentially identical at log K_{oc} values exceeding approximately 3.5.

Metals

The geochemical form, or speciation, of inorganic chemicals governs their fate, toxicity, mobility, and bioavailability in contaminated sediment and water. For cationic metals (e.g., cadmium, copper, lead, nickel, silver, and zinc) oxidation/reduction conditions in the sediment frequently provide a measure of potential metal bioavailability. For example, AVS present in pore water under reducing conditions can bind with cationic metals to form insoluble sulfide complexes which have limited bioavailability. For oxyanions (e.g., arsenic, chromium, selenium) limited predictive models exist for understanding bioavailability, although understanding oxidation/reduction conditions in site sediment allows for general prediction of chemical speciation, with resultant influence on chemical bioavailability.

The bioavailability of cationic metals (typically the lack of toxicity due to the metals evaluated) in sediment can be generally predicted by measuring the AVS and SEM in sediments. If the concentration of AVS is greater than the concentration of SEM in sediment on a molar basis, no toxicity due to the applicable cationic metals (cadmium, copper, lead, nickel, silver, and zinc) is expected (USEPA 2005c). AVS minus SEM (SEM – AVS) has proven to be a useful indicator of metal bioavailability and lack of toxicity to benthic organisms (Di Toro et al. 1992, Hansen et al. 1996, Di Toro 2008). Geochemically, the SEM – AVS approach predicts that under reducing conditions in sediment, the concentration and bioavailability of these six metals in pore water will be lowered due to precipitation as (or with) insoluble sulfide phases. Even under reducing conditions, however, metal sulfide phases have demonstrated bioavailability to infaunal organisms (Lee et al. 2000). Because the SEM – AVS method does not account for dietary metal uptake from sediment or other food sources, the sometimes poor correlation observed between benthic invertebrate tissue data and SEM – AVS predictions of metal bioavailability likely results from direct metal assimilation through ingestion (Lee et al. 2000).

Although SEM – AVS appears to be generally useful tool for assessing bioavailability under reducing conditions, factors controlling metal bioavailability in oxygenated sediments are less well defined. These factors include metal sorption to iron and/or manganese oxides, clay minerals, and sediment organic matter. For oxygenated sediments, the bioavailability of cations and oxyanions has been assessed via sequential extraction assays (e.g., Romaguera et al. 2008, Schaider et al. 2007). For these assays, at least one extractant is selected that either mimics physiological conditions in the digestive tract of representative organisms (as presented by USEPA 2007b, 2008b for extraction of bioavailable lead) or directly applies extracted gut fluids to sediment samples (Lawrence et al. 1999). Di Toro et al. (2005b) have also demonstrated that the BLM can be adapted to assess speciation and toxicity in sediments with low or no AVS component. In this approach, the BLM adopts the EqP approach to relate toxicity of sediment-associated metals to dissolved metal concentrations. For oxygenated systems, this approach assumes equilibrium between the critical metal concentration on the biotic ligand and the sediment organic carbon content (Di Toro et al. 2005b).

Mercury

In contrast to most cationic metals, reducing conditions provide less of a measure of bioavailability for mercury. An understanding of mercury bioavailability is typically determined by measuring methylmercury concentrations; methylmercury is a neurotoxin and the form of mercury that bioaccumulates in aquatic organisms. Mercury bioavailability can also be better understood by comparing mercury concentrations in abiotic matrices (sediment, surface water, pore water) to mercury levels in biota. Mercury bioavailability, particularly in its methylated form, may also be predicted from sediment, pore-water, or surface-water organic matter concentrations (Gorski et al. 2008, Lamberttson and Nillson 2006, Driscoll et al. 1995) although these predictions can be highly uncertain. More complex water body– or ecosystem-scale models can also be used to predict mercury bioavailability. These models typically focus on mercury body burdens and exposure risk to higher trophic level consumers, including fish species as well as piscivorous birds and wildlife (e.g., Gandhi et al. 2007, USEPA n.d. "SERAFM").

Radionuclides

An overview of the geochemical speciation, mobility, and bioavailability of radionuclides, as well as the significance of these data for environmental impact assessments, is presented by Salbu, Lind, and Skipperud (2005). Significant research on the bioavailability of radionuclides has also been conducted in the European Union for soils (Tamponnet et al. 2008) and sediments (IAEA 2004, 2010). For marine systems, the geochemical cycling and bioavailability of radioisotopes (including ^{51}Cr, ^{60}Co, and ^{65}Zn) has been recently reviewed (Livingston 2004) and includes presentation of radioisotope bioavailability to deposit feeding and filter feeding organisms. In circumpolar marine systems, bioavailability has been sparingly assessed in benthic and pelagic organisms (e.g., Nonnis et al. 2000) although research has both highlighted the role that sediment resuspension plays in the transfer of sediment-associated radionuclides to filter feeding mollusks (Borretzen and Salbu 2009) and observed that the distribution of radionuclides within the bodies of deposit-feeding mollusks was correlated with radionuclide partitioning (Hutchins et al. 1998). That is, radionuclides present in the aqueous phase were more commonly ultimately associated with mollusk shells, whereas radionuclides present in sediment/food were more commonly ultimately associated with mollusk soft tissues.

In freshwater systems, the bioavailability of radioisotopes has been assessed through experimental radioisotope additions to mesotrophic and eutrophic lakes (Bird et al. 1998) with results highlighting radionuclide partitioning between distinct tissue compartments and minimal effect of lake trophic status on radionuclide uptake by biota.

As with other inorganic analytes, bioavailability of radionuclides has been assessed through chemical extraction methods. This approach has been somewhat more commonly applied to soils (e.g., Kennedy et al. 1997) than to sediments (e.g., Lucey et al. 2007) although factors governing radionuclide lability and bioavailability function similarly in both environments. Dominant factors likely influencing radionuclide bioavailability to flora and fauna include organic matter content of the soil or sediment and the grain size distribution and magnitude of the clay-sized fraction (Vidal and Rauret 1993).

Ordnance Compounds

Ordnance-related compounds (i.e., explosives) are typically associated with military activities at munitions production sites or training ranges (Lotufo et al. 2009). The main compounds found in freshwater sediments at military sites include 2,4,6-trinitrotouene (TNT), 1,3,5-trinitrobenzene (TNB), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-

tetrazocine (HMX), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and their related transformation products. As with other contaminant classes, it is important to do a careful initial evaluation of any historical site data to refine study objectives and narrow the list of compounds that should be considered for comprehensive study.

Total sediment concentrations are not reliable for predicting bioavailability (and toxicity) of ordnance compounds because only that fraction dissolved in pore water is accessible to biota and, once ingested, that fraction is further exposed to degradation by digestive fluids (Lotufo et al. 2009). Because traditional chemical extractions are designed to determine the total amount of contaminant present in sediments, these methods likely overestimate that fraction accessible for organism uptake (i.e., bioavailability). Organism body burdens therefore provide a more realistic and scientifically sound basis for numerically defining bioavailability (Lotufo et al. 2009). However, measuring organism body burdens is complicated by the fact that absorbed ordnance compounds like TNT are subject to metabolic processes, yielding transformation products that favor sequestration in tissues, thereby reducing elimination efficiency (Bowen, Conder, and La Point 2006).

BCFs reflect the potential for contaminant accumulation in organism tissues, and through experiments with Mediterranean mussels, major ordnance compounds have been reported with relatively low BCFs of 1.67, 0.87, and 0.44 for TNT, RDX, and HMX, respectively, in keeping with their expected low bioaccumulative potential based on octanol-water partitioning (Rosen and Lotufo 2007). Trophic transfer potential to higher organisms was reported to be negligible for dietary TNT exposure in feeding experiments with channel catfish (*Ictalurus punctatus*), and TNT biotransformation products showed greater accumulation than did parent TNT (Belden et al. 2005).

Biomimetic approaches are designed to make chemically extractable sediment contaminants more reflective of bioavailable toxicant body levels than reflected through traditional solvent extraction techniques (Hermens et al. 2001). More recently, SPME devices were used to predict bioavailable TNT and its related transformation products in sediment (Conder and La Point 2005). SPME fibers coated with polymer act to bind dissolved contaminants thought to be reflective of bioavailable compounds. As an equilibrium sampling technique, SPME is both gentle and nondepletive, lending to its utility as a biomimetic (Bowen, Conder, and LaPoint 2006). SPME offers a range of polymer-coated fiber types, is durable enough for direct burial in sediment, yields low detection limits, and exhibits linear uptake relationships across toxicologically relevant sediment explosives concentrations (Conder et al. 2003). There is still work to be done to improve and refine SPME prediction of chemical concentrations in organisms, and it is important to keep in mind that these approaches reflect partitioning of chemicals, and as such, are of limited utility when other mechanisms of uptake may be active. Nonetheless, when seeking potential bioavailability measurement techniques for ordnance-related compounds in sediment, SPME could be a worthwhile option to consider.

Appendix C

Bioavailability Tools and Methods

BIOAVAILABILITY TOOLS AND METHODS

Appendix C-T1. Direct pore-water sampling devices

Method: Centrifugation		
Description: Collection of sediment followed by centrifugation. Filtration and/or flocculation of residuals are possibly necessary. **Measured endpoints:** Analysis of pore-water chemistry and comparison with ambient water quality criteria. If sufficient volume is collected, aquatic toxicity tests may be conducted using standard methods (e.g., *Daphnia* acute toxicity testing). **References:** USEPA 2001b, NFESC 2003	**Advantages:** Relatively inexpensive and can be done at most commercial labs. Conservative but generally accepted method by regulatory agencies. **Disadvantages:** Requires large volumes of sediment and ability to centrifuge large samples at ~10,000 g or higher. Limited sample volumes generated, especially for some sediment types. Can alter pore-water chemistry (i.e., redox).	**Analyte capability:** All analytes depending on sample volume
Method: Suction devices		
Description: A syringe, airstone, or tubes of varying length (e.g., Michigan sampler) with one or more sampling ports inserted into the sediment to the desired depth. Suction is applied via various means to directly retrieve the pore water sample. **Measured endpoints:** Analysis of pore-water chemistry and comparison with ambient surface-water quality criteria. If sufficient volume is collected, aquatic toxicity tests may be conducted using standard methods (e.g., *Daphnia* acute toxicity testing). **References:** ASTM E1391 2008; USEPA 2001b, n.d. “Measurement”	**Advantages:** Relatively inexpensive and can be done in situ or within most commercial labs. Conservative but generally accepted method by regulatory agencies. **Disadvantages:** In situ, low-flow rates in fine-grained substrates. Also need to prevent short-circuiting of overlying surface water. In the laboratory, large volumes of sediment are required (10:1). Limited sample volumes generated especially for some sediment types. Can alter pore-water chemistry (i.e., redox).	**Analyte capability:** All analytes depending on sample volume
Method: Piezometers (field)		
Description: Similar to laboratory suction devices, suction is applied via various means (usually a peristaltic pump) to directly retrieve the pore-water sample from a piezometer in the field. **Measured endpoints:** Pore-water concentrations. Concentration limit is method specific. **References:** USEPA n.d. “Measurement”	**Advantages:** Relatively easy to install and extract pore water. Can repeatedly sample from same location using dedicated tubing. **Disadvantages:** Can alter pore-water chemistry (i.e., redox). Need to ensure that overlying surface water is not being drawn. Sample volume dependent on achievable flow rate.	**Analyte capability:** All analytes depending on sample volume

Method: Trident probe (U.S. Navy)		
Description: Direct-push probe that also collects depth, temperature, and conductivity to determine the appropriate depth for pore-water sampling. **Measured endpoints:** Analysis of pore-water chemistry and comparison with ambient surface-water quality criteria. If sufficient volume is collected, toxicity testing may also be conducted using pore-water/surface-water methods (e.g., *Daphnia* acute toxicity testing). **References:** USEPA n.d. "Measurement," Chadwick and Hawkins 2008	**Advantages:** Can determine groundwater/ surface-water interface through changes in conductivity and temperature. **Disadvantage:** Limited familiarity and availability among commercial laboratories.	**Analyte capability:** Metals all analytes depending on sample volume
Method: Solid-phase microextraction—USEPA SW-846 Method 8272, ASTM D7363-07		
Description: Direct analysis of hydrophobic organics in sediment pore water. Small sediment sample (40 mL) centrifuged and dissolved solids flocculated in the laboratory. SPME fiber added to supernatant and then injected into GC. ASTM method same as SW-8272 except the analysis of alkylated PAHs is specified. **Measured endpoints:** Pore water at low concentrations (pg/mL). **References:** USEPA SW-846 Method 8272, Hawthorne et al. 2007	**Advantages:** Small sediment volume (40 mL) and low detection limits (pg/mL). Procedure does not involve revisiting the site. Removes the limitations imposed by using EqP. Large database relating aquatic toxicity to pore-water concentrations for comparison with site samples. **Disadvantages:** Fairly complex analytical and data interpretation technique. Method SW-8287 specifies the analysis of only 16 priority pollutants PAH compounds (not alkylated compounds).	**Analyte capability:** PAHs, PCBs, pesticides
Method: Air bridge		
Description: Works on the principle that organic compounds dissociate from sediments into water, diffuse into air, and then redissolve into clean water as freely dissolved compounds. Measures "truly dissolved" chemical constituents in water. **References:** Fernandez et al. 2009	**Advantages:** Method assesses freely dissolved hydrophobic concentrations of compounds such as PAHs and PCBs. **Disadvantages:** Slow process; larger molecular weight compounds may take weeks, if not months, to equilibrate.	**Analyte capability:** PAHs, PCBs, pesticides, energetic compounds (nonpolar organics

Appendix CT-2. Indirect pore-water sampling devices

Method: Diffusion equilibration on thin films		
Description: Thin (<1 mm) film of gel over a rigid support attains equilibrium with pore water. Measures metal concentrations in pore water, and the concentration limit is method specific. **References:** USEPA n.d. "Measurement"	**Advantage:** More rapid equilibrium than with peepers. **Disadvantage:** Need to extract sorbed compounds from the gel for analysis.	**Analyte capability:** Metals, mercury
Method: Dialysis bags		
Description: Contaminant diffuses into permeable dialysis material (polyvinylidene fluoride, polycarbonate) filled with water. Measures pore-water concentrations. Concentration limit is method specific. **References:** USEPA 2001b, n.d. "Measurement"	**Advantages:** Easy to install and extract pore water. **Disadvantages:** Requires modification to water within the bag for different sediment conditions.	**Analyte capability:** Metals, mercury, nonpolar organics

Method: Sediment peeper		
Description: Contaminant diffuses across a permeable membrane surrounding a fixed support filled with water. Measures pore-water concentrations. Concentration limit is method specific. **References:** ITRC 2004; USEPA 2006b, n.d. “Measurement,” 2001b	**Advantages:** Easy to install and extract pore water. Vertical distribution of contaminants with depth. **Disadvantages:** Requires modification to water within the bag for different sediment conditions. Low volume of pore water extracted.	**Analyte capability:** Metals, mercury, VOCs, PAHs, PCBs, pesticides, radionuclides, energetic compounds (nonpolar organics)
Method: Diffusion gradients in thin films (DGT)		
Description: Binding agent is selective to target ions in solution immobilized in a thin layer of hyrogel, surrounded by an ion-permeable hydrogel layer. Collects metal ions by diffusion, and measures/estimates contaminant flux in pore water. **References:** USEPA n.d. “Measurement”	**Advantages:** Rapid determination of flux (linear concentration gradient) in sediments. **Disadvantages:** Does not measure equilibrium pore-water concentration.	**Analyte capability:** Metals, mercury
Method: Semipermeable-membrane devices		
Description: Diffusion of hydrophobic contaminants across a semipermeable bag into a purified oil (e.g., triolein) which serves as a surrogate lipid. Integrates pore-water concentrations by averaging over a specified deployment period. Though not an equilibrium sampler, compound-specific flux rates are available. **References:** USEPA n.d. “Measurement”	**Advantages:** Relatively easy to deploy. Reverse extraction of dialysis tubing conducted by vendor. Measures “truly dissolved” pore-water constituents. Low (pg/L) concentration limits. **Disadvantages:** Does not measure pore-water concentration but rather an average concentration over time.	**Analyte capability:** PAHs, PCBs, nonpolar pesticides
Method: SPME fibers		
Description: SPME fibers are disposable glass fibers coated with µm poly(dimethylsiloxane). Fibers are cleaned by sonicating sequentially with hexane, acetonitrile, and water and are inserted directly into sediment in 5–7 cm lengths. Fibers are withdrawn after a set number of days, cut into small pieces, and transferred to autosampling vials, which are then filled with hexane and analyzed on a GC/MS. Measures pore water at low concentrations. **References:** Adams et al. 2007	**Advantages:** In situ or in vitro methods which determine pore-water concentrations and/or can be correlated with bioaccumulation. Low (<pg/mL) detection limits. **Disadvantages:** In situ procedures require site revisits. Methods require equilibrium time with sediments (14–28+ days), and also require method- and compound-specific EqP coefficients.	**Analyte capability:** PAHs, PCBs, nonpolar pesticides
Method: Polyoxymethylene (POM) film		
Description: Sorption onto polymer surface with pore-water concentration determined through compound-specific partition coefficients. Various in situ or in vitro methods are being developed and tested to indirectly measure pore-water concentrations and bioavailable fractions. **References:** Adams et al. 2007, Ghosh and Hawthorne 2010	**Advantages:** In situ or in vitro methods which determine pore-water concentrations and can be correlated with bioavailability. Low (<pg/mL) detection limits. **Disadvantages:** In situ procedures require site revisits. Methods require equilibrium time with sediments (14–28+ days) and also require method- and compound-specific EqP coefficients.	**Analyte capability:** PAHs, PCBs, pesticides, energetic compounds (nonpolar organics)

Method: Polyethylene devices		
Description: Passively accumulate hydrophobic organic compounds in proportion to their freely dissolved concentrations; require equilibrium with the sampled medium. Samples are time-weighted. Measures pore water at low (<pg/L) concentrations. **References:** Adams et al. 2007, Ghosh and Hawthorne 2010, Gschwend 2010	**Advantages:** In situ or in vitro methods which determine pore-water concentrations and can be correlated with bioavailability. Low (<pg/L) detection limits. **Disadvantages:** In situ procedures require site revisits. Methods require equilibrium time with sediments (14–28+ days) and also require method- and compound-specific EqP coefficients.	**Analyte capability:** PAHs, PCBs, nonpolar pesticides, energetic compounds (nonpolar organics)
Method: GORE® Modules		
Description: The GORE Module, a sorbent-based diffusion groundwater sampler, is a waterproof, vapor-permeable GORE-TEX® membrane within a deployment device. The membrane serves as the interface between an aqueous setting (groundwater) and the sorbent housed within the membrane tube. It measures groundwater concentrations (ppb). It has not been validated as a pore-water sampling device. **References:** ITRC 2007, USEPA 2000b	**Advantages:** Rapid equilibrium (hours), inexpensive, and easy to install. **Disadvantages:** Does not sorb higher-molecular-weight compounds; not useful for calculating TUs if higher-molecular-weight compounds are present. Has not been verified as an acceptable pore-water sampling device.	**Analyte capability:** VOCs

Appendix C-T3. Freshwater sediment toxicity testing and pore-water and elutriate tests

Tool/test species	Method	Duration	Measurement endpoints
Selected bedded-sediment freshwater toxicity tests			
Acute tests			
Hyalella azteca (amphipod)	ASTM 2005, 2008; USEPA 2000c	10–14 day	Survival
Chironomus spp. (midge)	ASTM 2005, 2008; USEPA 2000c	10 day	Survival, growth
Lumbriculus variegatus (oligochaete)	ASTM 2007b, USEPA 2000c	10 day	Survival
Hexagenia limbata (mayfly larvae)	ASTM 2005, 2008	10 day	Survival
Chronic tests			
Hyalella azteca (amphipod)	ASTM 2005, 2008; USEPA 2000c	28–42 day	Survival, growth, reproduction
Chironomus spp. (midge)	ASTM 2005, 2008; USEPA 2000c	20 day	Survival, growth
Chironomus spp. (midge)	ASTM 2005, 2008; USEPA 2000c	30 day	Life cycle
Hexagenia spp. (mayfly)	ASTM 2007b, USEPA 2000c	21 day	Survival, growth
Tubifex tubifex (tubificid oligochaete)	ASTM 2007b	28 day	Survival, growth, reproduction
Rana pipiens (frog)	ASTM 2007a	28 day	Survival, growth, reproduction
Xenopus (frog)	ASTM 2007a	28 day	Survival, growth, reproduction
Amphibian larvae	NAVFAC 2004	10 day	Survival, growth, reproduction
Bioaccumulation tests			
Diporeia spp. (amphipod)	ASTM 2007a	28 day	Survival, bioaccumulation
Lumbriculus variegatus (oligochaete)	ASTM 2007a, USEPA 2000d	28 day	Bioaccumulation
Selected freshwater pore-water and elutriate toxicity tests			
Daphnia magna	Pore water–ASTM 2001a	48 hour	Survival
Ceriodaphnia dubia	Pore water–ASTM 2001c	7 day	Survival, reproduction
Pimephales promelas (fathead minnow)	Pore water–ASTM 2001b	7 day	Survival, growth

Tool/test species	Method	Duration	Measurement endpoints
Selenastrum capricorntum (algae)	Elutriate–Weber et al. 1989	96 hour	Survival, reproduction
Ceriodaphnia dubia	Elutriate–Weber et al. 1989	7 day	Survival, growth
Pimephales promelas (fathead minnow)	Elutriate–Weber et al. 1989	7 day	Survival, growth
Salmo spp. (salmonid)	Elutriate–Weber et al. 1989	96 hour	
Selected bedded-sediment marine toxicity tests			
Acute tests			
Ampelisca abdita (amphipod)	ASTM 2007b, 2008; USEPA 1994c	10 day	Survival
Eohaustorius estuarius (amphipod)	ASTM 2007b, 2008	10 day	Survival
Rhepoxynius abronius (amphipod)	ASTM 2007b, 2008; USEPA 1994c	10 day	Survival, reburial
Grandidierella japonica (amphipod)	ASTM 2007b, 2008	10 day	Survival
Leptocheirus plumulosus (amphipod)	ASTM 2007b, 2008; USEPA 2001b	10 day	Survival
Corophium spp. (amphipod)	ASTM 2007b, 2008	10 day	Survival
Neanthes arenaceodentata (polychaete)	ASTM 2007b, 2008	10 day	Survival
Chronic tests			
Neanthes arenaceodentata	ASTM 2007b	28 day	Survival, growth
Armandia brevis		28 day	Survival, growth
Leptocheirus plumulosus (amphipod)	ASTM 2008, USEPA 2001b	28 day	Survival, growth, reproduction
Bivalve larvae (oyster, larvae)		48 hour	Larval development
Echinoderm (sea urchin, sand dollar)			
Bioaccumulation tests			
Macoma spp. (clam)	USEPA 1998b	28 day	Survival, bioaccumulation
Neanthes (Nereis) spp. (polychaete)	ASTM 2007a, 2007b	28 day	Bioaccumulation

Appendix C-T4. Modeling

Method: Equilibrium partitioning (EQP)		
Description: Assumes pore-water concentration equivalent to NRWQC FCV, then back-calculates a bulk sediment concentration (or OC-normalized sediment concentration) using a K_{oc} (or K_{oc} calculated from a K_{ow}) of the COC of interest (dissolved phase = OC-normalized total sediment concentration * partitioning coefficient). **References:** Di Toro et al. 1991, 2005a; Di Toro 2008; Hansen et al. 1996; USEPA 1994a, 2003d	**Advantages:** Easy to calculate. Is a low-cost screening tool. **Disadvantages:** Assumptions do not take into account the presence of anthropogenic carbon or other factors which may influence default partitioning coefficients.	**Analyte capability:** PAH, PCB, nonpolar pesticides, energetic compounds (nonpolar organics)

