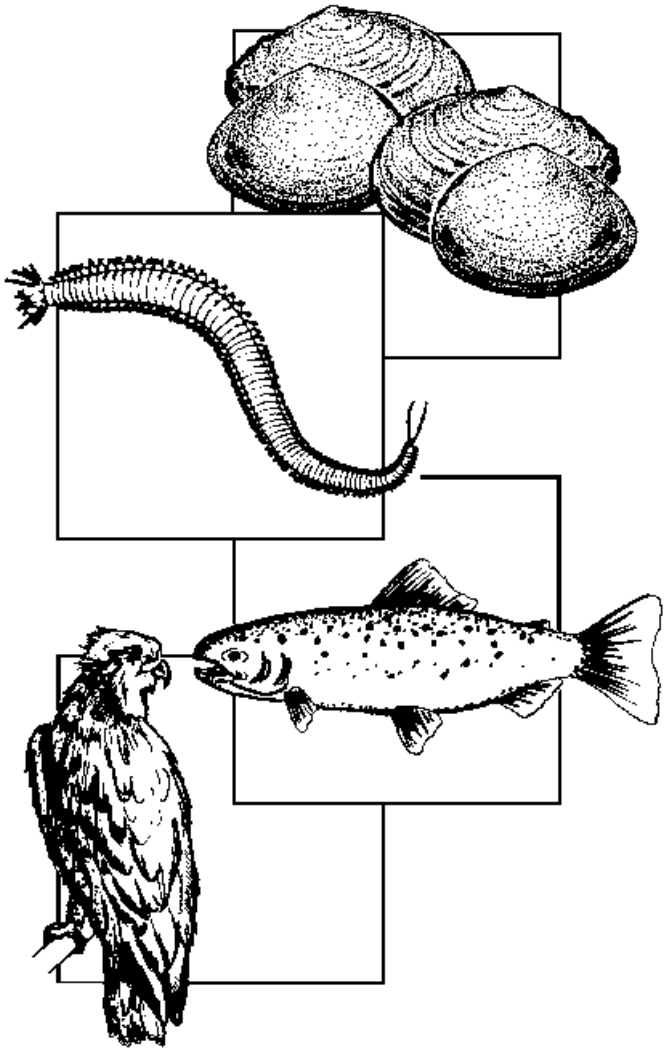
United States Environmental Protection Agency
Office of Water (4305)
Office of Solid Waste (5307W)
EPA-823-R-00-001
February 2000

EPA

Bioaccumulation Testing And Interpretation For The Purpose Of Sediment Quality Assessment

Status and Needs



BIOACCUMULATION TESTING AND INTERPRETATION FOR THE PURPOSE OF SEDIMENT QUALITY ASSESSMENT

STATUS AND NEEDS

February 2000

U.S. Environmental Protection Agency
Bioaccumulation Analysis Workgroup
Washington, DC 20460

This document has been approved for publication by the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This document describes existing knowledge on the use of bioaccumulation data as part of sediment quality assessments. It is not intended to serve as guidance or regulation. This document cannot impose legally binding requirements on EPA, States, Indian tribes, or the regulated community.

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ACKNOWLEDGMENTS

Valuable input or assistance was provided by the following EPA individuals: James Keating, Patti Tyler, Mindy Pensak, Tom Steeger, Jeneva Craig, Richard Healy, Robert Wood, Erik Winchester, Heidi Bell, Marjorie Wellman, William Tate, Kelly Eisenman, Kathy Davey, Jane Farris, Leanne Stahl, Rick Hoffmann, Bob Morcock, Keith Sappington, and Ted Dewitt. Technical support for completion of this document was provided under EPA contract #68-C98-111 by Tetra Tech, Inc. and their subcontractors EVS Environment Consultants, and SAIC.

The Bioaccumulation Analysis Workgroup, co-chaired by OW/OST and OSWER/OSW, consists of 40 people from EPA headquarters, regional offices, and research laboratories with scientific and/or programmatic experience related to bioaccumulation testing and interpretation and sediment quality.