Method: Narcosis model		
Description: Predicts toxic effects to benthic organisms from impacted sediments using a universal model that predicts toxicity based on a critical body burden that assumes the lipid compartment is the toxic target for Type I narcotic (hydrophobic) chemicals. **References:** USEPA 2003d, 2008b; Di Toro, McGrath, and Hansen 2000; Di Toro and McGrath 2000	**Advantages:** Model is validated across 156 chemicals and 33 aquatic species. TUs are assumed to be additive. Forms the basis of applying EqP to predict sediment toxicity assuming pore water is equivalent to final acute values (as the NOAEL endpoint). Is a low-cost screening tool. **Disadvantages:** Assumes that sediment toxicity is entirely the result of narcotic effects to benthic organisms when in reality other stressors may be contributing to adverse impacts.	**Analyte capability:** Type I narcotic chemicals (aliphatics, aromatics, alcohols, ethers, ketones, PAHs)
Method: Biotic ligand model		
Description: Variation of the free metal ion activity model that accounts for varying bioavailability of metals as a function of varying water chemistry. **References:** Di Toro et al. 2005b	**Advantages:** Accounts for toxicity variations due to changes in alkalinity, pH, and OC. **Disadvantages:** None reported or identified.	**Analyte capability:** Metals, mercury
Method: Simultaneously extracted metal/acid volatile sulfide (SEM/AVS)		
Description: Amorphous iron sulfide is measured as AVS; the metal in sediments that is potentially bioavailable is measured in the same extract and is termed "simultaneously extracted metals" (SEM). If AVS > SEM, then no toxicity is expected. If SEM > AVS, then toxicity may or may not occur. **References:** USEPA 2005c, Di Toro et al. 1990, Di Toro 2008, Hansen et al. 1996	**Advantages:** Easy to conduct; methods widely available from certified labs. Low-cost screening tool. **Disadvantages:** Recommended that field samples be taken as cores to avoid contact with air (which may oxidized reduced sulfides). Recent round robin of certified laboratories showed considerable variability in results.	**Analyte capability:** Divalent metals (Cd, Cu, Pb, Ni, Ag, Zn)
Method: Toxicity identification evaluation (TIE)		
Description: Series of aquatic toxicity laboratory tests that manipulate physical/chemical properties of sediment pore water to bind classes of chemicals and certain confounding factors, thus rendering them biologically unavailable. **References:** USEPA 2007b, NFESC 2003	**Advantages:** Can assist in identifying site-related COCs and/or confounding factors contributing to observed toxicity. **Disadvantages:** A precursor to the TIE test is a toxicity test—expensive and time-consuming. Does not address bioaccumulation issues. Small number of amendments to be cost-effective.	**Analyte capability:** Metals, VOCs, PAHs, PCBs, pesticides, radionuclides, energetic compounds (nonpolar organics)

Appendix C-T5. Tissue sampling and analysis

Method: Biota-sediment accumulation factor (BSAF)		
$\mathbf{C_{tss}/L = (C_s/TOC) * BSAF}$ where C_{tss} = tissue concentration at steady state (mg/kg) L = lipid content (g/g) C_s = sediment concentration (mg/kg) TOC = total organic carbon in sediment (g/g) BSAF = biota-sediment accumulation factor (g carbon/g lipid) **Links:** www.epa.gov/med/Prods_Pubs/bsaf.htm, http://el.erdc.usace.army.mil/bsafnew/BSAF.html	**Advantages:** Simple estimation tool that can use default USEPA values or develop site-specific factors based on measured tissue and sediment concentrations. Simple and easily performed using spreadsheet functions data set of BSAFs for nonionic organic chemicals exist from USEPA and the USACE. **Disadvantages:** BSAFs derived from literature sources do not reflect site-specific conditions. Site-derived BSAFs implicitly assume that all exposures occur within the area under investigation.	**Analyte capability:** PAHs, PCBs, nonpolar pesticides, dioxins, energetic compounds (nonpolar organics) **Applicable compound class:** Hydrophobic (nonionic) organics (PCBs, PCDDs, PCDFs, DDTs, PAHs, chlorinated pesticides)
Method: Bioaccumulation factor (BAF)		
Description: Ratio of the concentration in aquatic organism to its concentration in specific media (water, sediment, prey). Bioaccumulation is net uptake and retention of a chemical in an organism from all routes of exposure (diet, dermal, respiratory) and any source (water, sediment, food) in the natural environment. **References:** USEPA n.d. "ECOTOX," Weisbrod et al. 2007	**Advantages:** Simple estimation tool that can use default USEPA values or develop site-specific factors based on measured tissue and other site media concentrations. Can be used for all aquatic and aquatic-dependent wildlife. **Disadvantages:** BAFs derived from literature sources do not reflect site-specific conditions. Site-derived BAFs implicitly assume that all exposures occur within the area under investigation.	**Analyte capability:** PAHs, PCBs, nonpolar pesticides, dioxins, energetic compounds (nonpolar organics) **Applicable compound class:** Hydrophobic (nonionic) organics (PCBs, PCDDs, PCDFs, DDTs, PAHs, chlorinated pesticides)

<table>
<tr><td colspan="3"><i>Method: Biomagnification factor in predator/prey tissue</i></td></tr>
<tr><td>Description: Ratio of the chemical concentration of a predator divided by that of its prey. For HOCs, the concentrations are lipid normalized. For metals, the units are mg/kg wet weight. Biomagnification is said to occur when the BMF > 1.
References: USEPA n.d. “ECOTOX,” Weisbrod et al. 2007, USACE n.d., USEPA 1993</td><td>Advantages: Simple tool that may be used to estimate concentrations in higher trophic level fish, birds or mammals based on measured or previously reported BMFs. Can be used for all aquatic and aquatic-dependent wildlife.
Disadvantages: BMFs derived from literature sources may not reflect site-specific conditions. Site-derived BMFs implicitly assume that all exposures occur within the area under investigation.</td><td>Analyte capability: Metals, mercury, VOCs, PAHs, PCPs, pesticides, selenium, dioxins, radionuclides, energetic compounds (nonpolar organics)</td></tr>
<tr><td colspan="3"><i>Method: Gobas kinetic food web model</i></td></tr>
<tr><td>Description: Widely applied food web model that provides estimates of chemical concentrations in organisms of aquatic food webs from chemical concentrations in the water and the sediment.
Measured endpoints: A prediction of specific body burdens of organic COCs at specified trophic levels and at specified growth stages. Model allows user-specified aquatic food web that can include benthos, phytoplankton, and zooplankton. Recent work by Burkhart, Cook, and Lukasewycz (2005) suggests that model predictions are within a factor of 4 of simple BSAF predictions.
References: Arnot and Gobas 2004; Gobas 1993; Burkhart, Cook, and Lukasewycz 2005</td><td>Advantages: Variations of the algorithm have been adapted to both freshwater and marine systems, including the Great Lakes, Lower Fox River, Wisc., San Francisco Bay, Calif., and Willamette River, Ore. Relatively easy for those areas where model has been calibrated and validated (e.g., San Francisco Bay). Increasingly difficult for new systems. Model currently provides point estimates. A better method for quantifying uncertainty (e.g., Monte Carlo simulations) remains to be adequately demonstrated.
Disadvantages: Data-intensive to populate and calibrate the model. Steep learning curve if not well-versed in fugacity theory.</td><td>Analyte capability: Metals, PAHs, PCPs, nonpolar pesticides, PCBs, dioxins, energetic compounds (nonpolar organics)</td></tr>
<tr><td colspan="3"><i>Method: Bioaccumulation and Aquatic System Simulator (BASS)</i></td></tr>
<tr><td>Description: Model simulates bioaccumulation of chemical pollutants integrated with population and bioaccumulation dynamics of age-structured fish communities. Provides a prediction of specific body burdens of organic COCs at specified trophic levels and at specified growth stages. Model allows user-specified aquatic food web that can include benthos, phytoplankton, zooplankton, and multiple trophic levels of fish.
References: USEPA 2008b, Barber 2008</td><td>Advantages: Applied to PCB dynamics in Lake Ontario; salmonids, largemouth bass-bluegill-catfish communities of Lake Hartwell, S.C.; DDT bioaccumulation in caged channel catfish at various Superfund sites; and to simulate fish methylmercury bioaccumulation in the Florida Everglades.
Disadvantages: Data-intensive to populate and calibrate the model.</td><td>Analyte capability: Hydrophobic organic pollutants and metals that complex with sulfhydryl groups (e.g., Cd, Cu, Hg, Ni, Ag, Zn)</td></tr>
</table>

Method: Food web model for environmental risk assessment for mercury (SERAFM)		
Description: SERAFM is a steady-state spreadsheet-based model framework that predicts speciated mercury concentrations (Hg^0, Hg^{II}, MeHg, total Hg) in freshwater and sediments and total mercury concentrations in fish tissue. It includes the following measurement endpoints: • bulk sediment Hg concentration • fish tissue Hg • total and dissolved Hg in surface water • TOC and DOC in sediment and water • water-column particle size • water temperature, DO, pH **Test organism categories:** Freshwater omnivore and piscivorous fish at user-specified age classes. **References:** USEPA n.d. "SERAFM," Knightes 2008	**Advantages:** USEPA model that has general acceptance to predict the fate of mercury in aquatic systems and hazard indices for wildlife. **Disadvantages:** Does not consider controlling factors of methylmercury bioavailability in sediments. Requires assumption that sediments are source of Hg.	**Analyte capability:** Mercury
Method: Direct plasma residue assessment		
Description: Plasma from receptor organisms are collected from the field, brought to the laboratory, and measured for target chemical(s). **Measured endpoints** include plasma COCs and percent lipids. Principally used to test organisms to assess chemical levels in T&E species and/or juveniles. **References:** Arcand-Hoy and Bensen 1998	**Advantages:** Integrates all pathways of exposure and provides a direct number for assessing risks without killing receptor. **Disadvantages:** Sampling generally limited to few individuals. Resource-intensive. Plasma COCs not associated with specific toxicological effects.	**Analyte capability:** All classes of chemicals
Method: Direct tissue analysis		
Description: Receptor organisms are harvested from the field and brought to the laboratory, and tissues are measured for target chemical(s). **Measured endpoints** include the following: • bulk sediment COCs concentrations • tissue residue COCs • total and dissolved COCs in surface water • whole body vs. fillet (fish) • TOC and DOC in sediment and water • water-column particle size • fertilized eggs (optional) • lipids **Test organism categories** include fish, shellfish, amphibians, or reptiles. **References:** Puget Sound Partnership 1990, USEPA 2000c	**Advantages:** Integrates all pathways of exposure and provides a direct number for assessing risks. **Disadvantages:** Assumptions include all exposures are within contaminated area, which is not valid for mobile fish or crustaceans. Not suitable for T&E species. Moderate to difficult to implement. Requires capture (trawling, reel, beach seine) of suitable numbers and types of target receptors for evaluation in statistically meaningful way.	**Analyte capability:** All classes of chemicals

Method: In situ bioaccumulation studies		
Description: Surrogate receptor organisms are placed at the target site in cages either in contact with or directly above the sediment. After a specified period of time, the organisms are harvested and the tissues analyzed for COCs. The measurements include survival, tissue residue, and lipids. **Test organisms** include benthic organisms, small fish, clams, and mussels. **References:** USEPA 2000a	**Advantages:** Animals confined to a small, well-defined location. Site-specific exposures that integrate contaminant uptake over all media. **Disadvantages:** Surrogate organisms are often those used in bioassays and may not reflect uptake by site-specific organisms.	**Analytical capability:** Most classes of chemicals but typically PBT compounds
Method: Dietary assimilation efficiency		
Description: Absorption efficiency represents the net result of absorption and elimination. Feeding studies are designed to estimate absorption efficiency based on accumulated chemical residues. The fraction of the chemical retained in the organisms relative to that ingested is the assimilation efficiency, which measures chemical levels in food and residual in feces. Also may involve measuring chemical levels in target organism tissue, organelles, and in developing fetus. **Test organisms** are typically fish, birds, and mammals. **References:** Erickson et al. 2008	**Advantages:** Most direct measure of how much of a contaminant in food is retained by the target organism. **Disadvantages:** Difficult to adequately capture fish fecal matter. Useful for birds and mammals but can be time- and resource-intensive.	**Analyte capability:** All classes of chemicals

Appendix CT-6. Selected methods for sampling benthic invertebrate communities

Method: Passive artificial substrates		
Description: Artificial substrate samplers are designed to mimic natural substrates (e.g., gravel, cobble, small spaces) and provide an easily quantified sampling unit. In general, artificial substrate samplers primarily sample the epifaunal community, whereas grab samplers primarily sample the infaunal community. Artificial substrate samplers can provide both qualitative and quantitative samples of benthic macroinvertebrates. Ohio Environmental Protection Agency recommends using of Hester-Dendy artificial substrate samplers in streams and rivers, five samplers exposed for six weeks. **Measured endpoints:** EPT richness and diversity at family and genus level of taxonomic resolution. **References:** OEPA 1989, Johnson 2006, USEPA 2002d	**Advantages:** Mesh artificial substrate samplers are a good alternative to grab samplers when collecting animals for tissue residue analyses. Artificial substrate samplers made of mesh-filled chicken baskets are particularly good at collecting large numbers of animals because of the large number of interstitial spaces. **Disadvantages:** None reported.	**Analyte capability:** Epifaunal populations

Method: Benthic response index (BRI)		
Description: The BRI is the abundance-weighted average tolerance score of organisms occurring in a sample. **Measured endpoints:** Southern California Marine Bays: Reference: <39.96 Low disturbance: 39.96–49.14 Moderate disturbance: 49.15–73.26 High disturbance: >73.26 Polyhaline Central San Francisco Bay: Reference: <22.28 Low disturbance: 22.28–33.37 Moderate disturbance: 33.38–82.08 High disturbance: >82.08 **References:** Smith et al. 2003; California EPA 2008, 2009	**Advantages:** Indices remove much of the subjectivity associated with data interpretation. Indices provide a simple means of communicating complex information to managers, tracking trends over time, and correlating benthic responses with stressor data. **Disadvantages:** Requires development and calibration. Different benthic indices have been used at different times and different places, and results cannot be compared across regions because the various indices have not yet been rigorously compared and intercalibrated. Initial development of each existing benthic index was constrained by data limitations, and they would all benefit from refinement with additional data as well as independent validation. Differences in sampling procedures. Habitat factors such as seasonality and sediment type. Accuracy of identification of benthic organisms of performance of California benthic indices. Indices only one line of evidence in determining causality of impairment. Indices often used in conjunction with multiple lines of evidence.	**Analyte capability:** Species specific

Method: Index of benthic biotic integrity (IBI)		
Description: The IBI identifies community measures that have values outside a reference range. **Measured endpoints:** Southern California Marine Bays: Reference: 0 Low disturbance: 1 Moderate disturbance: 2 High disturbance: 3 or 4 Polyhaline Central San Francisco Bay: Reference: 0 or 1 Low disturbance: 2 Moderate disturbance: 3 High disturbance: 4 **References:** California EPA 2008, 2009	**Advantages:** Indices remove much of the subjectivity associated with data interpretation. Indices provide a simple means of communicating complex information to managers, tracking trends over time, and correlating benthic responses with stressor data. **Disadvantages:** Requires development and calibration. Different benthic indices have been used at different times and different places, and results cannot be compared across regions because the various indices have not yet been rigorously compared and intercalibrated. Initial development of each existing benthic index was constrained by data limitations, and they would all benefit from refinement with additional data as well as independent validation. Differences in sampling procedures. Habitat factors such as seasonality and sediment type not taken into account. Accuracy of identification of benthic organisms of performance of California benthic indices. Indices only one line of evidence in determining causality of impairment. Indices often used in conjunction with multiple lines of evidence.	**Analyte capability:** Species specific

Method: Relative benthic index (RBI)		
Description: The RBI is the weighted sum of (1) several community parameters (total number of species, number of crustacean species, number of crustacean individuals, and number of mollusk species) and abundances of (2) three positive and (3) two negative indicator species. **Measured endpoints:** Southern California Marine Bays: Reference: >0.27 Low disturbance: 0.17–0.27 Moderate disturbance: 0.09–0.16 High disturbance: <0.09 Polyhaline Central San Francisco Bay: Reference: >0.43 Low disturbance: 0.30–0.43 Moderate disturbance: 0.20–0.29 High disturbance: <0.20 **References:** California EPA 2008, 2009	**Advantages:** Indices remove much of the subjectivity associated with data interpretation. Indices provide a simple means of communicating complex information to managers, tracking trends over time, and correlating benthic responses with stressor data. **Disadvantages:** Requires development and calibration. Different benthic indices have been used at different times and different places, and results cannot be compared across regions because the various indices have not yet been rigorously compared and intercalibrated. Initial development of each existing benthic index was constrained by data limitations, and they would all benefit from refinement with additional data as well as independent validation. Differences in sampling procedures. Habitat factors such as seasonality and sediment type not taken into account. Accuracy of identification of benthic organisms of performance of California benthic indices. Indices only one line of evidence in determining causality of impairment. Indices often used in conjunction with multiple lines of evidence.	**Analyte capability:** Species specific

Method: River Invertebrate Prediction and Classification System (RIVPACS)		
Description: The approach compares the assemblage at a site with an expected species composition determined by a multivariate predictive model that is based on species relationships to habitat gradients (originally developed for British freshwater streams and adapted for California's bays and estuaries). **Measured endpoints:** Southern California Marine Bays: Reference: >0.90–<1.10 Low disturbance: 0.75–0.90 or 1.10–1.25 Moderate disturbance: 0.33–0.74 or >1.25 High disturbance: <0.33 Polyhaline Central San Francisco Bay: Reference: >0.68–<1.32 Low disturbance: 0.33–0.68 or 1.32–1.67 Moderate disturbance: 0.16–0.32 or >1.67 High disturbance: <0.16 **References:** Wright, Furse, and Armitage 1993; Van Sickle, Huff, and Hawkins 2006; California EPA 2008, 2009	**Advantages:** Indices remove much of the subjectivity associated with data interpretation. Indices provide a simple means of communicating complex information to managers, tracking trends over time, and correlating benthic responses with stressor data. **Disadvantages:** Requires development and calibration. Different benthic indices have been used at different times and different places, and results cannot be compared across regions because the various indices have not yet been rigorously compared and intercalibrated. Initial development of each existing benthic index was constrained by data limitations, and they would all benefit from refinement with additional data as well as independent validation. Differences in sampling procedures. Habitat factors such as seasonality and sediment type not taken into account. Accuracy of identification of benthic organisms of performance of California benthic indices. Indices only one line of evidence in determining causality of impairment. Indices often used in conjunction with multiple lines of evidence.	**Analyte capability:** Species specific

Method: Integration of benthic community		
Description: The median of all benthic index response categories shall determine the benthic line of evidence category. If the median falls between categories, it shall be rounded up to the next higher category. **Measured endpoints:** Reference: A community composition equivalent to a least affected or unaffected site. Low disturbance: A community that shows some indication of stress but could be within measurement error of unaffected condition. Moderate disturbance: Confident that the community shows evidence of physical, chemical, natural, or anthropogenic stress. High disturbance: The magnitude of stress is high. **References:** California EPA 2008, 2009	**Advantages:** Index performance was evaluated by comparing index assessments of 34 sites to the best professional judgment of nine benthic experts. None of the individual indices performed as well as the average expert in ranking sample condition or evaluating whether benthic assemblages exhibited evidence of disturbance. However, several index combinations outperformed the average expert. When results from both habitats were combined, two four-index combinations and a three-index combination performed best. **Disadvantages:** Requires development and calibration. Different benthic indices have been used at different times and different places, and results cannot be compared across regions because the various indices have not yet been rigorously compared and intercalibrated. Initial development of each existing benthic index was constrained by data limitations, and they would all benefit from refinement with additional data as well as independent validation. Differences in sampling procedures. Habitat factors such as seasonality and sediment type not taken into account. Accuracy of identification of benthic organisms of performance of California benthic indices. Indices only one line of evidence in determining causality of impairment. Indices often used in conjunction with multiple lines of evidence.	**Analyte capability:** Species specific

Method: Rapid bioassessment protocol (RBP)		
Description: Choice of qualitative and/or quantitative protocols (three tiers) for use in streams and rivers. Protocols used to determine whether a stream and associated habitat are supporting a designated aquatic life use, characterize the existence and severity of impairment, and identify the source of impairment. **Measured endpoints:** Macroinvertebrates: Taxa richness, family biotic index, ratio of scrapers, filtering collectors, ratio of EPT and chironomid abundances, % contribution of dominant family, EPT index. Fish: IBI, species richness and composition metrics, trophic composition metrics, fish abundance and condition metrics. **References:** Barbour et al. 1999	**Advantages:** Bioassessment provides indications of cumulative impacts of multiple stressors, not just water quality. Biological community condition reflects both short- and long-term effects, and directly evaluates the condition of the habitat and water resource. Biological data can be interpreted based on regional reference condition where single reference sites are lacking or inadequate. Properly developed methods, metrics, and reference conditions provide a tool that enables a direct measure of the ecological condition of a water body. Once a framework is in place for bioassessment, biological monitoring can be relatively inexpensive and easily performed with standard protocols and consistent training. **Disadvantages:** May be difficult to interpret results in areas impacted by urban/nonpoint contamination or areas impacted by numerous site discharges. Additional chemical and biological (toxicity) testing is usually needed to identify causal agent.	**Analyte capability:** Macro-invertebrate species

Method: Invertebrate community index (ICI)		
Description: ICI is a summary measure of 10 metrics representing aquatic macroinvertebrate community integrity and is evaluated and scored in relation to conditions at relatively undisturbed reference sites In this index, a site can receive a 6, 4, 2, or 0 score depending on how it compares to the specified reference site. **Measured endpoints:** Total number of taxa—species richness and diversity Number of mayfly taxa—pollution-sensitive species; greater proportion of taxa indicates higher environmental quality Number of caddisfly taxa—main component in larger, unimpacted waterways; wide range of pollution tolerances within taxa Number of Dipteran taxa—have wide range of tolerances to pollution; often only organism collected under heavily polluted conditions; greater proportion suggests lower stream quality Percent mayfly composition—easily affected by even minor disturbances; serves as measure of overall levels of stress and disturbance Percent caddisfly distribution—quickly absent under environmental stress; serves as a measure of stream stress Percent tribe Tanytarsini midge composition—often predominant group at minimally impacted sites; pollution tolerances are intermediate Percent other Dipteran and noninsect composition—includes noninsect invertebrates such as worms, isopods, snails, etc.; main community component in poor water-quality conditions; greater abundance indicates lower environmental quality Percent tolerant organisms—tolerant to toxic and organic pollution; greater proportion of organisms indicates lower overall environmental quality Number of qualitative EPT taxa—qualitative measure of habitat diversity and water quality; measures richness of mayfly (*Ephemeroptera*), stonefly (*Plecoptera*), and caddisfly (*Trichoptera*) taxa. **References:** OEPA 1989, USEPA 1992b	**Advantages:** Bioassessment provides indications of cumulative impacts of multiple stressors, not just water quality. Biological community condition reflects both short- and long-term effects and directly evaluates the condition of the habitat and water resource. Biological data can be interpreted based on regional reference condition where single reference sites are lacking or inadequate. **Disadvantages:** Additional chemical and biological (toxicity) testing is usually needed to identify causal agent.	**Analyte capability:** Invertebrates

Method: Macroinvertebrate aggregated index for streams (MAIS)		
Description: MAIS is a rapid bioassessment protocol similar to ICI. MAIS scores are based on macroinvertebrates collected with a prescribed number of kick and dip net sweeps. Organisms are identified to the family (rather than genus) level. Family-level identifications require more training than order level (e.g., EPT, etc.) but can be performed by individuals with an intermediate level of skill. Once macroinvertebrates are collected, identified, and enumerated, an MAIS index score ranging between 0 and 18 is generated from 9 aggregated macroinvertebrate metrics that describe the diversity and abundance of different groups. In the mid-Atlantic highlands, four narrative categories are assigned based on the scores 0–7 = very poor, 8–11 = poor, 12–15 = good, 16–18 = very good. **Measured endpoints:** The nine biological metrics that compose the final MAIS index score: • EPT richness: number of caddisfly, stonefly and mayfly families • *Ephemeroptera*: number of mayfly families • Percent *Ephemeroptera*: % abundance of mayflies • Percent five dominant taxa: five most dominant taxa combined • Simpson Diversity Index: integrates richness and evenness • Modified Hilsenhoff Biotic Index: Integrates abundance and taxa richness; taxa in latter are weighted by pollution tolerance scores • Number of intolerant taxa: number of families with tolerance values of 5 or less (very sensitive) • Percent scrapers: relative abundance of benthos that feed on periphyton • Percent haptobenthos: relative abundance of benthos that require clean, coarse, firm substrates **References:** Johnson 2006	**Advantages:** Bioassessment provides indications of cumulative impacts of multiple stressors, not just water quality. Biological community condition reflects both short- and long-term effects and directly evaluates the condition of the habitat and water resource. Biological data can be interpreted based on regional reference condition where single reference sites are lacking or inadequate. **Disadvantages:** Additional chemical and biological (toxicity) testing is usually needed to identify causal agent.	**Analyte capability:** NA