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EXECUTIVE SUMMARY

Persistent bioaccumulative chemicals are distributed in sediments throughout the United States, with sediments serving as both a sink and a reservoir for these chemicals. As part of their sediment management decisions, the U.S. Environmental Protection Agency (EPA) and other regulatory agencies are frequently required to interpret the environmental significance from laboratory and field studies. Decisions that require the interpretation of bioaccumulation data are complicated by numerous factors, including variability in chemical bioavailability due to seasonal and physicochemical conditions. It is no longer sufficient to know only whether chemicals accumulate because bioaccumulation itself is not an effect but a process. Regulatory managers must know whether the accumulation of chemicals is associated with or responsible for adverse effects on the aquatic ecosystem and human health. Another complicating factor is that EPA programs have different mandates, often requiring different applications and uses of bioaccumulation data.

EPA prepared this document to serve as a status and needs summary of the use of bioaccumulation data. The document is the result of a collaborative effort among the members of the EPA Bioaccumulation Analysis Workgroup. This document was also prepared to respond to increased interest in the fate and effects of persistent, bioaccumulative, and toxic (PBT) pollutants, as evidenced by the development of EPA's multimedia PBT Strategy.

The purpose of this document is to describe existing knowledge on the use of bioaccumulation data as part of sediment quality assessments. This document:

- Provides a comprehensive summary of existing knowledge on bioaccumulation.
- Provides a compilation of exposure and effects data for persistent, bioaccumulative chemicals.
- Discusses factors that affect the bioavailability of sediment-associated contaminants.
- Identifies how various programs currently use bioaccumulation data for sediment management decisions.
- Identifies issues and research needs for interpreting bioaccumulation data for the purpose of assessing sediment quality.

Factors Affecting Bioavailability

A wide range of physical, chemical, and biological factors have the potential to influence the bioavailability of sediment contaminants. The bioavailability of contaminants in sediment is a function of the type of chemical and the chemical speciation, as well as the behavior and physiology of the organism. The two basic routes of exposure for organisms are transport of dissolved contaminants in pore water across biological membranes, and ingestion of contaminated food or sediment particles with subsequent transport across the gut. For upper-trophic-level species, ingestion of contaminated prey is the predominant route of exposure, especially to hydrophobic chemicals. Uptake through ingestion of or direct exposure to water or sediment can also be important depending on the trophic level of the organism and the physical-chemical characteristics of the contaminant.

Physical Factors

Sediments are dynamic environments with a wide range of interacting processes with variable rates. The rate of mixing in surficial sediment layers by physical processes such as turbulence and bioturbation competes with the rate of sedimentation to determine the depth to which contaminated sediment will be buried. Diffusion and resuspension can also have a large impact on the bioavailability of sediment-associated contaminants either by re-exposing epibenthic filter feeders to contaminated particulates or by increasing the aqueous concentration of a contaminant via desorption from the particulates within the water column.

Chemical Factors

The characteristics of a chemical, such as its molecular size and polarity, determine to a large extent the degree of association of the chemical with particles and thus have an effect on bioavailability. Large, nonpolar chemicals, such as highly chlorinated polychlorinated biphenyls (PCBs), have low aqueous solubilities and a strong tendency to be associated with dissolved and particulate organic matter; therefore, they are less bioavailable, at least to non-sediment-ingestors. Small, ionic species such as certain metals have high aqueous solubilities and tend to be more bioavailable. Even between these extremes, chemical characteristics of contaminants have a large influence on bioavailability.

The concentration of total metals in sediment is generally not predictive of the bioavailability of these elements. Metals concentrations in interstitial water (i.e., pore water) have been correlated with biological effects. For several divalent metals in sediments, acid-volatile sulfide (AVS) appears to have a strong influence on cationic metal activity and toxicity.

For nonionic organic chemicals, the most important factor determining bioavailability is sorption to dissolved and particulate organic matter. Sediment-pore water partitioning of nonionic organic compounds is influenced by the organic carbon content of the sediment. Hydrophobicity is the most important chemical characteristic determining the bioaccumulation behavior of organic chemicals in aquatic systems, although some have suggested that activity coefficients in water are a better estimator. Octanol-water partitioning has become a common method for evaluating the potential of a contaminant to bioaccumulate; however, a major disadvantage of octanol-water partitioning is that experimental determination can be subject to very large measurement errors. It has been demonstrated that bioaccumulation can be predicted from octanol-water partitioning when the partition coefficient (log K_{ow}) lies between 2 and 6. There is also a relationship between the K_{ow} of a chemical and its potential for biomagnification, with uptake efficiency increasing with increasing log K_{ow} for values between 3 and 6. For compounds with a log K_{ow} greater than 6, uptake efficiency begins to decrease. The predictive relationships between K_{ow} and bioaccumulation or biomagnification potentials assume that the compound is not metabolized. If metabolism occurs, these correlations are not applicable, making interpretation more difficult.

Biological Factors

Bioaccumulation is a function of the bioavailability of contaminants in combination with species-specific uptake and elimination processes. Toxicity is determined by the exposure of an animal to bioavailable contaminants in concert with the animal’s sensitivity to the contaminant. These processes have been shown to be a function of the organism's lipid content, size, growth rate, gender, diet, and ability to metabolize or transform a given contaminant, as well as the chemical conditions of the surrounding medium. Other biological factors that can affect contaminant bioavailability include the burrowing and

feeding behavior of the individual organism or species. The depth to which an organism burrows, the type of feeding mechanism it uses (e.g., filter feeding, particle ingestion), the size range of sediment particles it consumes, and its diet all have a large influence on the concentration of contaminant to which the organism will be exposed.

Methods for Assessing Bioaccumulation

Two basic approaches exist to assess bioaccumulation: the first consists of methods that directly measure bioaccumulation, and the second consists of methods that model bioaccumulation. The selection of the appropriate approach is dependent on what questions are being asked, the type of environment, the species, and the contaminants of concern.

The following questions are useful in determining the most appropriate approach for evaluating bioaccumulation:

- *Is the goal to monitor existing bioaccumulation or to predict bioaccumulation under future exposure conditions?*
- *Is the test or model being used as a screening tool or as an accurate predictor?*
- *Is the goal to qualitatively identify which sediment compounds will bioaccumulate or to develop quantitative estimates of tissue concentrations for these compounds?*
- *Will conditions required to reach steady state be met?*
- *Are uptake routes in addition to sediment exposure likely to be important?*
- *Is a goal to determine or predict the time course of uptake and/or elimination?*
- *Is it required that local species be used in the assessment?*
- *Is more than one species to be tested?*
- *Will field or experimentally spiked sediments be used?*

Direct measurement, the simplest approach to assessing bioaccumulation in aquatic organisms, can be conducted using either laboratory-exposed or field-collected organisms. This approach minimizes or eliminates many of the problems associated with modeling. Important issues associated with laboratory measurements of bioaccumulation of chemicals from sediment include selection of an appropriate test species, sediment sampling and handling methods, conditions during exposure to the sediment, exposure duration, and statistical analyses. Measuring bioaccumulation at a particular site requires consideration of which test species to use, whether to examine natural populations or use transplanted populations, and how to compare bioaccumulation occurring under conditions at a potentially contaminated site with that occurring at a reference site.

The two main approaches to bioaccumulation model development are (1) an empirical approach in which laboratory or field data are interpreted to calculate parameters such as bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) and (2) a deterministic modeling approach that employs kinetic or equilibrium models in which the mechanistic aspects of bioaccumulation are considered, usually referred to as food web models. Empirical models include bioconcentration factors, BAFs, BSAFs, food chain multiplier, and theoretical bioaccumulation potential. Mathematical models or food web models can be grouped into two categories - equilibrium-based and kinetic approaches. Equilibrium models are usually referred to as “dynamic” because absolute thermodynamic equilibrium

between contaminant concentrations in biota, water, and sediments is rarely reached in a natural setting. Thus, the equilibrium-based models assume steady-state conditions between organisms and the environment. In contrast to equilibrium-based models, kinetic models describe bioaccumulation as the net effect of rate processes (uptake and loss of contaminant). General assumptions of kinetic models include constant uptake rate(s), instantaneous mixing within the compartment(s), and a negative exponential depuration process for all compartments. A newer bioaccumulation assessment tool currently being evaluated for its utility is the critical body residue approach. The critical body residue approach links body burdens in an individual organism to toxicological effects in that organism. Considerable interest exists in using the above tools to identify sediment concentrations associated with threshold tissue concentrations that are protective of aquatic organisms or their predators, including humans.