Method: Benthic infaunal abundance		
Description: This marine-specific method compares the relative abundance of site major taxa to reference-area taxa. A site is considered impacted if (1) the abundance of the Class Crustacea, Class Polychaeta, and Phylum Mollusca in the test sediment is statistically different (t test @ 0.05, www.socialresearchmethods.net/kb/stat_t.php) from the "reference sediment" and (2) the "test sediment" has less than 50% of any one of the major taxa relative to the reference sediment's mean abundance of any one of the major taxa. **Measured endpoints:** Abundance of the following major taxa: Class Crustacea, Class Polychaeta, and Phylum Mollusca. **References:** Washington Administrative Code 173-204	**Advantages:** Bioassessment provides indications of cumulative impacts of multiple stressors, not just water quality. Biological community condition reflects both short- and long-term effects and directly evaluates the condition of the habitat and water resource. Biological data can be interpreted based on regional reference condition where single reference sites are lacking or inadequate. **Disadvantages:** Additional chemical and biological (toxicity) testing is usually needed to identify causal agent.	**Analyte capability:** NA

Appendix C-T7. Surface-water quality models (fate and transport)

Method: Level I		
Description: Calculates the equilibrium distribution of a fixed quantity of conserved (i.e., nonreacting) chemical in a closed environment at equilibrium with no degrading reactions, no advective processes, and no intermediate transport processes. **Equilibrium:** 1-dimensional **Version:** March 2004 **Format:** Windows **References:** Mackay 2001 **Website:** www.trentu.ca/academic/aminss/envmodel/models/models.html	**Advantages:** None reported. **Disadvantages:** None reported.	**Analyte capability:** Organochlorines, other organic compounds
Method: Level II		
Description: Models a situation in which a chemical is continuously discharged at a constant rate and achieves a steady-state and equilibrium condition, at which the input and output rates are equal. **Equilibrium:** 1-dimensional **Version/released:** February 17, 1999 **Format:** Windows **References:** Mackay 2001 **Website:** www.trentu.ca/academic/aminss/envmodel/models/models.html	**Advantages:** None reported. **Disadvantages**: None reported.	**Analyte capability:** Organochlorines, other organic compounds

<table>
<tr><td colspan="3"><i>Method: Level III</i></td></tr>
<tr><td>Description: Describes the fate of a chemical continuously discharged at a constant rate and has achieved a steady-state condition in which input and output rates are equal but equilibrium between media is not assumed.
Steady state: 1-dimensional
Version/released: February 7, 2004
Format: Windows
References: Mackay 2001
Website: www.trentu.ca/academic/aminss/envmodel/models/models.html</td><td>Advantages: None reported.
Disadvantages: None reported.</td><td>Analyte capability: Organochlorines, other organic compounds</td></tr>
<tr><td colspan="3"><i>Method: Quasi</i></td></tr>
<tr><td>Description: Describes the steady-state behavior of an organic chemical in a lake subject to chemical inputs by direct discharge, inflow in rivers, and deposition from the atmosphere.
Steady state: 1-dimensional
Version/released: February 8, 2002
Format: Windows/Basic
References: Mackay 2001; Mackay, Joy, and Patterson 1983
Website: www.trentu.ca/academic/aminss/envmodel/models/models.html</td><td>Advantages: None reported.
Disadvantages: None reported.</td><td>Analyte capability: Organochlorines, other organics, metals</td></tr>
<tr><td colspan="3"><i>Method: Sediment</i></td></tr>
<tr><td>Description: Calculates the water-sediment exchange characteristics of a chemical based on its physical chemical properties and total water and sediment concentrations.
Steady state: 1-dimensional
Version/released: February 2004
Format: Windows
References: Rueber et al. 1987, Mackay 2001
Website: www.trentu.ca/academic/aminss/envmodel/models/models.html</td><td>Advantages: Useful for determining the likely fate of a chemical subject to transfer between a water column and a sediment compartment.
Disadvantages: None reported.</td><td>Analyte capability: Organochlorines, other organic compounds</td></tr>
</table>

<table>
<tr><td colspan="3"><i>Method: Exams</i></td></tr>
<tr><td>Description: Interactive computer software for formulating aquatic ecosystem models and rapidly evaluating the fate, transport, and exposure concentrations of synthetic organic chemicals.

Steady state to dynamic: 1-dimensional
Version/released: 2.98.04.06/2005
Format: Fortran

Website: www.epa.gov/ceampubl/swater/exams/exams2980406.html</td><td>Advantages: A “legacy” Fortran routine that is used extensively to model the fate, transport, and exposure concentrations of synthetic organic chemicals, including pesticides, industrial materials, and leachates from disposal sites. Often used to predict hazards of pesticides a priori. Can be integrated seamlessly into other model platforms.

Disadvantages: Steep learning curve and requires numerous input variables, some of which may have to be assumed.</td><td>Analyte capability: Organo-chlorines, other organic compounds</td></tr>
<tr><td colspan="3"><i>Method: SMPTOX4</i></td></tr>
<tr><td>Description: SMPTOX is a steady-state flow model that simulates transport and fate of chemical pollutants in suspended solids, dissolved in the water column, and in sediments.

Steady state: 1-dimensional
Version/released: 1995
Format: DOS

Supporting agency/developer: USEPA Center for Exposure Assessment Modeling

Reference: USEPA 1995b</td><td>Advantages: None reported.

Disadvantages: Steady-state predictions only. Nonpoint source loadings cannot be simulated. Does not consider daughter products or processes. Process kinetics is not simulated.</td><td>Analyte capability: Organo-chlorines, metals</td></tr>
<tr><td colspan="3"><i>Method: MIKE11-WQMIKE21-WQMIKE3W</i></td></tr>
<tr><td>Description: Generalized modeling package-1D(/2D/3D) water quality module.

Dynamic: 1-dimensional to 3-dimensional
Format: Geographic information system (GIS)

Supporting agency/developer: Danish Hydraulic Institute

Website: www.mikebydhi.com</td><td>Advantages: None reported.

Disadvantages: None reported.</td><td>Analyte capability: Hydraulic models of rivers and floodplains</td></tr>
</table>

Method: RATECON (Great Lakes Rate Constant Model)		
Description: Rate constant model for chemical dynamics, designed to predict the fate and recovery times of contaminants in the Great Lakes; similar to QWASI but not using the fugacity concept. **Dynamic:** 1-dimensional **Version/released:** 1991 **Format:** Basic **References:** Mackay et al. 1994 **Website:** www.trentu.ca/academic/aminss/envmodel/models/models.html	**Advantages:** None reported. **Disadvantages:** None reported.	**Analyte capability:** Developing a complete quantification of all processes, thus providing a decision support tool to improve management and remediation of aquatic systems by linking loading to concentration
Method: Watershed Analysis Risk Management Framework (WARMF)		
Description: Provides a roadmap to calculate total maximum daily loads for most conventional pollutants. **Dynamic:** 1-dimensional to 2-dimensional **Version:** 6.1/September 1, 2005 **Format:** Windows 95/98/ME/2000xp **Website:** **http://www.epa.gov/athens/wwqtsc/html/warmf.html**	**Advantages:** See website. **Disadvantages:** None reported.	**Analyte capability:** Coliform, TSS, biological oxygen demand, nutrients
Method: Water Quality Analysis Simulation Program (WASP6)		
Description: Helps users interpret and predict water-quality responses to natural phenomena and man-made pollution for various pollution management decisions. **Dynamic:** 1-dimensional to 3-dimensional **Version/released:** 7.41/June 7, 2010 **Format:** Windows 95/98/ME/2000xp **Website:** www.epa.gov/athens/wwqtsc/html/wasp.html	**Advantages:** None reported. **Disadvantages:** None reported.	**Analyte capability:** Metals (Hg), organo-chlorines, other organics
Method: AQUATOX–Dynamic, with food web		
Description: Predicts the fate of various pollutants, such as nutrients and organic chemicals, and their effects on the ecosystem, including fish, invertebrates, and aquatic plants. **Steady state to dynamic:** 2-dimensional **Version/released:** 3.0 **Format:** Windows **Website:** www.epa.gov/waterscience/models/aquatox/	**Advantages:** None reported. **Disadvantages:** None reported.	**Analyte capability:** Organo-chlorines, other organics

Method: ECOFATE		
Description: Includes a steady-state and a time-dependent model of the mass transport and food-web bioaccumulation of organic chemicals in aquatic ecosystems. It can be used to assess the distribution of chemical concentrations in water, sediment, and aquatic biota in real-world aquatic ecosystems. **Steady state to dynamic:** 1-dimensional to 2-dimensional **Version/released:** 1998 **Format:** Visual Basic for Windows 3.x platform **Website:** http://research.rem.sfu.ca/toxicology/models/models.htm	**Advantages:** None reported. **Disadvantages:** None reported.	**Analyte capability:** Organics

Appendix C-T8. Fish uptake calculation methods and models

Method: Sediment, receptor tissue equilibrium partitioning (EqP) or biota-sediment accumulation factor (BSAF)		
See Appendix C-T5.		
Method: Sediment, diet, water, receptor tissue bioaccumulation factor (BAF)		
Description: Ratio of the concentration in aquatic organism to its concentration in specific media (water, sediment, prey). Bioaccumulation is net uptake and retention of a chemical in an organism from all routes of exposure (diet, dermal, and respiratory) and any source (water, sediment, food) as typically occurs in the natural environment. Measured endpoints include concentration in organism and concentration in water (all sources). It can be conducted in laboratory or field. **Test organisms** include all aquatic and aquatic-dependent wildlife. **References:** USEPA n.d. "ECOTOX," Weisbrod et al. 2007	**Advantages:** Simple estimation tool that can use default USEPA values or develop site-specific factors based on measured tissue and other site media concentrations. Simple and easily performed using spreadsheet functions. **Disadvantages:** BSAFs derived from literature sources do not reflect site-specific conditions. Site-derived BSAFs implicitly assume that all exposures occur within the area under investigation.	**Analyte capability:** All classes of chemicals but especially applicable to divalent cation uptake
Method: Water, receptor tissue bioconcentration factor (BCF)		
Description: Bioconcentration is the process by which a chemical is retained in an aquatic organism following its absorption through respiratory and dermal surfaces from the surrounding water (does not include dietary exposure). Bioconcentration is measured under controlled laboratory conditions. **Measured endpoints** include concentration in organism, concentration (total and dissolved) in water. **Laboratory exposure test organisms** are typically fish, amphibians, and reptiles. **References:** USEPA n.d. "ECOTOX"	**Advantages:** Simple estimation tool that can use default USEPA values or develop site-specific factors based on measured tissue and other site media concentrations. Simple and easily performed using spreadsheet functions. **Disadvantages:** BCFs derived from literature sources may not reflect site specific conditions. Site-derived BCFs implicitly assume that all exposures occur within the area under investigation.	**Analyte capability:** All classes of chemicals

Method: Predator tissue, prey tissue biomagnification factor (BMF)		
See Appendix C-T5.		
Method: Estimation Program Interface (EPI) Suite™		
Description: The EPI Suite is a Windows-based suite of physical/chemical property and environmental fate estimation programs developed by the USEPA Office of Pollution Prevention Toxics and Syracuse Research Corporation. **Website:** www.epa.gov/opptintr/exposure/pubs/episuite.htm	**Advantages:** Facilitated by a database of >40,000 chemicals. **Disadvantages:** A screening-level tool not to be used if acceptable measured values are available.	**Analyte capability:** Screening-level estimates of physical/ chemical and environmental fate properties, the building blocks of exposure assessment
Method: Gobas kinetic food web model		
See Appendix C-T5.		
Method: Food web Bioaccumulation and Aquatic System Simulator (BASS)		
See appendix C-T5.		
Method: Food web Spreadsheet For Environmental Risk Assessment For Mercury (SERAFM)		
See Appendix C-T5.		
Method: Tissue/direct tissue residue assessments		
See Appendix C-T5.		
Method: Plasma/direct plasma residue assessments		
See Appendix C-T5.		
Method: Tissue/in situ bioaccumulation studies		
Description: Surrogate receptor organisms are placed at the target site in cages either in contact with or directly above the sediment. After a specified period of time, the organisms are harvested and the tissues analyzed for COCs. **Measured endpoints** include survival, tissue residue, COCs, and lipids. **Test organisms** are benthic organisms, small fish, and clams. **References:** USEPA 2000a	**Advantages:** Site-specific exposures that integrate contaminant uptake over all media. Relatively easy and inexpensive to implement. **Disadvantages:** Surrogate organisms are most often those used in bioassays and may not reflect uptake by site-specific organisms.	**Analyte capability:** All classes of chemicals

Method: Tissue/dietary assimilation efficiencies		
Description: Absorption efficiency represents the net result of absorption and elimination. Feeding studies are designed to estimate absorption efficiency based on accumulated chemical residues. The fraction of the chemical retained in the organisms relative to that ingested is the assimilation efficiency. **Measured endpoints** are COC levels in food and residual in feces. Also may involve measuring chemical levels in target organism tissue, organelles, and developing fetus. **Test organisms** include all, but most typically fish, birds, and mammals. **References:** Erickson et al. 2008	**Advantages:** Most direct measure of how much of a contaminant in food is retained by the target organism. **Disadvantages:** Difficult to adequately capture fish fecal matter. Useful for birds and mammals but can be time- and resource-intensive. Expensive and requires special laboratory procedures and animal husbandry.	**Analyte capability:** All classes of chemicals
Method: Direct tissue residue analysis		
See Appendix C-T5.		

Appendix C-T9. Wildlife calculation methods and models and direct measures

Calculation methods and models		
Method: Bioaccumulation and biomagnification		
Description: Estimation methods using measured or estimated COC in food or prey and published accumulation factors from the literature. **Measurement endpoints:** Estimated concentrations in receptor organisms. **Test organisms:** All. **References:** USEPA 2006b, Weisbrod et al. 2007, Van Wezel et al. 2000	**Advantages:** Simple, inexpensive method to estimate exposure levels. Readily implementable. **Disadvantages:** Does not include site-specific factors, including bioavailability.	**Analyte capability:** All chemical classes
Method: USEPA allometric food intake assessment		
Description: Allometric equations developed to estimate total oral dose of a chemical based on intake of food, water, or sediment with consideration of species home range, weight, consumption rates, and food preferences. **Measurement endpoints:** Daily oral dose to receptor organism. **Test organisms:** Originally developed for select birds and mammals, have been applied to a wide range of species including reptiles and marine mammals. **References:** Baron, Sample, and Suter 1999; Sample and Suter 1999	**Advantages:** Simple, inexpensive method to estimate exposure levels. Can be adjusted to consider bioavailability where information is available. Requires only a literature search and a spreadsheet calculation. **Disadvantages:** Does not include site-specific factors, including bioavailability.	**Analyte capability:** All chemical classes

Method: Bioenergetics-based modeling		
Description: Models constructed to estimate exposure based on estimating oral intake from the target receptors' bioenergetic requirements, contaminant assimilation efficiencies, tissue conversion factors, and clearance rates. **Measurement endpoints:** Estimated tissue residue concentrations. **Test organism categories:** Principally applied to avifauna. **References:** Norstrom et al. 2007, Nichols et al. 2004, Karasov et al. 2007	**Advantages:** Moderately complex modeling exercise that depends on effective parameterization of the model equations. Requires collaboration between knowledgeable bird ecologist, toxicologist, and computer modeler. **Disadvantages:** Model parameters are not available for all species, introducing uncertainty into the model estimates.	**Analyte capability:** Persistent organic compounds
Direct measures		
Method: Bioaccumulation and biomagnification		
Description: Evaluates uptake of a chemical into a predator relative to that of its prey. For HOCs, the concentrations are lipid normalized. For metals, the units are mg/kg wet weight. Biomagnification is said to occur when the BMF > 1. **Measurement endpoints:** Concentration in predator, concentration in prey % lipids. **Test organism categories:** Can be used for all aquatic and aquatic-dependent wildlife. **References:** Foley et al. 1988; Bergman et al. 1994; Leonards et al. 1997; Wolfe, Schwartzbach, and Sulaiman 1998	**Advantages:** May be used to estimate concentrations in higher trophic level fish, birds, or mammals based on measured or previously reported BMFs or to validate more complex food web models. **Disadvantages:** BMFs derived from literature sources may not reflect site-specific conditions. Site-derived BMFs implicitly assume that all exposures occur within the area under investigation.	**Analyte capability:** All
Method: Field tissue residue and effects assessments		
Description: Receptor organisms are harvested from the field and brought to the laboratory and tissues are measured for target chemical(s). Field observations can also include clutch size, eggshell thinning, fledge success. **Measurement endpoints:** Tissue residue COCs, lipids, whole body, clutch size, eggshell thickness, fledge success, subcellular biomarkers. **Test organism:** Most commonly applied to bird species. Whole-body measures not applicable for T&E species. **References:** Custer and Custer 1995, Custer et al. 1999, Anteau et al. 2007, Overman and Krajicek 1995	**Advantages:** Integrates all pathways of exposure and provides a direct number for assessing risks. **Disadvantages:** Assumes all prey consumed are within contaminated area, which may not be valid for all predators. Not suitable for T&E species. Moderately to difficult to implement. Requires capture of suitable numbers and types of target receptors for evaluation in statistically meaningful way.	**Analyte capability:** All chemical classes

<table>
<tr><td colspan="3"><i>Method: Site-specific in situ dietary intake/effect studies</i></td></tr>
<tr><td>Description: Nest boxes are placed immediately proximal to a contaminated site and monitored for reproductive effects. Measures include gut content identification and COC analysis, tissue analyses, clutch size, eggshell thickness, and reproductive success.

Measurement endpoints: Adult growth (weight), mortality, clutch size, eggshell thickness, fledge success.

Test organisms: Tree swallows, house wrens.

References: Custer et al. 1998, 2001, 2003, 2005</td><td>Advantages: Relatively inexpensive. Integrates multiple chemicals in prey organisms with direct measures of site-specific uptake and effects.

Disadvantages: Assumes dose is wholly dependent on foraging occurring within the contaminated site. Good assumption for large sites, not practicable for small sites.</td><td>Analyte capability: All chemical classes</td></tr>
<tr><td colspan="3"><i>Method: Site-specific ex situ dietary intake/effect studies</i></td></tr>
<tr><td>Description: Fish or other prey items from the contaminated site are collected, formulated into diets, and fed to surrogate species.

Measurement endpoints: Adult growth (weight), assimilation efficiency, COC uptake, mortality, litter or clutch size, pup weight gains, eggshell thickness

Test organisms: Minks and otters.

References: Sample and Suter 1999; Smits, Wobeser, and Schiefer 1995; Bleavens et al. 1984</td><td>Advantages: Integrates multiple chemicals in prey organisms with direct measures of uptake and effects.

Disadvantages: Expensive and can take considerable time if multiple generations are involved. Not suitable for T&E species.</td><td>Analyte capability: All chemical classes</td></tr>
<tr><td colspan="3"><i>Method: Direct toxicity assessments</i></td></tr>
<tr><td>Description: Target wildlife species are directly exposed to COCs in controlled laboratory environments.

Measurement endpoints: Adult growth (weight), assimilation efficiency, COC uptake, mortality, litter or clutch size, pup weight gains, eggshell thickness.

Test organisms: All species.

References: Flemming et al. 1985, Clark et al. 1987, Camardese et al. 1990</td><td>Advantages: Integrates multiple chemicals in prey organisms with direct measures of uptake and effects.

Disadvantages: Expensive and can take considerable time if multiple generations are involved. Not suitable for T&E species.</td><td>Analyte capability: All chemical classes</td></tr>
</table>

Method: Plasma COC assessments		
Description: Plasma from receptor organisms is collected from the field, brought to the laboratory, and measured for target chemical(s). **Measurement endpoints:** Plasma COCs, percent lipids. **Test organisms:** Principally used to assess chemical levels in T&E species and/or juveniles. **References:** Elliot et al. 2001, Bowerman et al. 2003, Strause et al. 2007	**Advantages:** Integrates all pathways of exposure and provides a direct number for assessing risks without killing receptor. **Disadvantages:** Sampling generally limited to few individuals. Resource-intensive. Plasma COCs not associated with specific toxicological effects. Moderately to difficult to implement. Requires capturing or accessing receptors and collecting samples, which may inflect damage on target species.	**Analyte capability:** All chemical classes
Method: Fur or feather COC assessment		
Description: Field collected fur or feathers are collected and analyzed for target COCs. **Measurement endpoints:** COCs, percent lipids. **Test organisms:** Principally used to assess chemical levels in T&E species and/or juveniles. **References:** Monteiro and Furness 1997; Scheuhammer et al. 1998; Burger, Lavery, and Gochfeld 1994, Lundstedt-Enkel et al. 2005	**Advantages:** Nonintrusive method for collecting and evaluating presence of COCs in wildlife. Relatively simple and low cost. **Disadvantages:** None reported.	**Analyte capability:** All chemical classes
Method: Dietary assimilation efficiencies		
Description: Absorption efficiency represents the net result of absorption and elimination. Feeding studies are designed to estimate absorption efficiency based on accumulated chemical residues. The fraction of the chemical retained in the organisms relative to that ingested is the assimilation efficiency. **Measurement endpoints:** Chemical levels in food and residual in feces. Also may involve measuring chemical levels in target organism tissue, organelles, and developing fetus. **Test organisms:** All, but most typically fish, birds, and mammals. **References:** None	**Advantages:** Most direct measure of how much of a contaminant in food is retained by the target organism. **Disadvantages:** Difficult to adequately capture fish fecal matter. Useful for birds and mammals but can be time- and resource-intensive.	**Analyte capability:** All chemical classes

Appendix D

Case Study Questionnaire and Summaries

CASE STUDY QUESTIONNAIRE AND SUMMARIES

CASE STUDY QUESTIONNAIRE

Development/Deployment

To document how bioavailability is currently being used in site evaluations, a case study questionnaire was developed and distributed to members of the ITRC Contaminated Sediments Team; ITRC State Points of Contact; ITRC Industry Affiliates Program members; and federal representatives, including USEPA, Departments of Defense and Energy, USACE, and USGS. The main goal of the survey was to identify sites that used measures of bioavailability to gain regulatory acceptance. Associated questions that the ITRC Contaminated Sediments Team wanted to answer through its review of case study information were as follows:

- What types of bioavailability assessments are being conducted at contaminated sediment sites throughout the United States?
- How does the evaluation of bioavailability within exposure pathways affect the risk management decisions for a site?
- How have bioavailability considerations been used at contaminated sediment sites to establish or alter cleanup levels or to dictate how risk to a receptor or group of receptors is managed?

The survey was developed through an iterative review and revision process covering several months. The team identified the survey objectives and survey audience and defined how the collected data would be used. The survey was beta-tested among team members and a number of selected respondents and modified accordingly. The final survey was reviewed and approved by the ITRC Team Leader Liaison and State Engagement Coordinator according to the "ITRC Technical Team Survey Development Planning Information, Guidance and Request Template." The survey information collection period lasted six weeks. The case study questionnaire was distributed in June 2008, and most responses were received by August 2008. Team members reviewed the questionnaires and developed a series of follow-up questions to establish how bioavailability was used at a site and to determine whether its use contributed to the development of cleanup levels. The results of follow-up questions were used to categorize the case studies according to the primary pathway where bioavailability was assessed and what tools were used during the assessment. The summary presented here represents only the information we received and is not intended to represent every sediment site throughout the United States.

Other sources of information are available. For instance, the Sediment Management Working Group has compiled a Major Contaminated Sediment Sites Database (www.smwg.org/MCSS_Database/MCSS_Database_Docs.html), which presents information on contaminated sediment remediation projects in the United States. This database was developed for major sediment sites and excludes smaller sites (e.g., those with contaminated sediment volumes less than 3000 yd^3). Viewers should also make note of the dates that the database has been updated, as some information may be out of date.