Important Bioaccumulative Chemicals

The difficulty associated with interpreting bioaccumulation data is exacerbated by a need to address chemical mixtures in sediments as they normally occur. Although progress is being made toward a mixture approach, these types of analyses are in the early stages of development. Hence, the discussion in this document is focused on individual bioaccumulative chemicals. The bioaccumulative chemicals of potential concern listed in this document were selected based on input from the EPA Bioaccumulation Analysis Workgroup and a review of various documents. These chemicals are known to be found in sediment and in animal tissues at levels associated with toxic effects. The document contains information in tabular format for 11 metals, 1 chlorinated phenol, 10 polycyclic aromatic hydrocarbons (PAHs), 13 pesticides, selected dioxins and furans, selected Aroclors and congeners of the PCB group, and total PCBs. Criteria for selecting an initial set of chemicals to be researched and summarized in this document included the following: (1) information was readily available; (2) the chemical was of immediate concern and known to bioaccumulate; (3) the chemical was representative of a group or class of compounds; and (4) the chemical was considered to be important in one or more EPA programs.

The chemical tables (Appendix) summarize information on chemical characteristics, including water solubilities, half-lives, and partition coefficients (log K_{ow} and log K_{oc}); human health concerns; wildlife and aquatic organism partitioning factors; and food chain multipliers. A brief profile of the chemical's toxicity, mode of action, and potential for bioaccumulation is also included. Daily intake levels of concern for the protection of human health were compiled, including estimated values for carcinogenic endpoints (slope factors) and noncarcinogenic endpoints (reference doses) for the oral ingestion exposure pathway, and EPA’s carcinogenic classifications are provided. Factors affecting partitioning of the chemical in relation to wildlife and aquatic organisms, food chain multipliers (biomagnification factors), toxic effects and mode of action, and other information were compiled from various sources.

The data in the chemical summary tables will be useful in addressing the following issues pertaining to bioaccumulation:

- *What species are potentially available for testing?*
- *How should we account for differential partitioning of bioaccumulative contaminants among tissues?*
- *How can bioaccumulation methods be used to assess population-level effects?*
- *How can tissue-specific residue levels be coupled with chronic toxicity response data to develop dose-response relationships for bioaccumulative contaminants?*

Agency Information on Bioaccumulation Data Collection and Interpretation

Bioaccumulation of toxic persistent organic contaminants by aquatic organisms is an ongoing concern for EPA and other agencies. This review identifies a variety of EPA programs that interpret bioaccumulation data to help assess sediment quality. Specialized activities within each of these programs represent a broad spectrum of approaches that address specific statutory mandates as well as the goals of EPA's Contaminated Sediment Management Strategy. Table 1 summarizes the uses of bioaccumulation data by various EPA programs for the interpretation of sediment quality.

Several different activities are overseen by the various agencies, with each activity emphasizing a different need or issue associated with collecting and using bioaccumulation data. Research on bioaccumulation and the use of bioaccumulation to assess sediment contamination are ongoing activities in OPPT, NHEERL, NERL, OERR, OSW, OST, OWOW, the Chesapeake Bay Program, and Regions 5 and 10. OPPT, OSW, OST, and OERR have been working on identifying, based on various chemical properties, chemical structure, and structure-activity relationships, which chemicals might bioaccumulate and cause adverse environmental effects. Bioaccumulation of sediment contaminants in fish that might be consumed by humans is a major concern in the development of water quality criteria for the protection of human health, and research is under way on the most appropriate methods for predicting bioaccumulation in fish and developing chemical-specific BSAFs for setting tissue residue-linked sediment chemical levels for the protection of human health, particularly for mercury.

Assessment procedures that the EPA is focusing on are specific bioaccumulation issues related to assessing contaminated sediments, which include

- The appropriateness of bioaccumulation evaluation methods and interpretation of test results to determine the acceptability of proposed actions.
- Improving consistency in methods used to determine potential bioaccumulative chemicals, effects concentrations for these chemicals, and use of background data to assess bioaccumulation.
- Pesticide evaluation.
- Screening methods and modeling procedures.
- Evaluating human health risks.