Results

A total of 35 case studies were received through the ITRC questionnaire from state and federal regulators as well as industry and other government interests. These also included information from an unpublished summary of cases compiled by Charles Menzie in 2008 in preparation for the SERDP-ESTCP Workshop on Bioavailability of Soils and Sediments (SERDP and ESTCP 2008). The case studies are briefly summarized in Table 9-1. A more detailed description and contacts for each case study is provided in this appendix.

From our limited number of sites reviewed, the benthic exposure pathway have been evaluated most often, followed by the human health and the pelagic pathways. Sediment chemistry and bioassays using benthic invertebrates are the most common tools used to assess bioavailability. Tissue sampling of various media (fish, bivalves, or other pelagic receptors) and pore-water chemistry were also commonly used to evaluate the bioavailability of contaminants at the sites reviewed. Pore-water chemistry was either predicted using EqP from bulk sediment, directly analyzed following centrifugation of bulk sediment, or measured using SPME or similar device.

In the majority of sites reviewed, more than one tool was used to assess a given exposure pathway. These tools included the following:

- bulk sediment chemistry
- pore-water chemistry, measured or derived through EqP toxicity testing
- tissue analysis
- bioaccumulation testing
- trophic modeling, including the derivation of BAFs/BSAFs
- benthic community survey
- SEM – AVS

An SQT approach (i.e., sediment chemistry, toxicity testing, and benthic community survey) was used at nine of the sites reviewed. COCs at the case study sites included the following:

- organics, including PAHs, PCBs, petroleum hydrocarbons, chlorobenzene/aromatic amines
- metals, including nickel, lead, copper, cadmium, arsenic, mercury, selenium

Bioavailability was incorporated in the decision-making process by helping to establish site-specific cleanup goals in approximately 50% of the case studies. For the other sites where bioavailability was assessed but not clearly used in decision making, it was generally reported that the cleanup goals or remedial decisions had not yet been made.

Summary

As previously mentioned, limited information regarding the case study information is provided in Table 9-1. This information includes the primary exposure pathways assessed, the COCs at the site, the methods or tools used to assess bioavailability, and whether the bioavailability information was used to make a regulatory site decision. More detailed summaries of each site reviewed, along with contact information for case managers and links to online documents, where available, are included below. These more detailed summaries may provide additional insight that is not included in the summary table.

D-1. BREMERTON NAVAL COMPLEX, OU B MARINE, BREMERTON, WASHINGTON

Dwight Leisle, 360-396-0935, Dwight.Leisle@navy.mil

Primary Pathway: Human health

Contaminants: PCBs and mercury

Tools: Bulk sediment chemistry, fish tissue chemistry, methylation process study

Methods: N/A

How Bioavailability Was Used: Bioavailability will be a consideration now that a supplemental HHRA has determined there is a risk associated with mercury. A mercury cleanup level has not yet been set.

Regulatory and Stakeholder Challenges: The primary risk driver at this site was established in 1999 as a human health risk to subsistence finfish harvesters from PCB concentrations in bottom fish. A cleanup goal was established for PCB concentrations in surface sediment, which was assumed to eventually result in a reduction in PCB concentrations in marine tissue. The PCB sediment cleanup goal was not risk based, and no bioavailability determination was made. The PCB cleanup goal was instead based on a cost-benefit analysis.

A supplemental HHRA, recently conducted as the result of a recommendation in the second Five-Year Review, found unacceptable risk to subsistence harvesters from mercury in fish and shellfish tissue. A mercury source study, conducted in parallel with the risk assessment, will include an evaluation of the mercury methylation processes at the site that will help characterize mercury bioavailability. The overall objective of this study is to describe and quantify the biogeochemical processes that lead to the bioaccumulation of methylmercury into the base of the pelagic food web, methylation of mercury in sediments, and the release of methylmercury and ionic mercury from the sediments. USGS is performing this study with an estimated completion date of September 2011. This study will assist in the establishment of a mercury cleanup goal.

D-2. BRADFORD ISLAND DISPOSAL SITE, BONNEVILLE DAM FOREBAY, CASCADE LOCKS, OREGON

Michael Gross, 503-808-4913, Michael.J.Gross@usace.army.mil

Site Description: Bradford Island is within the Bonneville Dam facility on the Columbia River, 40 miles east of Portland, Oregon. Various wastes associated with operations at the dam were disposed of on the island between the 1940s and 1980s. In 2000, electrical components were discovered in the river. These had apparently been dumped down the north slope of the island. Some of these contained PCBs. Three removal projects have been conducted between 2000 and 2007 to remove the equipment, debris, and contaminated sediment. Work is under way to evaluate the risk to human and ecological receptors posed by the remaining contamination.

Primary Pathway: Human health, pelagic, and benthic

Contaminants: PCBs

Tools: Bulk sediment chemistry, tissue, and surface-water chemistry

Methods: Contaminant concentrations in sediment, benthic tissue, and fish tissue are being used to evaluate baseline risk. Trophic models may also be used to calculate acceptable contaminant concentrations.

How Bioavailability Was Used: Bioavailability is being evaluated based on long-term monitoring of tissue levels.

Regulatory and Stakeholder Challenges: Diver-assisted suction dredging of sediment was conducted in 2007 in areas totaling approximately 1 acre, where PCB concentrations exceeded 500 µg/kg. Contaminant concentrations in sediment and crayfish have declined significantly over the past several years. However, the most recent samples of fish tissue (smallmouth bass) showed elevated PCB concentrations averaging 2900 µg/kg. Future sampling will be required to determine whether these concentrations decline.

D-3. BUFFALO RIVER, NEW YORK

Mary Beth Ross, USEPA Great Lakes National Program Office, 312-886-2253, Ross.Marybeth@epa.gov

Site Description: The Buffalo River is located in Buffalo, New York and discharges into Lake Erie. The lower 6.2 miles of the Buffalo River and the adjacent City Ship Canal (1.4 miles) have been identified as a Great Lakes area of concern. A legacy of industrial activity during the last 150 years has lead to elevated chemical concentrations in the river sediments, including PAHs, PCBs, mercury, and lead.

Primary Pathway: Human health, benthic, pelagic

Contaminants: Indicator contaminants included PAHs, PCBs, mercury, lead.

Tools: Bulk sediment and pore-water chemistry, AVS/SEM, toxicity tests, fish tissue chemistry, benthic taxonomy surveys

Methods: The determination of a site-specific toxicity unit for PAHs was based on USEPA's EqP approach using multiple data sets, including sediment toxicity testing and site-specific K_{oc} values. It also included an evaluation of USEPA's target lipid model approach using site-specific bioaccumulation data. The theoretical bioaccumulation potential model was used to understand the potential bioaccumulation of PCBs in fish tissue, and mercury and lead concentrations in Buffalo River fish tissue were compared to state criteria that have been determined to be protective of fish and piscivorous wildlife.

How Bioavailability Was Used: Multiple bioavailability tools were used to develop of a site-specific remedial goal for total PAHs, including pore-water measurements, sediment toxicity tests, bioaccumulation tests, and an evaluation of USEPA's target lipid model. The development of a PAH remedial goal was based on USEPA's EqP approach using site-specific partitioning information. Pore-water measurements demonstrated that aqueous PAH concentrations were less than what would have been predicted through models typically used to estimate chemical partitioning. For PCBs, a bioaccumulation potential model was used along with site-specific sediment chemistry data to determine a remedial goal that would be protective of fish-eating birds and mammals. Site-specific mercury and lead fish tissue data were compared to state criteria. Mercury and lead concentrations in Buffalo River fish tissue were well below the state criteria; thus, mercury and lead remedial goals were identified so that remedial options could be evaluated against current conditions. AVS/SEM also demonstrated very low metals bioavailability in Buffalo River sediment.

D-4. CAMP LEJEUNE IR SITE 89, MCB CAMP LEJEUNE, NORTH CAROLINA

Jonathon Weier, CH2M HILL, 770-485-7503, jweier@ch2m.com

Primary Pathway: Benthic, pelagic

Contaminants:

Tools: Bulk sediment and surface-water chemistry, trophic modeling, macroinvertebrate chemistry

Methods: Sediment compared to benchmarks and benthic macroinvertebrate survey data. Surface water compared to benchmarks for the protection of amphibians and survey data for fish and other water column receptors.

How Bioavailability Was Used: No cleanup was done. The evaluation resulted in a conclusion of no risk (see comments).

Regulatory and Stakeholder Challenges: We conducted a baseline ERA for Site 89 (a stream) due to exceedances of benchmarks for sediment and surface water. The assessment involved collection of substantial data at four site locations and four reference locations. This stream was physically impacted due to anthropogenic influences other than the release, and we wanted to control for that in our analysis. We collected data on the physical character of stream, chemistry (i.e., contaminants), macroinvertebrates, water-quality parameters, and fish community and did food chain modeling and comparison of media concentrations to benchmarks. This may not be a “classic” type of bioavailability study. I do think that the case can be made that field surveys of biota relative to reference can be a indirect way at getting to bioavailability and a very direct way of assessing risk. No cleanup was done. The evaluation resulted in a conclusion of no risk.

A reference comparison method was used to measure bioavailability. We characterized the faunal community at the site and compared it to reference conditions, controlling for physical conditions of the watercourse. Cluster analysis was used to demonstrate the comparability of the reference and site stream sampling locations. Basically, we demonstrated the reference and site stream conditions in terms of physical character and biota were similar, suggesting that the release did not have any discernable effect. Mainly, the assessment of the physical features of the stream and the biota data collected in the field were used in the comparison study.

D-5. CASS LAKE, ST. REGIS WOOD TREATMENT PLANT, CASS LAKE, MINNESOTA

Timothy Drexler, 312-353-4367, drexler.timothy@epa.gov

The St. Regis Paper Company Superfund site is a former wood-preserving facility that operated 1957–1985. Groundwater, sediment, and soil on and in the vicinity of the site are contaminated as a result of the wood-preserving process and waste-disposal activities. The site consists of 125 acres within the exterior boundary of the Leech Lake Reservation, adjacent to the Chippewa National Forest, in the City of Cass Lake. Most of the site contamination is the result of pressure treatment of wood with pentachlorophenol. PCP affects the central nervous system, cardiovascular system, liver, and kidneys. Workers and some nearby residents may have been exposed to toxic levels of PCP when the plant was operating. Current concerns include soil contamination from PCP, PAHs, and dioxin/furans ("dioxin"). Dioxin/furans were impurities in the PCP. Dioxins cause cancers in soft tissues, neurological effects, immune system toxicity, and developmental disorders. The other concern, addressed by an existing treatment system, is groundwater contaminated with PAHs and PCP. Current activities at the site stem from reviews of response actions taken in the mid-1980s, some of which were found to be inadequate for protection of human health and the environment.

www.health.state.mn.us/divs/eh/hazardous/sites/cass/stregis/community.pdf

Primary Pathway: For human health risk, soil, sediment, surface-water, and groundwater exposures to residents were evaluated, including those with tribal lifeways, children, and workers. For ecological risk, direct uptake from sediment and water by aquatic invertebrates and fish was evaluated. Dietary uptake by piscivorous, herbivorous, or omnivorous birds, mammals, and reptiles was also studied.

Tools: Bulk sediment and surface-water chemistry, sediment bioaccumulation assays, field bioaccumulation (plant, benthic invertebrates, and fish), and sediment toxicity tests including AVS-SEM

Methods: A new cleanup method is, as yet, unknown since a revised cleanup decision has not been reached for this site. A USEPA ROD is due in 2011. However, site investigations used to generate data to support the human health and ecological risk assessments did include the evaluation of contaminant bioavailability as follows:

- laboratory bioaccumulation—28-day Asiatic clam (*Corbicula fluminea*) and oligochaete (*Lumbriculus variegates*)

- field bioaccumulation—fish, crayfish, wild rice, cattail roots, and mussels
- sediment toxicity tests—10-day midge (*Chironomus dilutes*) and 10- and 28-d amphipod (*Hyalella azteca*)

How Bioavailability Was Used: From an HHRA perspective, contaminant bioavailability from sediments was evaluated by measuring the concentrations of contaminants in various foodstuffs (such as wild rice, bivalves, and finfish including eggs) that are growing or living in or near contaminated sediments. Also, potential human exposure through incidental ingestion of contaminated sediments was also evaluated. Calculation of ingestion exposures considered contaminant-specific RBA ([absorbed fraction from soil/sediment]/[absorbed fraction from dosing medium in toxicity study]).

- Field bioaccumulation data were used directly in food-chain exposure models (fish, crayfish, mussels, cattail root, and wild rice organic contaminants) or used to derive site-specific BSAFs (wild rice metal contaminants).
- Laboratory bioaccumulation data were used directly in food-chain exposure models (*Corbicula* and *Lumbriculus*).
- Sediment toxicity tests provided a line of evidence of sediment risk.

Comments: With regard to ecological risk, bioavailability was not directly measured with the exception of AVS-SEM, which was used as a part of the sediment toxicity testing, but the influence of bioavailability was captured through measurement of site-specific laboratory and field bioaccumulation and sediment toxicity.

D-6 CENTRE COUNTY KEPONE, STATE COLLEGE, PENNSYLVANIA

Regulatory Agency: CERCLA/Pennsylvania Department of Environmental Protection
Frank Klanchar, 215-814-3218, Klanchar.Frank@epamail.epa.gov

Site Description: The 32-acre Centre County Kepone site, in State College, Pennsylvania, was a chemical manufacturing facility that produced the pesticide kepone in 1958, 1959, and 1963, and the pesticide mirex in 1973 and 1974. Process wastes were originally disposed of on site in a spray irrigation field, a concrete lagoon, and two earthen lagoons. Process wastes also were stored in drums on site. After leaks were discovered, the material in the lagoons was solidified and disposed of in the two earthen lagoons and capped. However, the material failed to solidify, and hazardous materials leached into the groundwater and surface water. Spring Creek is located adjacent to the site, and in 1982 a section of the creek was designated as a catch-and-release zone for fishing as a result of high levels of pesticides in fish.

Primary Pathway: Human health, benthic, pelagic

Contaminants: Mirex, kepone, photomirex

Tools: Bulk sediment chemistry, surface-water chemistry, fish tissue chemistry

Methods: Toxicity thresholds were identified or derived for relevant biota based either on existing or recommended guidelines (i.e., ambient water-quality criteria or sediment thresholds). Where published guidance was not available, toxicity thresholds were derived. The quotient method for characterizing potential risk was used [BAF = % lipid (K_{ow})/% carbon (K_{oc})]. Assuming receptors continuously inhabit the area, the ratio of measured (or estimated) exposure to the established (or estimated) toxicity threshold gives an indication of relative risk. Ratios of >1 were interpreted to indicate ecological risk, while ratios of <1 indicate negligible ecological risk.

How Bioavailability Was Used: The quotient method analysis showed ratios of >1 for all zones tested. Soil cleanup levels were set at the level established by USEPA to be protective of environmental receptors. Considering the BAF quotient, removal of sediment to meet USEPA's cleanup level would ensure that fish tissue levels do not exceed Food and Drug Administration (FDA)–established fish-tissue action levels for mirex and kepone of 100 µg/kg and 300 µg/kg, respectively. A fish-tissue and sediment monitoring program is in place to evaluate future contamination trends.

Comments: The ERA carried out in the RI used the surrogate approach, which involves extensive assumptions as the basis for the models. Many of the assumptions were unjustified, resulting in an ERA that is not protective of ecological receptors as a whole. For example, the ERA used the assumption that the OC level of the soil is 5% and the lipid content of the earthworm is 0.85%. The carbon content of the site soil ranges 1%–4%, and the lipid content of the earthworms is 1.5%. Using the reasonable assumption that the average carbon content of the soil is 2.5% and entering the values of 2.5 and 1.5 into the calculations to derive the bioaccumulation factor for earthworms, the results increase nearly fourfold [BAF = % lipid (K_{ow})/% carbon (K_{oc})]. These changes exert a change in the environmental effects quotient from the 0.05 contained in the RI to 9.5. Thus using actual site data for organic content and lipids made a huge difference in how the site was handled from a regulatory and cleanup perspective.

D-7. DIAMOND ALKALI–PASSAIC RIVER STUDY AREA, NEW JERSEY

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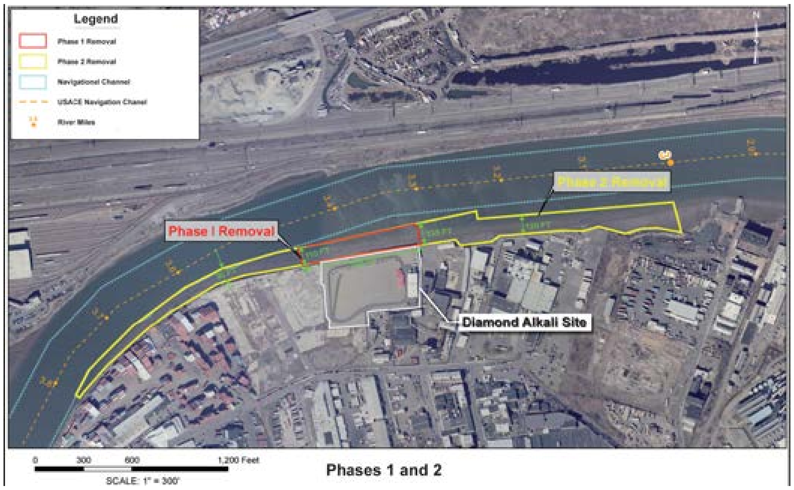
Site Description: From 1951 to 1969, the Diamond Alkali Company (subsequently known as the Diamond Shamrock Chemicals Company) owned and operated a pesticides manufacturing plant at Lister Avenue in Newark. The property has been used for manufacturing by numerous companies for more than 100 years. The mid-1940s marked the beginning of the manufacturing operations related to the current site conditions, including the production of DDT and phenoxy herbicides. Subsequent owners used the property until 1983, when sampling at the site and in the Passaic River revealed high levels of dioxin. Dioxin (also known as 2,3,7,8-tetrachlorodibenzo-p-dioxin, or TCDD) is an extremely toxic chemical and an unwanted by-product of the manufacture of certain chemicals which were produced at the site. USEPA added the site to the Superfund National Priorities List on September 21, 1984 because of hazardous substances present at the site and in the Passaic River, which borders the property.



The site comprises three parts: the former pesticides manufacturing plant and surrounding properties at 80 and 120 Lister Avenue, the Lower Passaic River Restoration Project Study Area, and the Newark Bay Study Area. Dioxin, pesticides, and VOCs, all of which can pose serious human health risks, were detected at the Lister Avenue properties. Occidental Chemical Corporation, a successor to the previous owner, the Diamond Shamrock Chemicals Company, performed interim cleanup work at the Lister Avenue properties and is performing a study of Newark Bay with USEPA oversight.

In 2004, USEPA formed a partnership with USACE, U.S. Fish and Wildlife Service (USFWS), NOAA, New Jersey Department of Environmental Protection (NJDEP0, and the New Jersey Department of Transportation and to conduct a joint study of the Lower Passaic River.

Primary Pathway: Human health, benthic, pelagic

Contaminants: PCBs, dioxin, dieldrin, chlordane, DDT, TCDD, mercury, copper, lead

Tools: Tissue chemistry, toxicity testing, BSAFs

Methods: Sampling of Passaic River sediments conducted during the RI/FS for the Diamond Alkali plant revealed numerous organic and inorganic compounds including, but not limited to, TCDDs and PCDFs, pesticides, PCBs, PAHs, and metals.

How Bioavailability Was Used: Bioavailability was factored into the risk assessment, but ultimately it was not used to determine a cleanup number. A feasibility study was performed to remove a major source of dioxin contamination from the lower Passaic River, eliminating the potential future threat that these harmful contaminants could pose to people's health and the environment. The agreement calls for 200,000 yd^3 of dioxin-laden sediment to be taken out of the river in the direct vicinity of the Diamond Alkali Superfund site in downtown Newark. This sediment is known to have the highest levels of dioxin in the lower Passaic. Cleanup levels are based on primarily the human health pathway through consumption of fish and crabs and secondly the benthic pathway.

Regulatory and Stakeholder Challenges: Direct contact exposures by sediment-associated receptors and indirect exposures associated with consumption of prey that have bioaccumulated sediment-borne contaminants. Bioavailability of contaminants were evaluated by looking at contaminant levels in biological tissue samples, toxicity testing, and development of site-specific BASF values. Sediment cleanup criteria have not been generated. Tissue testing and toxicity studies were used to measure bioavailability.

Comments: In June 2008, Occidental Chemical Corporation and USEPA signed an Administrative Order on Consent for a non-time-critical removal of approximately 200,000 yd^3 of contaminated sediment from the Passaic River in the vicinity of the former Diamond Alkali plant in Newark, to be done in two phases. Phase 1 will include the excavation of 40,000 yd^3 of contaminated sediment, which will be shipped off site for treatment and disposal. Phase 2 will include the excavation of 160,000 yd^3 of contaminated sediment.

For further information, visit www.epa.gov/region2/superfund/npl/diamondalkali.

D-8 FIFTEENMILE CREEK HERBICIDE SPILL THE DALLES, OREGON

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Regulatory Agency: Oregon Department of Environmental Quality (DEQ)

Site Description In August 2000, approximately 2600 gallons of herbicide spilled, and an unknown portion of this entered Fifteenmile Creek when the truck carrying it crashed on the bridge above. Approximately 1200 feet of the creek, from the accident site to the confluence with the Columbia River, was affected. The herbicide is Goal 2XL, and its active ingredient is oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene). Although not very harmful to mammals or birds, oxyfluorfen is toxic to fish and other aquatic life. The Oregon Department of Fish and Wildlife estimates that about 5500 fish died as a result of the accident. Almost all of these were juvenile Pacific lamprey, which spend the first four to six years of their lives burrowed in sediment. Oxyfluorfen preferentially partitions to OC in sediment in aquatic environments. Emergency response measures focused on preventing contamination from escaping into the Columbia River. Remedial measures involved placement of booms, sandbag dams, and water-filled fabric dams; diversion of creek water from the affected area; and removal of contaminated sediment by suction dredging and dry excavation.

Primary Pathway: Benthic, wildlife

Contaminants: Oxyfluorfen

Tools: Bulk sediment chemistry, tissue chemistry, toxicity testing, histopathology

Methods: Effects on aquatic invertebrates were determined based community impairment using macroinvertebrate studies and toxicity using laboratory bioassays. Effects on larval lamprey were evaluated based on population density upstream and downstream and histopathology studies. Effects on other fishes were evaluated based on histopathology studies and in situ caged fish studies to measure survival rates and bioaccumulation. Impacts on terrestrial wildlife were based on ingestion doses.

How Bioavailability Was Used: Bioavailability was measured based on site-specific ratios between concentrations in sediment, water, and biota (juvenile lamprey burrowing in sediment and trout that were held in cages in the water column for 30 days).

Regulatory and Stakeholder Challenges: No information.

D-9. FOX RIVER

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www.epa.gov/region5/sites/foxriver

Site Description: The Fox River and Green Bay Site includes an approximately 39-mile section of the Lower Fox River, from Lake Winnebago downriver to the mouth of the river, and all of Green Bay, totaling approximately 2700 square miles. This stretch of the river and bay flows through or borders Brown, Door, Kewaunee, Marinette, Oconto, Outagamie, and Winnebago Counties in Wisconsin and Delta and Menominee Counties in Michigan. The site has been divided into discrete areas (OUs). The river portion of the site comprises OU-1 through OU-4, and the bay portion of the site is designated OU-5 for purposes of site management. PCBs, the primary risk driver, are contained in sediment deposits located in the river and the bay. More than 75 COPCs (metals, PCBs, dioxins, pesticides, and PAHs) were identified in the screening-level risk assessment conducted to evaluate which chemicals in the system pose the greatest degree of risk to people and ecological receptors.

Primary Pathway: Human health and pelagic

Tools: Bulk sediment chemistry, toxicity tests, benthic community surveys, bioaccumulation/ bioassays, SEM/AVS

Methods: For benthic infauna, calculated HQs based on PCB SQOs were high. Benthic community analyses showed dominance of pollution-tolerant oligochaetes and chironomids. Sediment bioassays on bulk sediments collected from the same locations as benthic infaunal samples showed toxicity using the amphipod *Hyalella azteca*, the oligochaete *Lumbriculus* *variegatus*, the chironomid *Chironomus riparius*, and the mayfly *Hexagenia limbata*. Pore-water toxicity was also indicated in acute and chronic bioassays on the alga *Selenastrum capricornutum*, the invertebrate *Ceriodaphnia dubia*, the bacterium *Photobacterium phosphoreum* and the fathead minnow *Pimephales promelas*. Measured body burdens in native infauna showed uptake of PCBs but not dioxins or PAHs. By most measures, PCBs were impacting benthic resources. However, a TIE conducted on sediments from OU-4 and Green Bay demonstrated that ammonia, not PCBs, was responsible for most of the observed effects (Ankley, Katko, and Arthur 1990).

SEM/AVS ratio and metal concentrations in pore water revealed the bioaccumulation of copper, lead, zinc, cadmium, nickel, and chromium by *L. variegatus* held for an extended time in various sediment samples from the lower Fox River, Wisconsin.

How Bioavailability Was Used: PCBs were included as COCs for the ROD but did not factor into the setting of the remedial action levels for any of the OUs. The systemwide remedial action level was set to 1 ppm with a goal of achieving a surface-weighted average concentration (SWAC) of 0.25 ppm. It has been estimated that the removal of the contaminated sediment above 1 ppm will result in a SWAC of 0.26 ppm for OU-3 and of 0.16 ppm for OU-4.

Comments: The major components of the selected remedy include (1) removal of about 6,475,800 yd^3 of contaminated sediment containing over 27,575 kg (60,660 pounds) of PCBs from OU-3 and -4 using environmental dredging techniques and (2) MNR of the residual PCB contamination remaining in dredged areas, undisturbed areas, and OU-5 until the concentrations of PCBs in fish tissue are reduced to an acceptable level. The long-term monitoring program covers various media (e.g., water, tissue, and sediment) throughout OU-3, -4, and -5 to determine the effectiveness of the remedy.

D-10. GLENBROOK NICKEL–COOS BAY

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Site Description: Glenbrook Nickel Company operated a nickel ore unloading, drying, and crushing facility on water-front property in Coos Bay. Ore was offloaded into receiving hoppers located on a free-standing dock, and over time ore and ore dust from the crushing operation collected in the bay sediments near the dock.

Primary Pathway: Benthic

Contaminants: Nickel

Tools Used: Bulk sediment chemistry, grain size analysis

Methods: Nickel concentrations in uncontaminated sediments Coos Bay exceed the SQO, so the responsible party planned to use tissue sampling and bioavailability to establish a cleanup goal. However, due to the many uncertainties in the toxicity and bioavailability of nickel to benthic organisms and in the interests of time, the responsible party ultimately chose to base the sediment cleanup on background. Because background nickel concentrations varied with grain size (concentrations of nickel were lower in coarser sediments than in finer sediments), background was established relative to percent fines. Based on sediment quality data from a number of sampling events, the team found a linear, inverse relationship between nickel concentrations and sediment grain site (figure below), indicating that the coarse sediments near the sites dock exceeded background values.

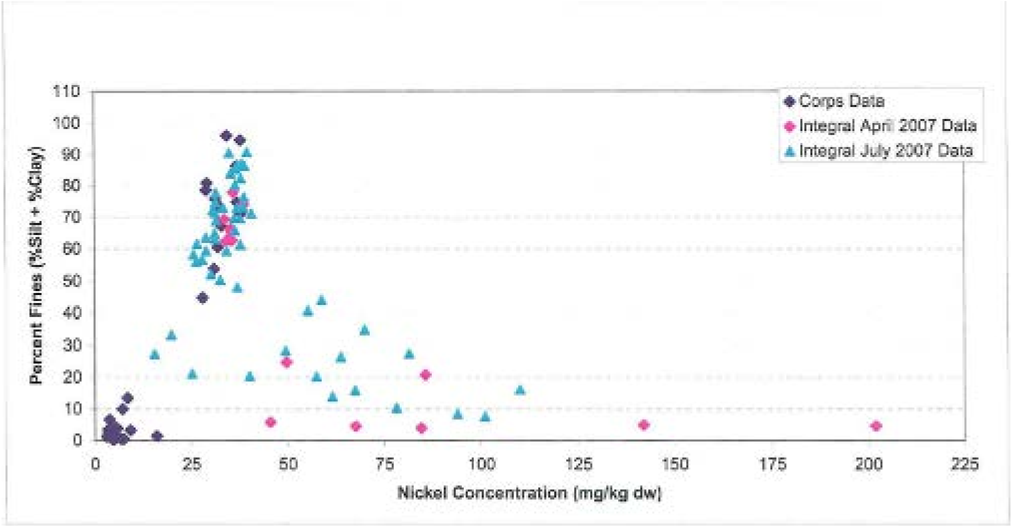

Figure 2. Nickel vs. Percent Fines in Sediment

How Bioavailability Was Used: Bioavailability was not directly used in the cleanup level. Grain-size-adjusted background values for nickel were used as cleanup goals. Nickel concentrations in the immediate site area (between the docks and the site shoreline) were higher than expected relative to percentage fines. To the extent that this reflects a higher bioavailability of nickel near the site, cleanup did address contaminant bioavailability.

Regulatory and Stakeholder Challenges: The site contact indicated that if literature values describing unacceptable levels for nickel in clams or oysters could have been found, they would have relied on tissue sampling instead of background for cleanup levels.

Comments: Ultimately, a rather large population (>10,000) of native Oregon oysters were discovered during preparation work just before the sediment removal action took place, indicating that the high concentration (up to about 200 mg/kg, compared to the SQO of 16 mg/kg) was not affecting the oyster population.

D-11. HACKENSACK RIVER, STUDY AREA 7, JERSEY CITY, NEW JERSEY

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Site Description: Study Area 7 (SA7) is a 34-acre parcel in Jersey City, New Jersey, located on the eastern shore of the Hackensack River, at the confluence of the Hackensack River and Passaic Rivers entering Newark Bay. SA7 had been used for industrial and commercial purposes for more than 100 years. Elevated chromium concentrations in SA7 sediment is partly attributable to the historic disposal of chromium ore processing residue generated during chromate production.

Primary Pathway: Human health, benthic, pelagic

Contaminants: Chromium

Tools: Bulk sediment and pore-water chemistry, AVS/SEM, benthic tissue analyses, in situ and laboratory toxicity and bioaccumulation testing, benthic community assessment

Methods: Various tools were used to assess chromium bioavailability, each of which contributed to a "multiple lines of evidence" evaluation that demonstrated the speciation, stability, and toxicity of chromium in SA7 sediments, as further described below.

How Bioavailability Was Used: Multiple bioavailability studies were used to evaluate potential environmental and human health risks associated with the presence of chromium in SA7 sediment and select an appropriate remedy for the site. Results from the sediment chemistry and biological evaluations showed conditions at SA7 favored the presence of the stable, insoluble trivalent chromium Cr(III) and not the toxic, water-soluble form hexavalent chromium Cr(IV). For example, AVS levels demonstrated reducing conditions in which chromium occurs as Cr(III) and not Cr(IV), and results from the pore-water analyses showed no detection of Cr(VI) in any of the pore-water samples, even when sediment total chromium concentrations were >370 mg/kg (NOAA's ER-M for chromium). Chromium levels in benthic tissue collected in the vicinity of SA7 did not differ from benthic tissue chromium concentrations collected from reference locations further north in the Hackensack River, the lower Passaic River, and in Newark Bay. Likewise, benthic community survey results showed the abundance of organisms and the composition of species in the vicinity of SA7 was similar to reference locations. These results along with additional lines of evidence, demonstrated very low bioavailability of chromium in study area sediments and supported a sediment remedy of capping and MNR.

D-12. HOLTRACHEM, ORRINGTON, PENOBSCOT COUNTY, MAINE

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Regulatory Agency: RCRA

Site Description: HoltraChem is a former chlor-alkali facility with multiple contaminants. The Penobscot River is adjacent to the site, and mercury was deposited in the river water and sediment. The river is tidal with an 11-foot tidal swing. The site is at the point in the river where it switches from being primarily salt water to primarily freshwater A wedge of salt water moves up and down in the site depending on the season. Bioavailability was used as one component of the cleanup decision relating to mercury. Mercury sediments from the cove in front of the site were used to conduct 28-day bioavailability toxicity testing. A site investigation determined that the HoltraChem property, including parts of the Penobscot River, is contaminated with mercury, chloropicrin, and several VOCs. Additional investigation will be done into the presence of additional areas of mercury contamination and PCBs.

Primary Pathway: Benthic, water-column vertebrates and invertebrates, human health

Contaminants: Mercury

Tools Used: Bulk sediment chemistry, toxicity testing, benthic community (macroinvertebrate) surveys, bioaccumulation/bioassay

Methods: Mercury toxicity to macroinvertebrates, reproduction, conversion of Hg in sediment to methylmercury in the site environment using co-located samples.

How Bioavailability Was Used: An assessment was made to determine what concentration of Hg was needed to avoid establishing a fish advisory. The May 2009 updates of Phase I and II Reports of the Penobscot River Study prepared by Bodaly et al. (2009) at the request of Judge John Woodcock of U.S. District Court (District of Maine), Bangor, Maine confirmed that there was extensive harm to the river and bay south of the plant site as a result of mercury contamination. The studies were conducted to determine whether mercury levels in fish, shellfish, and wildlife found in the lower Penobscot River (Maine) and in Penobscot Bay are of concern with regard to possible human consumption or the species themselves, particularly in relation to the location of the HoltraChem site.

Comments: At the present time remedial options for the sediments are being negotiated. The cleanup goals for sediments include dredging of the most highly contaminated area of the river sediments—just under an acre—near the plant's outfall pipe and several acres of more moderate contamination in an adjacent cove. In areas of the river below the southern cove, there are significantly lower concentrations of mercury. The on-site sediments that are highly contaminated will also be excavated and/or buried. Excavated soils would be either disposed of off site or consolidated on site under a cap designed to prevent infiltration and the discharge of contaminants. Additional investigation will be done into the presence of additional areas of mercury contamination and PCBs.

D-13. HORSESHOE ROAD AND ATLANTIC HIGHLANDS SUPERFUND SITE, NEW JERSEY

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Primary Pathway: Benthic, wildlife, and pelagic

Contaminants: Arsenic

Tools: Bulk sediment chemistry, tissue chemistry, toxicity testing, bioassessment survey, macroinvertebrate survey, bioaccumulation tests, sediment toxicity test

Methods: The AET approach and back-calculation from food chain models were used to develop site-specific risk-based sediment remediation goals. Risk-based goals were developed for numerous ecological receptors, but the most conservative cleanup number was used.

How Bioavailability Was Used: Risk-based remediation goals for marsh sediments were generated for several receptors using the AET approach. Both acute (survival) and chronic (reduction in biomass) endpoints were evaluated via sediment toxicity testing for the freshwater black worm, *Lumbriculus variegatus*, and the terrestrial earthworm, *Eisenia fetida*. Data from the black worm, as the more sensitive species tested, was used in setting the cleanup goal. A risk management decision made by USEPA/NJDEP enforced the use of the most conservative cleanup goal for the marsh environment (risk to black worm = 32 mg/kg arsenic).

A remediation goal for in-river sediment was calculated to be 192 ppm based on sediment toxicity tests using *Leptocheirus plumosus*; however, the actual cleanup goal was modified to 100 ppm to take regional background concentrations into account.

Risk-based remediation goals were also developed for the marsh wren and muskrat using site-specific insect and plant tissue data, respectively, and back-calculation from food chain models. Since these cleanup goals were less conservative than those for the black worm, they were not selected as the final remediation goal.

Comments: Bulk sediment chemistry, toxicity testing (USEPA protocol methods), 28-day chronic toxicity test on Raritan River sediment (test organism = *L. plumosus*), macroinvertebrate surveys (USEPA RBPs), tissue chemistry (tissue collection from Phragmites, small mammals, terrestrial invertebrates, fiddler crabs, estuarine minnows), bioaccumulation/bioassay (marsh and Raritan River sediments—black worm (*L. variegatus*) and earthworm (*E. fetida*). The AET approach was used to develop site-specific risk-based goals. The AET is determined for each

COC and is defined as the concentration above which a specific biological effect is always found. In other words, the AET is the highest concentration with no effect. It is determined from sediments/soil chemistry data and sediment/soil toxicity test results that show statistically significant adverse effects. The black worm was picked as a sensitive species since it was a marsh environment and that species was more indicative of the terrestrial nature of that marshland. The remedial design was initiated in September 2009 for the marsh and river sediments.

D-14. IMPERIAL REFINERY, ARDMORE CARTER COUNTY, OKLAHOMA

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Katrina Higgins-Coltrain, Remedial Project Manager, USEPA Region 6, 214-665-8143
Regulatory Agency: CERCLA/USEPA/Oklahoma DEQ

Site Description: The Imperial Refining Company (IRC) Superfund Site is the location of a 72-acre abandoned former petroleum refinery that operated 1917–1934. Numerous tanks and buildings were present on the site during refinery operation, but all of the tanks and most of the buildings were dismantled sometime between 1934 and 1948, leaving the property in much the same condition as it is in today, mixed wooded areas and open fields.

IRC is located on either side of State Highway 142 in northeast Ardmore, Oklahoma. In 1934 IRC declared bankruptcy and ceased operations and dismantled all tanks and storage equipment by 1948. Numerous pits, piles, and water impoundments are contaminated with metals and refining wastes. The site was listed on the National Priorities List in July 2000. The remedial process is a three-stage progression that defines the nature and extent of contamination, establishes the engineering plan to remedy the problems, and constructs the selected remedy for Superfund sites.

Primary Pathway: Benthic

Contaminants: PAHs

Tools: Bulk sediment chemistry, toxicity testing, BSAFs, and tissue chemistry

Methods: Sediment chemistry and BSAFs were used to estimate tissue concentrations. The toxicity testing was used to identify ponds where an unacceptable risk was present.

How Bioavailability Was Used: Bioavailability was not used directly. Toxicity study data drove the cleanup with removal of sediment in areas where an unacceptable risk was present. Based on the low survival rate results in the toxicity study and lack of associated site-specific chemistry, these areas will be removed, and a second effects level for benzo(a)pyrene of 0.782 mg/kg will be used as the pond sediment cleanup level. This value is analogous to an LOAEL.

Comments: Sediment concentration and toxicity studies data were used in the measurement/ calculation of bioavailability. No benthic invertebrate tissue data were collected. The COPEC concentration in benthic invertebrate tissue was assumed to be equivalent to the COPEC dry weight concentration in sediment multiplied by a BSAF obtained from the literature. The 90th percentile BSAFs for all organisms developed by ORNL (Bechtel Jacobs 1998) were used to conservatively estimate COPEC concentrations of benthic invertebrate tissue. Benthic invertebrates were assessed as an important part of the diet of the raccoon and the marsh wren potentially using the ponds, Sand Creek, and wet areas for foraging. The toxicity studies conducted in the ERA showed a significant and immediate risk to sediment-dwelling organisms in the on-site ponds. Survival rates during the toxicity studies were less than 70%. Based on the low survival rate results in the toxicity study and lack of associated site-specific chemistry, a second effects level for benzo(a)pyrene of 0.782 mg/kg will be used as the pond sediment cleanup level. This value is analogous to an LOAEL.

D-15. INDUSTRI-PLEX SUPERFUND SITE, WOBURN, MASSACHUSETTS

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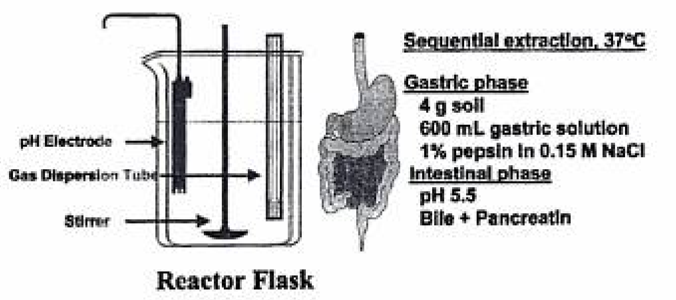

Source: Dr. Nick Basta, School of Environment and Natural Resources, Ohio State University

Primary Pathway: Human health

Contaminants: Arsenic

Tools: In vivo extraction to estimate RBA

Site Description The Industri-plex site was once occupied by the former Merrimac Chemical Co., which was once the nation's leading producer of lead arsenate, the main insecticide used in apple orchards in the 19th century. Prior to completion of the HHRA, an arsenic bioavailability study was performed to assist in the quantification of sediment risks. An in vitro extraction test was first performed on fine-sieved sediment obtained from four locations along the Aberjona River to measure the amount of arsenic that dissolves in a reactor that simulates the stomach fluid of humans. The amount of arsenic that solubilizes after 1 hour was used as a preliminary indicator of potential of the in vivo RBA. The results from this test indicated arsenic from dried material was more bioavailable than that from wet sediment. Microprobe analysis suggested that the presence of iron oxide was associated with higher arsenic concentrations and lower in vitro bioaccessibility, while the presence of the iron-zinc sulfate complexes saw lower arsenic concentrations and higher in vitro bioaccessibility.

Based on the in vitro tests, sediment test material samples TM2 and TM3 were measured to have arsenic levels of 313 and 676 mg/kg, respectively. Varying weights of each material were fed in dough balls to three groups (N = 4/dose) of immature swine so that the target doses were equivalent to 300, 600, and 900 µg/animal/day. When exposure began (day 0), the animals were about 6 weeks old and weighed an average of about 12.1 kg. Samples of urine were collected from each animal for three consecutive 48-hour periods on days 6/7, 8/9, and 10/11 of the study. Positive controls were fed equivalent doses of sodium arsenate. Laboratory analyses were submitted in a blind fashion, and measurements accounted for all forms of arsenic (i.e., As(III), As(V), and methylated species). The RBA of arsenic in the sediment samples was calculated by dividing the absolute bioavailability (ABA = amount absorbed/amount ingested) of the three test sediments by the ABA of the sodium arsenate. The RBA of TM2 and TM3 were 37% and 51%, respectively. The risk assessment toxicity factors were, accordingly, adjusted using the most conservative relative bioavailability factor of 0.51 (i.e., USEPA IRIS reference dose was divided by 0.51, and the cancer slope factor multiplied by 0.51).

Source: Dr. Stan Casteel, College of Veterinary Medicine, University of Missouri

D-16. INDIAN RIVER POWER PLANT, MILLSBORO, DELAWARE

Regulatory Agency: Delaware Department of. Natural Resources and Environmental Control
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Primary Pathway: Benthic

Contaminants: PAHs

Tools: Bulk sediment chemistry, pore-water estimates using EqP, and narcosis theory

Methods: TU approach

How Bioavailability Was Used: Cleanup levels based on the EqP-TU approach were calculated for intertidal sediments contaminated with NAPL and dissolved-phase, diesel-range organics that resulted from a diesel fuel spill from a leaking underground pipeline into the Indian River sediments. The pipeline was taken out of service, and a sheet pile wall with sealed interlocks was installed to preclude the future migration of residual oil into the river sediments. Subsequent investigation work consisted of identifying the extent of impact, assessing risk to aquatic receptors, implementing a remedial action, and restoring the shoreline.

For each sample collected during the investigation of impact extent, bulk sediment chemical measures of PAH parent compounds and alkylated homologs were first normalized to the TOC concentrations at each corresponding sample point. Pore-water concentrations of these compounds were then predicted using EqP and were subsequently divided by analyte-specific acute and chronic values calculated from narcosis theory. For each sample, the TUs for individual compounds were summed to yield total acute and chronic TUs. TUs >1 indicated that pore-water exposure concentrations were potentially high enough to cause toxicity to benthic organisms. The state required excavation of all sediments with chronic TUs >1, which corresponded to a total PAH cleanup criterion of 2 mg/kg. In total, approximately 480 yd^3 of sediment was ultimately removed from the Indian River shoreline, and confirmatory samples indicated that the calculated cleanup criteria were met. Excavated sediments were replaced with clean material of similar grain-size composition and were allowed to be naturally reworked and contoured over several tidal cycles prior to revegetation efforts.

Comments: A long-term monitoring program was subsequently established to ensure that the remedial efforts would remain protective of ecological receptors and included regular visual site inspections to monitor erosion and health of vegetation, photomonitoring of vegetative growth and site development, vegetation sampling for various parameters, and sediment sampling for PAHs and TOC.

D-17. JOHNSON LAKE, PORTLAND, OREGON

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Regulatory Agency: Oregon DEQ

Site Description: Johnson Lake extends over 18 acres and is directly connected to the Whitaker Slough, which in turn flows to the Columbia Slough, a quiescent waterway located south of the Columbia River. Several environmental investigations have been conducted at the site, beginning in 1994 with the collection of three sediment samples from Johnson Lake as part of a broader sediment sampling event conducted by the City of Portland for the Columbia Slough project. Analytical results indicated elevated PCBs, metals, and PAHs in lake sediment. Follow-up investigations conducted between 1998 and 2004 confirmed the sediment contamination and provided information on contaminant distribution. In 2005 and 2007, Owens conducted additional sediment sampling of the lake for chemical characterization and bioassays. Tissue samples were also collected and analyzed to assess the degree to which bioaccumulative contaminants were present in lake biota.

Primary Pathway: Benthic, human health, wildlife

Contaminants: PCBs, metals, PAHs, PHCs

Tools: ODEQ concluded that sediment contamination in Johnson Lake poses an unacceptable risk to human health based on the risk associated with ingestion of PCB-contaminated fish. ODEQ calculated a potential excess lifetime cancer risk via this pathway of 1×10^{-4} using risk associated with individual PCB congeners. Pertinent assumptions used in this evaluation include the following:

- a fish ingestion rate of 45 g/day based on a Columbia Slough consumption survey
- an assumption that fish caught from Johnson Lake would make up approximately 11% of the diet of someone who regularly fishes from the Columbia Slough
- no contaminant losses during cooking
- consideration of dioxin-like cancer risk posed by particular PCB congeners

Tissue concentrations of PCB congeners were also predicted to cause unacceptable risk to birds, and bioassays suggested toxicity to benthic organisms in one area of the lake.

Methods: Bulk sediment and tissue chemistry, toxicity testing

How Bioavailability Was Used: A comparison of tissue levels to a weighted-average sediment concentration throughout the lake was used to develop a site-specific BSAF. This value was used to estimate the area of sediment that would require remediation such that the residual lakewide sediment concentration would result in a projected risk of 1×10^{-5} excess cancer risk based on human ingestion of fish. Source control and natural recovery were expected to bring the concentration down even further over time.

Comments: Additional sediment data were collected during remedial design to better determine the depth of sediment that would need to be removed and improve PCB concentration delineation. These data indicated that a much larger volume of sediment would need to be remediated to achieve the lakewide goals established in the original ROD. Consequently, the remedial action was reevaluated, and the ROD amended to require thin-layer capping of the entire bottom of the lake. Permitting is currently under way, and the capping is expected to occur in the summer of 2011. The ROD can be viewed at http://www.deq.state.or.us/Webdocs/Forms/Output/FPController.ashx?SourceId=1311&SourceIdType=11.

D-18. LAKE HARTWELL (SANGAMO-WESTON/TWELVEMILE CREEK/LAKE HARTWELL SITE, OU 2), PICKENS, SOUTH CAROLINA

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Agency: USEPA Region 4

Primary Pathway: Human health via fish consumption, benthic

Contaminants: PCBs

Tools: Bulk sediment, sediment deposition, and bioaccumulation modeling; fish and benthic tissue chemistry

Site Summary: The affected areas are a 7-mile stretch of Twelvemile Creek and 56,000-acre Lake Hartwell (man-made reservoir created by the construction of Hartwell Dam across the Savannah River) (USEPA 2004b). Twelvemile Creek is the primary tributary into the headwaters of the lake and contains three masonry impoundments (private dams) along its length. Sediment in both Twelvemile Creek and Hartwell Lake contains PCBs that originated from a Sangamo Weston capacitor plant that discharged PCB-containing wastewater into Town Creek, a tributary to Twelvemile Creek. Sediment PCB concentrations in the lower 7-mile stretch of Twelvemile Creek, interchangeably known as the Twelvemile Creek Arm and Seneca Creek Arm, and a depositional area, were originally measured in the 1–3 ppm range at the surface and higher in deeper sediments. Portions of the Twelvemile Creek Arm were found to contain up to 61 ppm PCBs. In 1991/92, maximum PCB concentrations measured in sediment core samples from the upper section of Lake Hartwell (where Twelvemile Creek enters) exhibited concentrations of 5–11 ppm; PCB concentrations in sediment in the lower part of the lake were typically <1 ppm.

In June 1994, a ROD was issued for the site that specified MNR supplemented by institutional controls as the selected remedy. The selected target cleanup standard for sediment was 1 ppm PCBs based on technical feasibility; the affected area covers approximately 730 acres with a total estimated volume of 4.7 million yd^3 of PCB-contaminated sediment. For fish, the FDA action level of 2 ppm PCBs was selected, also based on technical feasibility. A carcinogenic risk-based approach was evaluated by determining the concentration levels in largemouth bass that would result in acceptable risk to anglers through ingestion of fish. Using USEPA risk assessment methods, a fish tissue concentration of 0.036 ppm was associated with a 10^{-4} risk. The risk-based fish cleanup goal of 0.036 ppm was determined to be technically impracticable. Natural recovery of largemouth bass within Hartwell Lake to below the FDA action level of 2 ppm PCBs was predicted by modeling to occur within 12 years (by 2004).

Methods: Sediment cores were collected in Lake Hartwell and provided data used to determine the vertical profile of PCBs in the sediment column. These data indicated that higher PCBs were being buried beneath sediment with lower PCB concentrations. Two long-term fate and bioaccumulation models were constructed to enable predictions of PCB concentrations in sediment and fish in Lake Hartwell over time under various potential remedial approaches. A water-quality model was developed to determine the fate of PCBs in the system over time, and results of this model indicated that PCB concentrations in the water column and sediment of Lake Hartwell would generally decrease over time, even in the absence of any intrusive remediation. The primary mechanisms for PCB reductions over time were boundary transport and burial. A bioaccumulation model was also constructed to complement the water-quality model and to estimate PCB concentrations in fish tissue over time. The results from this model indicated that largemouth bass PCB levels would decrease to <2 ppm (in fish weighing greater than 3.4 kg) in 12 years under an MNR scenario. Results from these models were used in establishing the ROD for the site.

How Bioavailability Was Used: Bioavailability was used at this site to determine that PCBs in lake sediment are generally higher at depth and lower at the sediment surface where PCBs would be bioavailable. Modeling was employed to estimate the fate of PCBs over time and the modeling showed that bioavailable PCBs are expected to reduce over time, resulting in lower PCB levels in lake water and resident fish species. Results of monitoring at the site since the 1994 ROD are summarized below.

Annual biota and sediment monitoring has been implemented in the spring of each year since 1994. This effort has included (1) surface sediment sampling at 21 locations in Twelvemile Creek and Lake Hartwell; (2) fish tissue analyses at six stations in Lake Hartwell for largemouth bass, catfish, and hybrid bass; (3) fish tissue analyses on forage fish species at three locations in Lake Hartwell; and (4) 28-day caged corbicula analyses at seven stations in Twelvemile Creek. Reportedly, sediment data indicate that surficial sediment PCB concentrations in Twelvemile Creek have decreased steadily since 1990 due to ongoing physical processes such as burial, mixing/dispersion, and PCB dechlorination. However, the USEPA Five-Year Review of the site performed in 2004 concluded that, although sediment concentrations continue to measurably decrease, PCB concentrations in largemouth bass, channel catfish, and hybrid bass have not responded as measurably to the decreased surface sediment trends.

A 2006 technical agreement between the Natural Resource Trustees and the principal responsible party, Schlumberger Technology Corporation, requires among other things the removal of two of three dams (Woodside 1 and 2) on the Twelvemile Creek Arm of Lake Hartwell. An Explanation of Significant Differences was issued in 2009 to support this aspect of the project as it is expected to enhance the ongoing natural transport of clean sediment downstream to speed burial of the PCB-contaminated sediment in Lake Hartwell.

D-19. MCCORMICK AND BAXTER, PORTLAND, OREGON

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Regulatory Agency: USEPA/ODEQ

Site Description: The McCormick & Baxter Creosoting Company site operated 1944–1991, treating wood products with creosote, pentachlorophenol, and inorganic (arsenic, copper, chromium, and zinc) preservative solutions. Historically, process wastewaters were discharged directly to the Willamette River, and other process wastes were discharged to ground surface, contaminating soil and groundwater across the site.

An impermeable, subsurface barrier wall surrounding 18 acres of the site was installed in 2003 to contain a large portion of the primary source areas of groundwater contamination and minimize horizontal seepage of creosote into the Willamette River. The site remedy was complete in September 2005 and includes a soil cap over approximately 40 acres of land and a sediment cap over approximately 22 acres of contaminated sediments beneath the Willamette River. Creosote continues to be recovered at the site by manual methods; approximately 6300 gallons has been recovered since 1996.

Primary Pathway: Human health, benthic, pelagic

Contaminants: PAHs, pentachlorophenol, metals

Tools: Bulk sediment chemistry, surface-water chemistry, fish tissue chemistry, toxicity tests

Methods: Fish and crayfish surveys were conducted at this site (Pastorok et al. 1994). To assess the effects of the residual creosote-derived contaminants including PAHs and dioxins, the assessment included sediment chemistry, bioassays, tissue residues in fish and crayfish and fish histopathology. Sediment chemistry and toxicity testing indicated that a substantial area of the Willamette River sediments proximal to the site was likely to be toxic (USEPA 1996n). By contrast, tissue residue values for PAHs in crayfish (*Pacifastacus leniusculus*) and large-scale sucker (*Catastomus macrocheilus*) collected near the site show slight elevations of dioxins/ furans and low-molecular-weight PAHs compared with fish and crayfish samples collected in other parts of the Willamette River. Visual examination of fish tissue showed no adverse effects from exposure to site-related contaminants other than mild inflammation, which was also observed in fish collected in other areas of the Willamette River.

How Bioavailability Was Used: Sediment chemistry and bioassay data, as well as continuing NAPL discharges from sediments to the Willamette River, were used as the basis for the remedial action at this site. The ROD required containment of NAPL by means of NAPL recovery with a subsurface barrier wall contingency and a (permeable) sediment cap (USEPA 1996n). During remedial design of the sediment cap, an organophylic clay was specified for placement over the remaining NAPL seep areas.

Comments: The Oregon Department of Human Services issued a health advisory for commercial harvesting of crayfish taken within 1000 feet of the site shoreline in 1991. Crayfish collected on 2003 before the sediment cap construction contained approximately twice the health advisory criteria of 0.9 ppt for 2,3,7,8-TCDD TEQ. Crayfish samples taken in 2006 and 2008, after the sediment cap was constructed, contained less than half the health advisory criteria. The advisory was lifted in 2009.

DEQ is now conducting SPME sampling to establish a baseline concentration of PAH contaminants in pore water within the sediment cap sand. Using that and previous pore-water data obtained using conventional Henry samplers, DEQ will consider future SPME sampling events to compare to the SPME baseline to ensure that the sediment cap is continuing to perform as designed.

D-20. MOCKS POND INDIANA STEEL AND WIRE—MOCKS POND AREA, MUNCIE, INDIANA

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Primary Pathway: Human health, benthic, fish

Contaminants: Metals

Tools: Bulk sediment and surface-water chemistry, benthic, plankton, wildlife and fish surveys, fish tissue chemistry, pore-water sampling

Methods: Screening of sediment analytical data against Indiana Tier II residential cleanup goals and sediment ecological screening benchmarks, screening of surface water analytical data against surface-water quality standards, comparison of fish tissue concentrations with background fish tissue concentrations from the White River and USEPA Region III risk-based concentrations, comparison of pore-water concentrations with surface-water ambient water quality criteria

How Bioavailability Was Used: Bioavailability was evaluated as part of a human health and ecological risk assessment by measuring metals in the whole bodies and filets of pelagic fish species. Pore-water concentrations were collected as part of a post-remedial monitoring program to evaluate the effectiveness of the remedy (i.e., partial excavation followed by placement of a sand cap) in preventing exposures to residual metals impacts in the sediment.

Regulatory and Stakeholder Challenges: Mocks Pond is an abandoned limestone quarry in Muncie, Indiana, which had formerly received lime-stabilized, spent, pickle-liquor sludge related to the manufacture of galvanized (zinc-coated) wire products composed of iron, and other insoluble metal hydroxides. The resultant “sediment” was a very fine iron-rich material with low TOC. While constituents of interest in the pond included select heavy metals (e.g., antimony, arsenic, cadmium, chromium, copper, lead and zinc) at concentrations exceeding their respective sediment screening values, previous testing suggested that the materials deposited in the bottom of the pond were stabilized and not biologically available.

Ecologically, the pond bottom consisted principally of unconsolidated sediment that was largely devoid of organic material and bottom-dwelling macroinvertebrates. As a result, bottom-feeding fish species (e.g., carp, catfish) were not common in the pond. Also, despite the presence of shallow, permanently submerged habitat, the margins of the pond were devoid of rooted or floating vascular vegetation (e.g., cattails).

In contrast to the sediment conditions, surface water exhibited relatively good quality (i.e., metals concentrations in surface water were below screening criteria). The pond contained a relatively diverse and healthy water-column aquatic community including a variety of pelagic fish, snapping turtles, and other turtle species and a diverse aquatic-dependent wildlife community. Institutional controls for human exposure were in place in the form of a large fence surrounding the site.

It was hypothesized that sludge-sediment itself would not support aquatic life and that the metal hydroxides were not biologically available through dissociation in pore water or surface water. While the physical/chemical conditions in the deposited materials were not conducive for benthic-dependent insects or fish, metals in the sediments were believed to be biologically unavailable to upper trophic level organisms. Human health and ecological risk assessments were completed to test this hypothesis. Bioavailability was evaluated as part of a human health and ecological risk assessment by measuring metals in the whole bodies and filets of pelagic fish species. The risk assessment activities determined that lead concentrations in sediment and arsenic concentrations in fish tissue may pose a significant consumption risk to construction workers and recreational anglers, respectively.

Based on the results of the risk assessment studies, a decision was made to dredge the sludge-impacted sediment to a clear water depth of 10 feet followed by placement of a sand cap with the objective of establishing a suitable habitat for benthic reestablishment and for potential future access to the site for recreational purposes. A remedial goal of the project was to demonstrate that the metals present in the residual impacted sediment were biologically unavailable following dredging and placement of a sand cap over the entire pond bottom.

Bioavailability was subsequently evaluated following implementation of the remedy as part of a post-remedial monitoring program designed to monitor cap performance (i.e., ability to restrict the migration of constituents into the biotic zone) by measuring metals concentrations in pore water. Large-volume “peepers” were used to collect pore-water samples. These devices consisted of dialysis tubing filled with reagent-grade water placed into a protective sheath and then inserted into the sediment to a depth of 10 cm. In addition, surface-water and sediment sampling was completed as part of the post-remedial monitoring to assess functional effects on the water column community and to confirm isolation of the residual metals-impacted sediment, respectively. Results from the post-remedial monitoring confirmed that metals were tightly sequestered and not partitioning into pore water or surface water.

The primary risk driver at this site was established in 1999 as a human health risk to subsistence finfish harvesters from PCB concentrations in bottom fish. A cleanup goal was established for PCB concentrations in surface sediment, which was assumed to eventually result in a reduction in PCB concentrations in marine tissue. The PCB sediment cleanup goal was not risk based, and no bioavailability determination was made. The PCB cleanup goal was instead based on a cost-benefit analysis.

A supplemental HHRA recently conducted as the result of a recommendation in the second Five-Year Review found unacceptable risk to subsistence harvesters from mercury in fish and shellfish tissue. A mercury source study, conducted in parallel with this risk assessment, includes an evaluation of the mercury methylation processes at the site to help characterize mercury bioavailability. The overall objective of this study is to describe and quantify the biogeochemical processes that lead to the bioaccumulation of methylmercury into the base of the pelagic food web, methylation of mercury in sediments, and the release of methylmercury and ionic mercury from the sediments. USGS is performing this study with an estimated completion date of September 2011. This study will assist in the establishment of a mercury cleanup goal.

D-21. MYRTLE STREET EMBAYMENT, LOWER DUWAMIWSH WATERWAY, WASHINGTON

Regulatory Agency: USEPA Region 10

Primary Pathway: Benthic, human health

Contaminants: PCE, TCE, DCE, VC

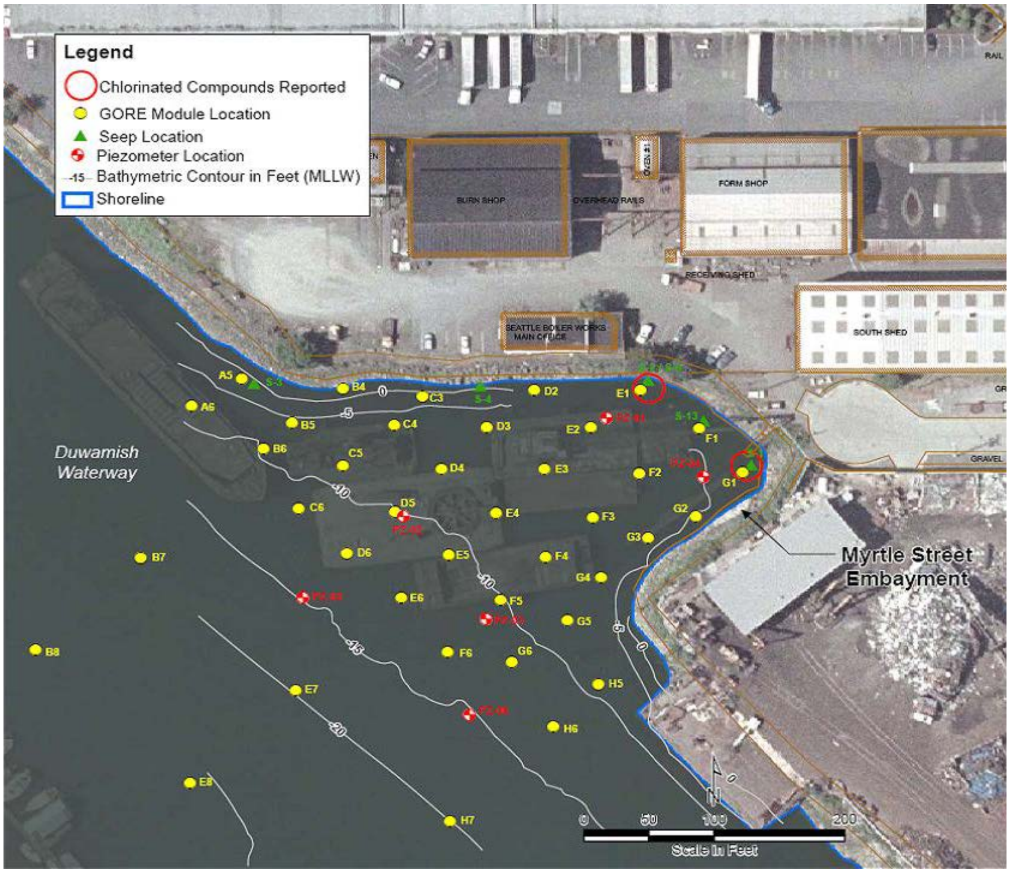
Tools: Diffusion-based samplers in pore water

Site Summary: The Lower Duwamish Waterway Superfund site investigation focused principally on bedded-sediment contamination, but the site is also considered to be impacted by continuing releases to the system from surface-water and subsurface-groundwater discharges. Groundwater releases were principally evaluated by sampling seeps during low-tide sequences and by placing piezometers and peepers in the sediment. These approaches were not effective at all locations due to the need for rapid characterization over tidal cycles at a finer spatial grade. Peepers placed subtidally were also not thought to adequately capture VOCs at one particular site, the Myrtle Street Embayment Study Area.

Two overlapping discharging solvent plumes were identified at the Myrtle Street Embayment: a shallow aerobic plume that was mostly PCE and TCE and a deeper anaerobic plume of daughter compounds such as DCE and VC. Wells located 50 feet inland indicated that the plumes ranged from the top of the aquifer (at about 10 feet bgs) to more than 45 feet bgs. The groundwater well concentrations were up to 1000 times groundwater cleanup levels, while in-seep samples concentrations were up to 100 times cleanup levels. However, as the freshwater plume encountered the tidal salt water wedge, the groundwater discharge area narrowed and rose over the wedge. In the process, the discharge area where benthic infauna would be exposed narrowed from 35 vertical feet to about 10 vertical feet. USEPA and the Washington Department of Ecology were concerned that the “worst” groundwater was discharging deeper in the waterway and therefore polluting the sediments.

Diver-placed diffusion samplers (GORE® Modules) were used to characterize the discharge to the embayment through localized seeps and generalized upwelling beneath the embayment. GORE Modules consist of GORE-TEX® membrane tubes housing hydrophobic adsorbents which capture and measure VOCs, and SVOCs. The modules were housed in a sediment insertion probe and inserted into the sediments (see Table C-T2). They were deployed in a systematic close-grid fashion across the embayment, known seeps, and potential critical discharge areas (see photo). Over multiple tide cycles, the samplers were able to identify an expanded seep discharge face near the top of the saltwater wedge but demonstrated lack of a subtidal embayment discharge.

How Bioavailability Was Used: The results demonstrated that there was no complete transition from groundwater to the bioactive layer of the sediment zone. Therefore, a complete exposure route did not exist between the contaminated groundwater seeping into the bay and the estuarian benthic community. The investigation showed an incomplete exposure pathway to subtidal organisms, and, although a direct measure of bioavailability could not be discerned, the lack of detection of COPECs by the GORE Modules did prove the null hypothesis, i.e., that potential receptors were not exposed and therefore there can be no risk to these receptors or their predators in the waterway. Without the investigation, the discharge area would have been assumed to be lower and more diffuse that it actually was, making it likely that additional biological sampling would have been placed in areas where exposure was limited.



D-22. MOFFETT FIELD, CALIFORNIA, HANGER 1, SITE 29

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Site Description: Hangar 1 was constructed in 1932 to house the giant airship U.S.S. Macon. Its floor space covers 8 acres (the equivalent of 10 football fields) and it stands 200 feet high. Over the years, the hangar provided space for maintenance of aircraft, training facilities, and offices for both the Army and Navy. Hangar 1 is part of the property transferred to National Aeronautics and

Space Administration Ames Research Center in 1994. It formerly housed the Moffett Field Historical Society Museum and was used as a display space for air shows, open houses, and various commercial and public functions.

The building materials and paint used to construct Hangar 1 contain PCBs, asbestos, lead, and zinc. The hangar is aging, and its paint and building materials are deteriorating. As a result, the contaminants in these materials moved into the environment around the hangar and, ultimately, reached Site 25 sediments in a storm-water retention pond and storm-water settling basin (located at nearby wetlands) through the Moffett Field storm drain system. To ensure the protection of human health and the environment, in 2003 the Navy completed an interim control measure called a time-critical removal action, which included applying a specialized coating to the exterior surface of Hangar 1 to seal the materials on the building surface.

In 2007, the Navy issued a draft revised engineering evaluation/cost analysis (EE/CA) recommending removal of the Hangar 1 siding and coating the structural steel frame. The previous EE/CA (2006) had recommended complete demolition of the hangar. The revised EE/CA was finalized in July 2008. In January 2009, the Navy signed an action memorandum declaring that the Navy will proceed with the proposed EE/CA alternative, removing the siding and coating the frame. The Navy has prepared cleanup action work plans and has initiated actions in 2010 with a completion date of 2011.

Primary Pathway: Benthic

Contaminants: PCB Aroclor 1268, asbestos, and lead

Tools: Bulk sediment chemistry, tissue chemistry, bioaccumulation testing, food chain modeling

Methods: Site-specific BAF and food chain model used to back-calculate sediment cleanup numbers

How Bioavailability Was Used: The relative bioavailability was determined by establishing the relationship between benthic organisms and sediment concentrations.

Comments: Sediment bioassays were used to estimate bioaccumulation. The estimated bioaccumulation was used to calculate a site-specific BAF, which was then used to back-calculate an acceptable sediment value.

D-23. ONONDAGA LAKE, ONONDAGA LAKE, NEW YORK

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Site Description: Onondaga Lake itself is a 4.6-square-mile, 3000-acre lake, approximately 4.5 miles long and 1 mile wide, with an average water depth of 36 feet. The lake has two deep basins, a northern basin and a southern basin, that have maximum water depths of approximately

62 and 65 feet, respectively. The basins are separated by a saddle region at a water depth of approximately 56 feet. Most of the lake has a broad, near-shore shelf in water depths of less than 12 feet. This near-shore shelf is bordered by a steep, off-shore slope in water depths of 12–24 feet.

Source: www.dec.ny.gov/chemical/34481.html

Primary Pathway: Human health and benthic

Contaminants: Metals, PAHs, PCBs

Tools Used: Bulk sediment chemistry, pore-water chemistry, toxicity testing, macroinvertebrate surveys, tissue chemistry, bioaccumulation/bioassay

Methods: Bioavailability was used in the form of bioaccumulation pathway analysis for mercury to address the risk to wildlife and humans from consumption of contaminated fish. To the extent that acute toxicity test reflect bioavailability, PRGs were developed based on site-specific SECs for the most sensitive species tested.

How Bioavailability Was Used: Separate PRGs based on site-specific SECs were developed for benthic, wildlife, and human health protection.

Toxicity Testing: Acute sediment toxicity testing procedures (which imply but do not directly measure bioavailability) using benthic macroinvertebrates (*Hyalella azteca* and *Chironomus tentans*) were used to establish PRGs for COCs (metals [including mercury], aromatics, chlorinated benzenes, PAHs, and PCBs). *C. tentans* were found to be the more sensitive test, and acute toxicity data were used to develop the five site-specific SECs that included ER-L, TEL, ER-M, PEL, and AET. From the geometric mean of these five SECs, a single consensus-based PEC was calculated for each contaminant. The SECs and PECs do not consider the potential effects that could occur throughout the food web as a result of bioaccumulation. However, bioaccumulation is considered in the development of PRGs for fish tissue and for a sediment quality value for mercury.

Bioaccumulation: Mercury in fish is derived from a combination of food sources such as benthic macroinvertebrates, uptake from the water column through skin or gills, and incidental intake of suspended particles in the water column. Together, these exposure pathways result in the bioaccumulation of mercury in fish. To address the risk to wildlife and humans from consumption of contaminated fish, a bioaccumulation sediment quality value (BSQV) was developed for this contaminant, based on the most sensitive ecological receptor for assessing bioaccumulation.

Comments: The ROD can be viewed at www.dec.ny.gov/chemical/34481.html. The sediment PRG is based on five site-specific SECs and one consensus-based PEC for the chemicals of potential interest evaluated in the RI and risk assessments. The SECs and PECs were calculated using data from acute sediment toxicity testing using benthic macroinvertebrates. To evaluate sediment quality in Onondaga Lake, toxicity of the sediment to sediment-dwelling (benthic) invertebrates was tested. Laboratory tests involved exposing the midge *C. tentans* and the amphipod *H. azteca* to Onondaga Lake sediments and observing their growth and survival. Since the results for *C. tentans* were found to be the more sensitive test, these acute toxicity data were then used to develop the following five site-specific SECs:

- Effects range-low—The concentration that represents the lowest 10th percentile of the concentrations at which toxic effects were observed. At concentrations below the ER-L, toxic effects are rarely expected.
- Threshold effects level—The geometric mean of the concentration that represents the lowest 15th percentile of the concentrations at which toxic effects were observed and the 50th percentile (median) of the concentrations at which no toxic effects were observed. At concentrations below the TEL, toxic effects are rarely expected.
- Effects range-median—The concentration that represents the 50th percentile (median) at which toxic effects were observed. At concentrations above the ER-M, toxic effects are likely to occur.
- Probable effects level—The geometric mean of the ER-M and the 85th percentile of the concentration distribution for the no-effects data. At concentrations above the PEL, toxic effects are likely to occur.
- Apparent effects threshold—The concentration of a chemical in sediment above which a particular toxic effect (e.g., increased mortality or decreased biomass) is always significant compared to reference concentrations. At concentrations above the AET, toxic effects are predicted to always occur.

The geometric mean of these five Onondaga Lake SECs was calculated to provide a single consensus-based PEC for each contaminant. At concentrations above the PEC, adverse effects in sediments are expected to frequently occur. The derivation of these site-specific values is presented in the Onondaga Lake baseline ERA. SECs and PECs were calculated for each of the chemicals of potential interest in the baseline ERA. For mercury, the following SEC values were calculated: 0.51 mg/kg for ER-L, 0.99 mg/kg for TEL, 2.8 mg/kg for ER-M, 2.84 mg/kg for PEL, and 13 mg/kg for AET. Based on these five SECs, the PEC for mercury is 2.2 mg/kg. As discussed in the baseline ERA, the SECs and PECs do not consider the potential effects that could occur throughout the food web as a result of bioaccumulation. However, bioaccumulation is considered in the development of PRGs for fish tissue and for a sediment quality value for mercury.

<u>Bioaccumulation</u>: The mercury in fish is derived from a combination of food sources such as benthic macroinvertebrates, uptake from the water column through skin or gills, and incidental intake of suspended particles in the water column. Together, these exposure pathways result in the bioaccumulation of mercury in fish. To address the risk to wildlife and humans from consumption of contaminated fish, a BSQV was developed for this contaminant; the BSQV of 0.8 mg/kg represents a concentration in sediments that, if not exceeded, is predicted to result in mercury concentrations in fish below levels of concern for wildlife that consume fish. The

selected BSQV for mercury of 0.8 mg/kg was based on the most sensitive ecological receptor for assessing bioaccumulation. This value is expected to be protective of other ecological receptors and adult human consumers of fish.

D-24. OPERABLE UNIT 1, MARINE CORPS AIR STATION, NORTH CAROLINA

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Commissioned in 1942 as Cunningham Field, Marine Corps Air Station (MCAS) Cherry Point is located in southeastern Craven County, North Carolina. The installation covers approximately 13,164 acres on a peninsula north of the Core and Bogue Sounds and south of the Neuse River. The station's primary mission is to maintain and operate support facilities and services to the 2nd Marine Aircraft Wing, Naval Aviation Depot, and Naval Hospital.

Environmental impacts at the site stem from past waste disposal and storage practices of industrial chemicals, waste, and fuels. These past practices at MCAS Cherry Point have resulted in several contaminated groundwater plumes and soil contamination from numerous smaller waste-disposal units.

Primary Pathway: Benthic

Contaminants: Organics, metals

Tools: Bulk sediment chemistry, toxicity testing, benthic community surveys, tissue chemistry, bioaccumulation

Methods: Used amphibian and invertebrate sediment toxicity test and used data for the most sensitive (invertebrate) to set cleanup level. The amphibian test was cost-effective in reducing the uncertainty and showing amphibians not at risk.

How Bioavailability Was Used: Amphibians were unaffected in 10-day exposures and determined to be not at risk. Data for the more sensitive invertebrate (midges) effects was used to set cleanup level.

Comments: The COCs are mixed contamination (metals, organics). Toxicity identification evaluation tests were not performed; therefore, the toxicity tests would represent exposure to mixed contamination. Amphibians were considered because they are present at the site and are important ecological receptors. Northern leopard frog tadpoles were used in the amphibian studies and are expected to have similar sensitivity to southern leopard frogs, which are more prevalent in the study area. Other than toxicity data, it is unclear what method was used to measure/calculate bioavailability (i.e., BCF, BAF, BSAF, SEM/AVS). However, on follow-up, respondent noted that usually SEM/AVS is a typical component of Navy ERAs.

D-25. PEARL HARBOR SEDIMENT, HAWAII

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Primary Pathway: Benthic, human health, fish and water-column invertebrates, birds

Contaminants: Metals, PCBs, PAHs, chlorinated pesticides

Tools Used: Bulk sediment chemistry, tissue chemistry, pore water, toxicity tests, benthic community surveys, bioaccumulation/bioassay, BSAFs, surface-area weighted-average concentration, GIS-based kriging interpolation

Methods: The relationship between sediment and benthic receptors was used in the risk assessment. Sediment, tissue chemistry, surface-weighted average concentration, and GIS-based kriging were used to delineate areas for further consideration in the FS stage.

How Bioavailability Was Used: AVS-SEM analysis was used to evaluate metal bioavailability in the RI Addendum. A cleanup level has not been established yet; it is still in the RI stage.

Regulatory and Stakeholder Challenges: The project is still in the RI stage, so no cleanup levels have been established. Updated bioavailability was evaluated using collocated sediment and tissue chemistry in the RI Addendum, using linear fit relationships between TOC-normalized sediment and lipid-normalized tissue data. Cleanup levels will be developed in the FS stage based on risks to human health, ecological receptors, and background. See www.epa.gov/waterscience/pc/csnews/csnews18.html.

D-26. PHILADELPHIA RESERVE BASIN, PENNSYLVANIA

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Site Description: The Philadelphia Naval Reserve Basin at the Philadelphia Naval Business Complex is a mooring basin used for inactive Navy vessels. The basin opens to the Schuylkill River 0.5 km north of the confluence of the Schuylkill and Delaware Rivers and serves as a moorage for the Navy’s inactive ships. A history of industrial use has led to the investigation of possible ecological impacts due to pollutant releases from Navy operations. Concurrently, the Navy mission required deepening of the basin to allow deeper draft vessels to be accommodated by April 2008. Hence, an additional focus of the study was to address the navigation dredging requirements.

Primary Pathway: Human health, benthic, wildlife, pelagic

Contaminants: Metals (copper), PCBs, PAHs

Tools: Bulk sediment, pore-water, and tissue chemistry; SEM/AVS; macroinvertebrate survey; bioaccumulation tests; sediment toxicity test

Methods: Used SEM/AVS to predict metals availability. Presence of PCBs in fish tissue was used as an indicator of its bioavailability.

How Bioavailability Was Used: Bioavailability used as a line of evidence in determining contaminant risk at sampling stations. The bioavailability study influenced and demonstrated the need for the development of an ecology-based inorganic (copper) cleanup goal and the human health-based organic (PCBs) cleanup goal. Fish tissue was collected as an indirect measure of bioavailability, and site-specific information was used in the human health risk assessment, which was used to develop the cleanup goal.

Comments: The bioavailability study influenced and demonstrated the need for the development of an eco-based inorganic (copper) cleanup goal. The same could also be said for the human health–based organic (PCBs) cleanup goal. We collected fish tissue as part of the study (indirect measure of bioavailability), and site-specific information was used in the HHRA, which was used to develop the cleanup goal. Bioavailability was used as a line of evidence in determining the risk of sampling stations.

The metals partitioning and bioavailability study assessed dissolved and particulate phases of metals in elutriates prepared from Reserve Basin sediments to describe differences with respect to water-quality criteria. This information provided a more detailed evaluation of the reduction in ecological risks afforded by removing sediments with concentrations greater than the PRGs. Results indicated that elutriate preparations had greater dissolved-metal concentrations than occurs in situ from sediments to pore water. Therefore, risk conclusions based on elutriate preparations are likely conservative with respect to predictions of in situ solubility and toxicity from copper in Reserve Basin sediments.

Bioavailability of copper was further investigated in light of seasonal AVS concentrations. AVS can sequester divalent metals such as copper and is therefore compared to SEM concentrations; an excess of AVS with respect to SEM indicates potential for divalent metals to be bound in the sulfides and unavailable to ecological receptors. Results indicated seasonally (spring) low AVS may be insufficient to completely sequester metals in the sediment, contributing to increased pore-water concentrations and potential for toxic effects. Results helped justify the derivation of the PRG for copper to protect ecological receptors.

Some of the measures we took at this site can be viewed as costly to some people; often this is the type of data that we need to collect at complex sediment sites to ensure that we are following Navy policy and guidance.

D-27. PORTLAND HARBOR, OREGON

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Site Description: Portland Harbor is a heavily industrialized stretch of the Willamette River north of downtown Portland, Oregon, that was listed on the National Priorities List in December 2000. Sediments in the river are contaminated with various toxic compounds, including metals, PAHs, PCBs, chlorinated pesticides, and dioxin. Levels of these pollutants in the river appear to be highest near contaminated sites that sit adjacent to the river on the shore (often referred to as “upland” sites). Contaminant sources include petroleum refining, gas manufacturing, pesticide manufacturing, steel production, port activities including dry-dock operations, storm-water runoff, and many other current and historical industrial activities.

Primary Pathway: Benthic, pelagic, human health, wildlife

Contaminants: Dioxins and furans, PCBs, pesticides, PAHs, total petroleum hydrocarbons, metals, tributyltin

Tools Used: Bulk sediment chemistry; surface-water, pore-water and benthic/pelagic tissue chemistry; toxicity testing. Clam tissue was collected from the site and analyzed with co-located sediment. In addition, 28-day bioaccumulation testing with the oligochaete *Lumbriculus variegates* and the clam *Corbicula fluminea* were undertaken for several areas of concern within the study area. Crayfish whole-body tissue was also analyzed at many locations. Several species of fish were analyzed, including sculpin, smallmouth bass, black crappie, peamouth, northern pike minnow, large-scale sucker, carp, juvenile Chinook salmon, Pacific lamprey ammocoetes, and juvenile white sturgeon to provide empirical measures of bioaccumulation and exposure for different receptors areas of the site.

Methods: It is anticipated that BSAFs will be developed using the data. For the benthic pathway the principal responsible parties have developed a predictive toxicity model that characterizes the relationship between sediment chemistry and benthic invertebrate toxicity. For some species, a site-specific Gobas model was developed to predict tissue concentrations.

How Bioavailability Was Used: This site consists of several different sites that are physically distinct from one another in terms of bioavailability and COCs. Therefore, cleanup levels for benthic risk will likely consider empirically derived estimates of toxicity along with predictive models. For bioaccumulative COCs, a food web model was used to back-calculate initial sediment PRGs. Cleanup levels have not yet been set.

Regulatory and Stakeholder Challenges: This is a large CERCLA site and is still in the RI phase. See the following link for site status and updates: www.deq.state.or.us/lq/cu/nwr/portlandharbor/index.htm. See the following link for more information about the benthic toxicity testing: http://yosemite.epa.gov/R10/OEA.NSF/af6d4571f3e2b1698825650f0071180a/100a7a3d5fe2ebf388256c78007a66bb?OpenDocument

D-28. PRIVATE RESIDENCE IN PENNSYLVANIA

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Primary Pathway: Benthic

Contaminants: VOCs, PAHs

Tools Used: Bulk sediment chemistry and screening values, followed by a bioassessment evaluation possibly using RBA protocol

Methods: Temporal trends of the bioassessment survey were used to determine whether additional cleanup was necessary. This was a release with some cleanup following the release.

How Bioavailability Was Used: Direct bioavailability measurements not used in cleanup level. COPCs assessed for bioavailability are #2 heating oil compounds, specifically, benzene, toluene, ethyl benzene, cumene, naphthalene, fluorene, and phenanthrene. Surface-water and sediment samples were collected during the course of this investigation. The surface-water analytical results were compared of our Chapter 16 surface-water quality standards. Sediment results were compared to the NOAA SQuiRT table TEL/PEL values as well as the USEPA assessment and remediation of contaminated sediments TEL/TEC values. Since the surface-water and sediment samples exceeded several of their respective standards/screening values, an ecological assessment of the stream was completed by a qualified biologist on two occasions. These investigations monitored the diversity and quantity of benthic macroinvertebrate species as well as signs of impacts from #2 fuel oil (sheen, free product, etc.). Ultimately the final decision concerning the status of the stream/sediments was based on observations of the overall health of the stream. Due to the size and nature of the stream, it was determined that remediation beyond the initial response activities would be more detrimental than allowing the remaining fuel oil to attenuate naturally. Initially, the stream was determined to be “moderately impaired.” Within a year, however, the stream had rebounded to “nonimpaired” status. Under Kansas Act 2 program, all of the exposure pathways must be addressed, including impacts to the critters, ecology, humans, etc.

D-29. SODA LAKE, WYOMING

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Site Description: The Soda Lake Area RFI focused on identifying the extent and nature of impacts in soil, groundwater, surface water, and sediments in both the Inlet Basin and Main Lake. The purpose of the sediment and pore-water investigations was to define the nature and extent of former refinery-related COIs in the Inlet Basin and Main Lake. The lines of evidence used for the evaluation included screening media concentrations against conservative surface-water, sediment, pore-water, and phytotoxicity screening levels. Additional lines of evidence included modeling of PAHs and mercury bioaccumulation, total PAH toxicity using narcotic toxicity and OC normalization, and evaluation of sediment bioassays.

Primary Pathway: Benthic, pelagic, wildlife

Tools: Bioassays, bulk sediment chemistry, trophic modeling, pore-water and tissue chemistry

Methods:

Sediment Screening Level Evaluation

- Organic COIs detected in surface and subsurface sediments included pyrene, benzene, chrysene, phenanthrene, benzo(a)anthracene, fluoranthene, naphthalene, total xylenes, and phenol. Phenol was the only organic compound present that exceeded benthic ecological high screening criteria. All other detected organic COIs exceeded the benthic low screening criteria only, and the stations that exhibited these compounds were further tested using solid-phase bioassay tests.
- Metal COIs detected in Main Lake sediment included arsenic, cadmium, chromium, mercury, nickel, and zinc. Cadmium, chromium, nickel, and zinc concentrations exceeded the benthic ecological low screening criteria. Metals that exceed the ecological low screening criteria did not show a pattern consistent with a refinery source, indicating these metals are of natural origin.
- COIs present in pore water included acetone, phenol, carbon disulfide, arsenic, antimony, manganese, selenium, silver, and vanadium. Acetone is believed to be a laboratory artifact. As discussed above, the metal distribution was ubiquitous throughout the lake; metals are of natural origin.

Solid-Phase Bioassay Testing was conducted to measure acute and subchronic toxicity of surface sediments. In addition, pore-water chemical testing was conducted on those stations that underwent bioassay testing. Low-level toxicity and nonrecurring toxicity in some samples were observed and could be related to laboratory artifacts and procedures.

- Bioassays were conducted on surface-sediment stations to further evaluate risk to benthic and epibenthic organisms. There was no consistency between the stations where chemical data exceeded screening levels and where the bioassays showed potential effects. Low-level toxicity and nonrecurring toxicity were observed in some samples and could be related to laboratory artifacts and procedures.
- There were differences between the control bioassays when compared to bioassays from site sediments; the bioassay data indicate there are no acute risks and negligible subchronic risk to benthic and epibenthic organisms near the underflow weir. Chronic risks were not evaluated.

Benthic and Epibenthic Community Evaluations: Organisms were evaluated for growth in the site sediments compared to control sediments, and the comparison was indeterminate. However, growth was observed in the area of potential impact indicating population growth and survival.

- Quantitative benthic community surveys within the Main Lake showed low diversity but high abundance. Low diversity was believed to be attributed to poor-quality habitat (low oxygen, high ammonia, and sulfide content of sediment).
- Qualitative assessments of epibenthos showed a rich and diverse assemblage, including sensitive *Odonata*, *Ephemeroptera*, *Plecoptera*, in addition to the daphnids, copepods, and amphipods described above.

Equilibrium Partitioning Evaluations

- Site total PAHs were evaluated relative to OC-normalized total PAH threshold effects criteria (Swartz 1999) and showed no exceedances.
- Probability modeling was conducted and demonstrated that there were negligible risks to benthic invertebrates from sediment PAH in the Main Lake, based on a "worst-case" analysis.
- Total and alkyl PAHs were evaluated relative to USEPA's narcotic toxicity criteria, when a conservative estimate (factor of 16) of unmeasured, alkyl PAHs was included. Only one location exceeded the toxicity criteria, based on nondetected data with an elevated detection limit.

How Bioavailability Was Used: Bioavailability measures were used to show selenium is not in the bioactive zone and is not migrating up the food chain. The data show that COIs are present in the Main Lake sediments and pore waters. The results of the toxicity testing of Main Lake sediments suggest that there is negligible to no acute or subchronic toxicity of the Main Lake sediments to the test organisms. The lines of evidence indicate there is negligible to no risk to aquatic invertebrates based on risk evaluations, which is also supported by the presence of epibenthic and benthic invertebrates. For the Main Lake, multiple lines of evidence approach contributed to the selection of NFA as the site remedy. A copy of the remedy decision can be found at http://deq.state.wy.us/shwd/HW/Downloads/fact%20sheets/2012/RD3final011002.pdf.

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D-30. FORMER SPRINGFIELD GAS WORKS, MASSACHUSETTS

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Site Description: The former Springfield Public Works Facility, located at 274 Taylor Street, consisted of six buildings on 5.6 acres of land. The brick masonry buildings, owned by the City of Springfield, were constructed between 1907 and 1923 and were used for storage, painting, vehicle maintenance, and offices. Prior to its use as a public works facility, the land hosted a variety of uses during the 1800s, including housing, coal sheds, an asphalt-mixing plant, and railroad facilities belonging to the New York and North East Railroad. Sanborn maps (digital maps) indicate that the city operated a wagon shed and carriage house on the property during the late 1800s. The entire property was used by the Springfield Department of Public Works 1924–1999, when all of the buildings were demolished.

Primary Pathway: Benthic

Contaminants: PAHs

Tools Used: Bulk sediment chemistry, pore-water chemistry (using SPME), and toxicity testing.

Methods: Chemical measurement of total dissolved PAHs was used as a predictor of PAH bioavailability.

How Bioavailability Was Used: In progress—the principal responsible party plans to use bioavailability data to proposed flexibility in interpreting visible harm and readily apparent harm to focus remediation on areas that pose actual threats to the environment.

Comments: The State of Massachusetts thinks that pore water is a better indicator than bulk sediments, and that is what it was primarily focusing on.

D-31. FORMER GENERAL MOTORS NORTH TARRYTOWN ASSEMBLY PLANT, NEW YORK

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Primary Pathway: Benthic

Contaminants: Chromium, copper, lead, mercury, zinc

Tools: Bulk sediment chemistry, SEM/AVS, pore water, benthic community survey, tissue chemistry, toxicity testing, bioaccumulation tests, sediment toxicity test

Methods: Sediment chemistry exceeded New York screening levels, triggering latest round of testing. Cleanup level will be established after current round of testing is completed.

How Bioavailability Was Used: Cleanup levels are not yet established pending latest round of testing. The samples collected will help get to that point. Data collected included SEM/AVS, pore water, benthic community survey, bioaccumulation (clams/mussels, where they were encountered during sampling), sediment toxicity.

Regulatory and Stakeholder Challenges: AVS typically might be compared to the sum of five SEMs (cadmium, copper, nickel, lead, zinc). However, the respondent indicated through follow-up that nickel was not a COC at the site and thus would not have been included in any AVS comparisons. Mercury was listed as a COC, but according to respondent, bioavailability for mercury was not assessed.

D-32. TECTRONIX BEAVERTON CREEK, WASHINGTON COUNTY, OREGON

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Regulatory Agency: Oregon DEQ

Site Description: Oregon DEQ is overseeing investigation and remediation of the Tektronix Beaverton Creek site. A portion of the property undergoing investigation includes the location of the former RCRA treatment, storage, and disposal unit located adjacent to an urban stream. An investigation of sediment in Beaverton Creek was done to refine a remedial alternative presented in the feasibility study.

Beaverton Creek is a channelized, fourth-order urban stream that flows east to west through the southern portion of the property. The creek enters the site after flowing through residential neighborhoods and, after leaving the site, flows through a commercial area before flowing into the Tualatin Hills nature park located about ½-mile downstream, and eventually discharges to the Tualatin River.

Historic operations at the Tektronix, Inc., Beaverton campus included management of process chemicals, chemical treatment, metal recovery, and process waste. Sludge was generated as a result of waste management and was land-applied at various locations around the campus. These historic practices resulted in releases to Beaverton Creek and elevated concentrations of metals that have been measured in sediments during the site RI.

Based on elevated concentrations of metals in sediment, it was initially presumed that remedial action would be required. However, planning for sediment remedial action demonstrated a variety of complexities. Metals were detected at elevated concentrations in sediment throughout the stretch of Beaverton Creek flowing through and downstream of the site, as well as in stream bank soil, suggesting wide-scale remediation might be required. In addition, implementation risk associated with resuspending sediments and potentially mobilizing contaminants that might subsequently be transported toward the Tualatin Wildlife Refuge was an issue associated with removal. ODEQ recommended further, more detailed consideration of toxicity and bioavailability of contaminants as a means to refine the scope of any potential remedial action in sediment.

Primary Pathway: Benthic

Contaminants: Cadmium, copper, chromium, lead, mercury, nickel, silver, zinc

Tools: Bulk sediment chemistry, AVS-SEM, and bulk sediment toxicity bioassays

Methods: The bioavailability and sediment toxicity study consisted of two primary, sequentially implemented elements of investigation: First, additional sediment samples were collected for analytical chemistry, including bulk sediment metals concentrations and measurement of AVS and SEM as metrics that could be related to the bioavailability, and hence potential for toxicity. Second, toxicity tests were performed in a subset of these samples based on consideration of the potential for toxicity as measured by AVS-SEM, total metals, and spatial representativeness throughout the relevant stretch of Beaverton Creek.

How Bioavailability Was Used: Sediment samples for analytical chemistry were collected at 20 locations throughout the study reach, and two upgradient reference samples. Two toxicity tests, the 10-day mortality sediment toxicity test with the amphipod *Hyalella azteca* and the 10-day growth and mortality sediment toxicity test with the midge *Chironomus dilutus*, were performed on 13 surface sediment samples collected at a subset of 11 locations within the site and at the two upstream locations. Average bulk sediment concentrations measured in 2007 were similar to those measured in the 2004 sampling event, although the spread or range in values was narrower than those collected in 2004.

According to USEPA guidance, the sum of the molar concentrations of SEM cadmium, copper, lead, nickel, silver, and zinc may be used as a predictor of potential toxicity. The USEPA guidelines state that benthic organisms in freshwater sediments should be adequately protected if the sum of the molar concentrations of SEM cadmium, copper, lead, nickel, silver, and zinc is less than or equal to the molar concentration of AVS (i.e., SEM – AVS < 1).

As a second metric, the presence of OC was considered along with AVS, and the SEM – AVS difference was normalized by the f_{oc} in sediment. Again, according to USEPA guidance, any sediment for which the SEM – AVS difference normalized by the f_{oc} is <130 μmol/g_{oc} should pose low risk of adverse biological effects. For any sediment where the SEM – AVS difference normalized by the f_{oc} is >3000 μmol/g_{oc}, adverse biological effects resulting from cadmium, copper, lead, nickel, silver, and zinc may be expected.

As measured by these evaluative criteria, the sediment results indicated a low potential toxicity but did not clearly rule out potential for toxicity in most samples. Therefore, follow-up toxicity testing was performed.

Toxicity Testing: Based on interpretive criteria currently in use, none of the sediment samples had an adverse effect on amphipods or midges based on the *H. azteca* mortality endpoint or *C. dilutus* growth endpoint. Based on the C. *dilutes* mortality endpoint, a few of the samples did show a weak response. Using the RSET and USEPA interpretive criteria, the results did not appear to be attributable to any measure of metals in the sediments.

In summary, the bulk sediment chemistry data indicated exceedances of screening criteria. Additional measures of bioavailability were collected and suggested an overall low potential for toxicity. Toxicity testing performed to validate and further clarify this prediction indicated no toxicity that could be related to any measured sediment metal concentrations. Therefore, it was concluded that site sediments do not pose risks to benthic organisms and sediment remediation was deemed unnecessary.

D-33. TRI-STATE MINING DISTRICT, KANSAS

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Regulatory Agency: USEPA

Site Description: The Tri-State Mining District lies in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma. For nearly 50 years, it was the world's richest producer of lead and zinc ores. More importantly, it was located next to the coalfields of southeastern Kansas. Coal was essential for smelting, the process of removing spelter—metallic zinc—from ore. The first zinc smelter in Kansas was built in Wier City in 1870.

Primary Pathway: Benthic

Contaminants: Cadmium, lead, zinc

Tools Used: Bulk sediment chemistry, pore-water chemistry, toxicity test (using mussels and clams)

Methods: Toxicity testing using site-collected sediment and pore water

How Bioavailability Was Used: A cleanup level is planned to be calculated based on sediment and pore-water concentrations that correspond to a 10%–20% nonsurvival rate for benthic organisms (clams and mussels).

Comments: The work plan will be completed soon and the USEPA Remedial Project Manager (David Drake, 913-551-7626, drake.dave@epa.gov) will provide when finalized.

D-34. VANDENBERG AIR FORCE BASE (AFB), SITE 5 CLUSTER (BEAR CREEK POND)

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Site Description: Installation Restoration Program (IRP) Site 5 Cluster includes Bear Creek Pond, a freshwater emergent/aquatic habitat covering approximately 15 hectares. This habitat consists of Bear Creek Pond and a portion of lower Bear Creek, an ephemeral creek. Although the pond is generally undisturbed, it is downgradient of and receives surface-water runoff from the formerly active launch pads at IRP Sites 5 (Space Launch Complex 3 East) and 6 (Space Launch Complex 3 West). Potential sources of contamination include chlorinated solvents and metals from sandblast grit. Metals were investigated as primary sources of risk in sediments of Bear Creek Pond. The frequency of inundation, duration, and depth of surface water in the pond vary from year to year; during some years the pond contains little or no water. In some years, Bear Creek Pond provides potentially suitable habitat for a variety of wildlife, including benthic and aquatic invertebrates, amphibians, and shorebirds. Several metals in pond sediments were initially predicted to pose potential risks to benthic invertebrates. However, sediment bioassays did not provide any evidence of adverse impacts to invertebrates. These results indicate that there is a negligible risk to benthic invertebrates at Bear Creek Pond as compared to ambient conditions.

Primary Pathway: Benthic

Contaminants: Metals

Tools Used: Bulk sediment chemistry, toxicity testing

Methods: Eight sediment samples were collected for sediment toxicity bioassays. Ten-day survival and growth bioassays using the amphipod *Hyallela azteca* were performed on four sediment samples from Bear Creek Pond and four upstream reference locations. These bioassays did not show any adverse effects to the test species in comparison to reference sediments collected from upgradient areas of Bear Creek. These results were supported by bulk sediment chemistry analyses, which included AVS analysis.

How Bioavailability Was Used: Bioavailability was indirectly assessed by toxicity testing. These sediment bioassays indicated that there is a negligible risk to benthic invertebrates at Bear Creek Pond as compared to ambient conditions. In addition, AVS analyses indicated that metals in site-specific sediments likely exhibit limited bioavailability.

Reference: Tetra Tech, Inc. 2002. "Results of Sediment Bioassays Performed for the Site 5/7 Sediment Bioassay Focused Feasibility Study, Vandenberg Air Force Base, California." Letter to

Capt. Sean O’Brien, Department of the Air Force, HQ AFCEE/ERD, Brooks Air Force Base, Texas, 28 March.

D-35. WASHINGTON NAVY YARD, D.C.

Stephen Geiger, 703-297-9118, steve.geiger@aecom.com

Site Description: The Washington Navy Yard (WNY) opened officially in 1799, and ship building and repair operations were ongoing by 1822. During the 1800s, ordnance production, research, and other industrial activities were prevalent at the yard. In 1886, the WNY was redesignated as the Naval Gun Factory. During the next 20 years, considerable expansion of the WNY occurred, and production of ordnance remained the primary operational activity at the facility during this time. Significant areas of adjacent marshlands were filled to accommodate the WNY.

Wastes generated at the site include metals used in ordnance production and paint-spraying, solvents use in cleaning, cyanide and phenols use in the cooling process, creosote used in wood treatment, petroleum products and wastes, and PCB-containing oils in storage tanks and electrical equipment. Contamination also likely occurred during storage and handling of raw materials. Sediment sampling of the river showed elevated concentrations of PAHs. The WNY is on the National Priorities List as a hazardous waste site.

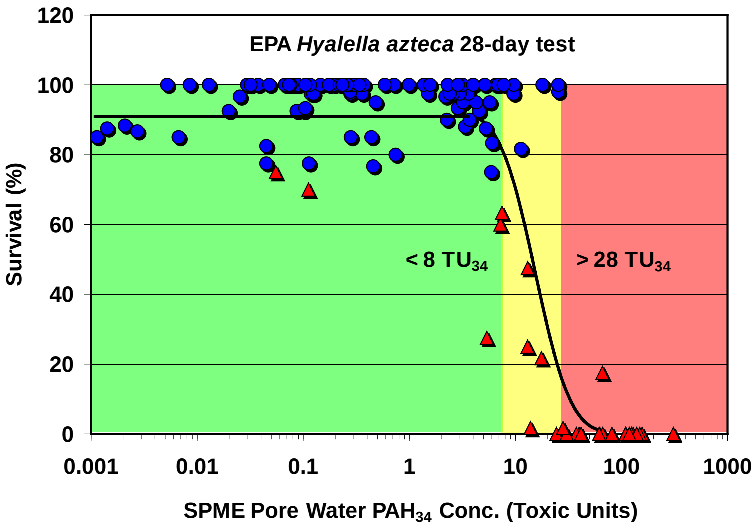
A field demonstration was conducted under Environmental Security Technology Certification Program (ESTCP) to assess the applicability of using a direct method of analyzing PAHs in sediment pore water as a robust method of evaluating the bioavailability of PAHs to benthic invertebrates.

Primary Pathway: Benthic

Contaminants: PAHs

Tools: Bulk sediment chemistry, direct analysis of pore-water chemistry using SPME, and benthic invertebrate toxicity testing

Methods: USEPA provides a tiered conceptual approach for evaluating the bioavailability of PAHs to benthic invertebrates in the document *Evaluating Ecological Risk to Invertebrate Receptors from PAHs in Sediments at Hazardous Waste Sites* (Burgess 2007). This demonstration project estimated the bioavailability of sediment PAHs using the USEPA's tiered approach. The first tier was the comparison of total PAH concentrations to sediment quality thresholds (threshold and probable effects levels) as well as estimating PAH pore-water concentrations using EqP and then comparing the estimated pore-water concentrations to biota-specific effects concentrations (FCVs). The second tier compared pore-water PAH concentrations that were directly analyzed using SPME (USEPA SW-846 Method 8272/ASTM Method D-7363-07) and comparing these to the FCVs. The third tier was aquatic toxicity testing using a surrogate benthic invertebrate *Hyalella azteca*.



How Bioavailability Was Used: The sediment quality thresholds overestimated the toxicity of the sediments when compared to the results of the aquatic toxicity tests, indicating that the use of these thresholds alone would have resulted in an incorrect decision. The use of EqP also overestimated the toxicity of the sediments (i.e., TUs were all >1 although only one sample was toxic to *H. azteca*). The SPME direct analysis of pore water method accurately predicted the results of the aquatic toxicity tests (i.e., TUs <1 where there was no toxicity to *H. azteca*, and TUs >1 where there was toxicity).

Comments: The demonstration results agree with those from other field sites (mostly manufactured gas plants and smelter sites), which show that the use of total PAH concentrations does not accurately reflect the bioavailability of PAHs when anthropogenic carbon is present and that a direct pore-water analysis method is a better and more accurate option for evaluating PAH bioavailability to benthic organisms in industrial/urban waterways.

Appendix E

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Appendix F

Glossary

GLOSSARY

background (reference conditions). When used in sediment characterization studies, refers to both the concentrations of COPC that are not a result of the activities at the site undergoing assessment and the locations of the background areas (MacDonald and Ingersoll 2002). Therefore, there are two types of background recognized by USEPA and many states: naturally occurring background and anthropogenic background. Users should verify whether their state and/or USEPA region has different definitions and requirements for assessing background conditions as part of environmental site assessments.

bioaccessible. Describes the fraction of a chemical that desorbs from its matrix (e.g., soil, dust, wood) in the gastrointestinal tract and is available for absorption. The bioaccessible fraction is not necessarily equal to the relative bioavailability but depends on the relation between results from a particular in vitro test system and an appropriate in vivo model.

bioaccumulation factor (BAF). The ratio of COPC in tissue to the COPC concentration in an external environmental phase (i.e., water, sediment, or food) (Spacie, Mccarty, and Rand 1995). The BAF is typically assumed to be measured or expressed on a steady-state basis. For applications to the water phase, the BAF is best determined from field data where sampled organisms are exposed to chemical measured in the water and their diet. For applications in reference to the sediment and food phases, the BAF is expressed using concentrations in the tissue and environmental phase on a wet weight basis or dry weight basis, i.e., (µg/g of ww tissue)/(µg/g of ww food), (µg/g of dw tissue)/(µg/g of dw food), and (µg/g of dw tissue)/(µg/g of dw sediment). This definition of BAF is used for metals, organometallic compounds, and organic compounds.

For clarity, the BAF is expressed with the units in subscripts. For the concentration in the tissue phase, the numerator (N subscript) is the basis of the tissue phase (L for lipid-normalized, WW for wet weight, and DW for dry weight bases). For the environmental phase, the denominator (D subscript) is the basis for the water (FD for freely dissolved, T for total, and D for dissolved/filtered water), food (WW for wet weight and DW for dry weight), or sediment (WW for wet weight, and DW for dry weight) phases. Some commonly used BAF expressions are as follows:

- $BAF_{L/FD}$ = where concentrations in tissue and water are on a lipid and freely dissolved basis, respectively
- $BAF_{WW/T}$ = where concentrations in tissue and water are on a wet weight and total basis, respectively
- $BAF_{DW/DW}$ = where concentrations in tissue and sediment are both on a dry weight basis

bioavailability. The relationship between external (or applied) dose and internal (or resulting) dose of the chemical(s) being considered for an effect (NRC 2003).

bioavailability processes. Individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments (NRC 2003).

bioconcentration factor. The ratio of the steady-state COPC concentration in an aquatic organism (CB) and the COPC concentration in water (C_W) determined in a controlled laboratory experiment where the test organisms are exposed to chemical in the water (but not the diet). In the subscript, the numerator (N) is the basis of the tissue phase (L for lipid-normalized, WW for wet weight, and DW for dry weight bases) and denominator (D) is the basis for the water phase (FD for freely dissolved, T for total, and D for dissolved/filtered water). Commonly used BCF expressions are as follows:

- $BCF_{L/FD}$ = where concentrations in tissue and water are on a lipid and freely dissolved basis, respectively
- $BCF_{WW/T}$ = where concentrations in tissue and water are on a wet weight and total basis, respectively
- $BCF_{DW/T}$ = where concentrations in tissue and water are on a dry weight and total basis, respectively

biomagnification factor (field based). The ratio of the chemical concentrations in an aquatic or terrestrial organism (CB) and in the diet of the organism (C_D) determined from field-collected animals that are exposed to chemical in air, water and diet. The numerator (N) is the basis of the tissue phase (L for lipid-normalized, WW for wet weight, and DW for dry weight bases) and denominator (D) is the basis for the diet (L for lipid-normalized, WW for wet weight, and DW for dry weight bases). Two commonly used BMF expressions are as follows:

- $BMF_{L/L}$ = where concentrations in tissue and diet are on a lipid basis
- $BMF_{WW/WW}$ = where concentrations in tissue and diet are on a wet weight basis

biomagnification factor (laboratory based). The ratio of the steady-state chemical concentrations in an aquatic or terrestrial organism (CB) and in the diet of the organism (C_D) determined in a controlled laboratory experiment, where the test organisms are exposed to chemical in the diet (but not water or air). In the subscript, the numerator (N) is the basis of the tissue phase (L for lipid-normalized, WW for wet weight, and DW for dry weight bases) and denominator (D) is the basis for the diet (L for lipid, WW for wet weight, and DW for dry weight bases). Commonly used BMF expressions are as follows:

- $BMF_{L/L}$ = where concentrations in tissue and diet are on lipid basis
- $BMF_{WW/WW}$ = where concentrations in tissue and diet are on wet weight basis
- $BMF_{DW/DW}$ = where concentrations in tissue and diet are on dry weight basis

biomimetic device. A diffusion-based sampler that is designed to "mimic" an aquatic organism (e.g., a semipermeable-membrane device is dialysis tubing filled with a purified fish oil like triolein).

biota sediment accumulation factor (BSAF, kg of organic carbon/kg of lipid). Ratio of the chemical concentration in an aquatic organism (CB, in g chemical/kg lipid) and in the sediment from the site where the organism was collected (C_S, in g chemical/kg organic carbon) determined from field or laboratory data: $BSAF = C_B/C_S$.

bulk concentration. In water, the total COPC concentration in a bulk (unfiltered) sample of water (kg of COPC/L of water). In sediment, the total COPC concentration in a bulk sediment sample (kg COPC/kg dry sediment).

carbon normalization. For sediment, dividing a bulk organic COPC concentration (e.g., mg/kg fluoranthene) by the fraction of TOC measured in the same sample (e.g., 0.02 g carbon/ g sediment, or 2% TOC).

contaminant(s) of potential concern (COPC). In a risk assessment, a substance detected at a hazardous waste site that has the potential to affect receptors adversely due to its concentration, distribution, and mode of toxicity (USEPA 1997b). COPCs are generally categorized operationally, i.e., based on how they are measured in the analytical laboratory. "Inorganic" COPCs generally address metals, elements, and unique inorganic compounds such as perchlorate. "Organic" COPCs include VOCs (such as acetone, benzene, trichloroethylene, etc.), SVOCs (such as chlorophenols, chlorobenzenes, phthalate esters, etc.), pesticides (e.g., atrazine, DDT, toxaphene), PCBs, and polychlorinated dibenzodioxin and dibenzofurans.

diffusion sampler. A semipermeable membrane or dialysis tube filled with distilled water or gel, which relies on solute gradient to establish equilibrium between pore water and the sampler.

diffusive flux. A law describing the diffusion that occurs when solutions of different concentrations come into contact with molecules moving from regions of higher concentration to regions of lower concentration. Fick's law states that the rate of diffusion dn/dt, called the "diffusive flux" and denoted J, across an area A is given by $dn/dt = J = -DA\partial c/\partial x$, where D is a constant called the "diffusion constant," $\partial c/\partial x$ is the concentration gradient of the solute, and dn/dt is the amount of solute crossing the area A per unit time. D is constant for a specific solute and solvent at a specific temperature. Fick's law was formulated by the German physiologist Adolf Eugen Fick (1829–1901) in 1855.

diffusive gradient in thin films (DGT). A sampler that is typically filled with a gel that is designed to target a specific compound (e.g., binding of metals).

dissolved concentration. In water, the concentration of COPC in filtered water, traditionally defined as water that will pass through a 0.45 µm filter.

epibenthic. On or above the sediment/water interface.

epifauna. Benthic invertebrates that live almost exclusively on or upon the benthic substrate. The substrate can range from soft silt or clay in a lentic environment to sand, gravel, pebbles, cobble and/or boulders in a lotic environment.

equilibrium partitioning theory. A theory developed in the late 1980s as a means of predicting toxicity of PAHs to sediment-dwelling organisms. It posits that the toxicity to sediment organisms is directly proportional to the amount of unbound PAH dissolved in sediment pore water.

final chronic value. See Section 4.1.3.2.

food-web magnification factor. See *trophic magnification factor*.

freely dissolved. The concentration of the chemical that is freely dissolved in water, excluding the portion sorbed onto particulate and dissolved organic carbon (kg of chemical/L of water). Freely dissolved concentrations can be estimated with an empirical equation with knowledge of the K_{poc} and K_{doc} and can be measured with passive samplers, e.g., POM, SPMD, SPME, and PE.

fugacity. A measure of a chemical potential in the form of "adjusted pressure." It reflects the tendency of a substance to prefer one phase (liquid, solid, or gas) over another and can be literally defined as "the tendency to flee or escape."

fugacity samplers. Polymeric materials inserted into sediment that accumulate hydrophobic organic compounds in proportion to their surface area.

gavage. Introduction of nutritive material into the stomach by means of a tube.

hyporheic zone. A region beneath and lateral to a stream bed, typically where there is an intermixing of shallow groundwater with surface water. This region is generally heterogeneous and difficult to define along the breadth and length of a stream.

infauna. Benthic invertebrates that live almost exclusively in or below the sediment/water interface. These are generally tube- or burrow-dwelling organisms that feed at either the sediment/water interface or burrow and ingest sediments and/or sediment-dwelling organisms.

ligand. Complexing chemical (ion, molecule, or molecular group) that interacts with a metal to form a larger complex (USEPA 2003a).

lipid-normalization. The COPC concentration in tissue (kg of chemical/kg of wet tissue) divided by the concentration of lipid in that tissue (kg of lipid/kg of wet tissue) or the COPC concentration in tissue (kg of chemical/kg of dry tissue) divided by the concentration of lipid in that tissue (kg of lipid/kg of dry tissue).

macroinvertebrate. Any organism that will, after sieving out surface water and fine suspended matter, be retained on a 0.5 mm mesh (No. 35 Standard Sieve) screen.

octanol-water partition coefficient (K_{ow}, unitless). The ratio of a chemical concentration in 1-octanol (C_o) and water (C_w) in an octanol-water system that has reached a chemical equilibrium: $K_{ow} = C_o/C_w$.

organic carbon normalization. See Michelsen 1992.

pore water. Water located in the interstitial compartment (between solid-phase particles) of bulk sediment.

receptor. A plant, animal, or human that is typically the focus of a risk assessment following the direct or indirect exposure to a potentially toxic substance.

reference location (control). An aquatic sediment system unaffected by COPCs which can be used in a baseline comparison of like parameters in a similar contaminated system. See *background*.

resuspension flux. The movement of a contaminant through a liquid (or gaseous media) upon resuspension of contaminated sediments.

screening. The comparison (by ratio, usually the environmental medium concentration divided by a benchmark, standard, criterion, etc.) of site conditions to a screening value. Often this is synonymous with “compare to a list that is readily available.”

sediment quality guideline (SQG). Same as SQV except a guideline is typically issued by a regulatory agency or, in rare cases, promulgated via a state law.

sediment quality objective (SQO). Same as SQV and SQG in some state-specific standards and rules.

sediment quality value (SQV). A numerical (bulk concentration) benchmark below which a lesser adverse effect (or no adverse effect) is anticipated and above which a greater adverse effect is anticipated.

soil screening level. See “Regional Screening Table” at www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm.

stakeholder. Affected tribes, community members, members of environmental and community advocacy groups, and local governments.

sulfhydryl. Thiol is a compound that contains the functional group composed of a sulfur atom and a hydrogen atom (-SH). Being the sulfur analogue of an alcohol group (-OH), this functional group is referred to either as a "thiol group" or a "sulfhydryl group."

toxicity unit. A unit formerly synonymous with "minimum lethal dose" but which, because of the instability of toxins, is now measured in terms of the quantity of standard antitoxin with which a toxin combines. See www.biology-online.org/dictionary/Toxic_unit.

trophic magnification factor, or food-web magnification factor (TMF, or FWMF, unitless). The average factor by which the normalized chemical concentration in biota of a food web increases with each increase in trophic level. The TMF is determined from the slope (m) derived by plotting the logarithmically transformed (base 10) lipid-normalized chemical concentration in biota vs. the trophic position of the sampled biota (as $TMF = 10^m$).

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Appendix G

Acronyms

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ACRONYMS

ABA	absolute bioavailability
AET	apparent effects threshold
AF	accumulation factors
AFB	Air Force Base
ARAMS	Adaptive Risk Assessment Modeling System
ASE	accelerated solvent extraction
ATL	acceptable tissue levels
AVS	acid volatile sulfides
BAF	bioaccumulation factor
BASS	Bioaccumulation and Aquatic System Simulator
BCF	bioconcentration factor
bgs	below ground surface
BLM	biotic ligand model
BMF	biomagnification factor
BSAF	biota-sediment accumulation factor
BSQV	bioaccumulation sediment quality value
CA	cost analysis
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
COI	contaminant of interest
COPC	contaminant of potential concern
COPEC	contaminant of potential environmental concern
CSCL	chemical stressor concentration limit
CSM	conceptual site model
DCE	dichloroethene
DDE	dichlorodiphenyldichloroethene
DDT	dichlorodiphenyltrichloroethene
DEQ	Department of Environmental Quality
DGT	diffusive gradient in thin films
DOC	dissolved organic carbon
DQO	data quality objective
DTPA	diethylenetriaminetetraacetic acid
EcoSSL	ecological soil screening level
EDTA	ethylenediaminetetraacetic acid
EE	engineering evaluation
EMNR	enhanced monitored natural recovery
EPI	Estimation Program Interface
EPT	*Ephemeroptora* (mayflies), *Plecoptera* (stoneflies), and *Trichoptera* (caddisflies)
EqP	equilibrium partitioning
ERA	ecological risk assessment
ERED	Environmental Residue Effects Database
ER-L	effects range low

ER-M	effects range median
ESB	equilibrium sediment benchmark
ESTCP	Environmental Security Technology Certification Program
FCV	final chronic value
FDA	Food and Drug Administration
FGETS	Food and Gill Exchange Transport System
FID	flame ionization detector
f_{oc}	fraction of organic carbon
FS	feasibility study
GC/MS	gas chromatograph/mass spectrometer
GETS	Gill Exchange and Transport System
GIS	geographic information system
HHRA	human health risk assessment
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HOC	hydrophobic organic chemical
HPAH	high-molecular-weight polycyclic aromatic hydrocarbon
HQ	hazard quotient
IBI	index of benthic biotic integrity
ICI	invertebrate community index
IRIS	Integrated Risk Information System
IRP	Installation Restoration Program
ITRC	Interstate Technology & Regulatory Council
K_{oc}	organic carbon–water partition coefficient
K_{ow}	octanol-water partition coefficient
LEL	lowest effects level
LOAEL	lowest observable adverse effects level
LPAH	low-molecular-weight polycyclic aromatic hydrocarbon
MCAS	Marine Corps Air Station
MCB	Marine Corps Base
MET	minimum effects threshold
mgd	million gallons per day
MNR	monitored natural recovery
NAPL	nonaqueous-phase liquid
NFA	no further action
NFESC	Naval Facilities Engineering Service Center
NJDEP	New Jersey Department of Environmental Protection
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observable adverse effects level
NRWQC	national recommended water quality criteria
OC	organic carbon
ODEQ	Oregon Department of Environmental Quality
ORNL	Oak Ridge National Laboratory
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PBT	persistent, bioaccumulative, and toxic

PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PCE	tetrachloroethene
PCP	pentachlorophenol
PDMS	polydimethylsiloxane
PE	polyethylene
PEC	probable effects concentration
PED	polyethylene device
PEL	probable effects level
PHC	petroleum hydrocarbon
POM	polyoxymethylene
PRG	preliminary remediation goal
PUP	Plant Uptake Program
R^2	coefficient of determination
RAGS	*Risk Assessment Guide for Superfund*
RAL	remedial action level
RAO	remedial action objective
RBA	relative bioavailability
RBP	rapid bioassessment protocol
RCRA	Resource Conservation and Recovery Act
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RFI	RCRA facility investigation
RI	remedial investigation
ROD	record of decision
SEC	sediment effects concentration
SEL	severe effects level
SEM	simultaneously extracted metals
SERAFM	Spreadsheet-Based Ecological Risk Assessment for the Fate of Mercury
SERDP	Strategic Environmental Research and Development Program
SFE	supercritical fluid extraction
SL	screening level
SLC	screening level concentration
SLERA	screening level ecological risk assessment
SLV	screening level value
SOC	sedimentary organic content
SPMD	semipermeable-membrane device
SPME	solid-phase microextraction
SPI	sediment profile imaging
SQAL	sediment quality advisory level
SQC	sediment quality criteria
SQG	sediment quality guideline
SQO	sediment quality objective
SQT	Sediment Quality Triad
SQuiRT	Screening Quick Reference Table

SQV	sediment quality value
SSL	soil screening level
SSLC	species screening level concentration
SVOC	semivolatile organic compound
SWAC	surface-weighted average concentration
TCE	trichloroethene
TCDD	tetrachlorodibenzo-p-dioxin
T&E	threatened and endangered
TEC	toxic effects concentration
TEL	threshold effects level
TEQ	toxic equivalent
TET	toxic effects threshold
TIE	toxicity identification evaluation
TLC	thin-layer chromatography
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotouene
TOC	total organic carbon
TSMD	Tri-State Mining District
TSS	total suspended solids
TU	toxic unit
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
USFWS	U.S. Fish and Wildlife Service
VC	vinyl chloride
VOC	volatile organic compound
WDEQ	Wyoming Department of Environmental Quality
WES	Waterways Experiment Station
WNY	Washington Navy Yard