OERR, OSW, GLNPO, and a number of international organizations are focusing on the use of bioaccumulation information to identify and evaluate sediments for remediation efforts. Clean-up levels for several Superfund sites have been based on the presence of bioaccumulative contaminants.

Table 1. Summary of Uses of Bioaccumulation Data by Various EPA Programs for the Interpretation of Sediment Quality

Agency Program	Components of Contaminated Sediment Management					
	Research	Assessment	Remediation	Dredged Material Management	Prevention	Outreach
Office of Prevention, Pesticides, and Toxic Substances (OPPTS)						
Office of Pesticide Programs (OPP)		O				
Office of Pollution Prevention and Toxics (OPPT)	O	O			O	O
Office of Research and Development (ORD)						
National Health and Environmental Effects Research Laboratory (NHEERL)	O	O				O
National Exposure Research Laboratory (NERL)	O	O				
Office of Solid Waste and Emergency Response (OSWER)						
Office of Emergency and Remedial Response (Superfund) (OERR)	O	O	O			
Office of Solid Waste (OSW)	O	O	O		O	
Office of Water (OW)						
Office of Science and Technology (OST)	O	O			O	O
Office of Wetlands, Oceans, and Watersheds (OWOW)	O	O	O	O	O	O
Office of Wastewater Management (OWM)					O	
Chesapeake Bay Program (CBP)	O	O	O	O	O	O
Great Lakes National Program Office (GLNPO)		O	O	O		
Office of Air and Radiation (OAR)		O				

The regions are using a number of approaches to target remediation of contaminated sediments; many are evaluating the fish ingestion pathway. Bioaccumulation tests with other organisms (small mammals, clams, amphibians) are also used during the evaluation of ecological risk.

Preventing the release of bioaccumulative contaminants is of concern to OPPTS, OSW, OST, OWM, the Chesapeake Bay Program, OWOW, and numerous countries around the world. OPPT is using its screening and prioritizing procedures to determine those chemicals which might accumulate in sediments and pose risks so that dangerous levels of loadings can be targeted. Under the Waste Minimization National Plan, OSW and OPPT are developing a tool that would prioritize chemicals in hazardous waste based on persistence, bioaccumulation potential, toxicity, and quantity. OWOW and OST use bioaccumulation data in the control of discharges of bioaccumulative chemicals under the CWA. Several international conferences have been held to examine methods for reducing or eliminating persistent organic and metal pollutants, some of which have resulted in agreements.

The dissemination of information pertaining to the bioaccumulation of chemicals has been important for OPPT, OST, OWOW, the Chesapeake Bay Program, NHEERL, and all EPA regions. OPPT recently released a draft multimedia strategy to reduce risks from exposures to priority PBT pollutants through increased coordination among EPA national and regional programs and various stakeholders. OST has published a series of documents on the analysis of fish tissue concentrations of contaminants and the use of such data to determine risks to humans from consumption of fish, as well as providing a database listing all fish and wildlife consumption advisories currently operating in the states. OWOW's outreach efforts include educating the public about the ocean- and coast-related programs and making program information readily available to the public. The toxics characterization of tidal tributaries of the Chesapeake Bay being performed by the Chesapeake Bay Program will be used as an outreach tool to put information in the hands of the public in order to target appropriate areas for additional monitoring and management activities.

Issues and Research Needs for Interpreting Bioaccumulation Data for the Purpose of Sediment Quality Assessment

The interpretation of bioaccumulation data will require an understanding of the relationship between environmental media concentrations, tissue concentrations, and effects on specific organisms or consumers of those organisms. Several issues and research needs have been identified by EPA's Bioaccumulation Analysis Workgroup and attendees of EPA's National Sediment Bioaccumulation Conference (September 11-13, 1996). These issues and needs have been grouped according to topic and include the following:

- Methods—*Laboratory and field methods for assessing bioaccumulation*
  Needs include standardization of methods and approaches, further identification of appropriate species for pathways of concern, and field validation of laboratory methods.

- Chemical Identification—*Identification of bioaccumulative chemicals*
  Needs include identifying a screening procedure for bioaccumulative contaminants, developing additional BAF and BSAF values to assign to known persistent bioaccumulators, or to identify potential ones, and better understanding the bioavailability processes of chemicals in sediments.

- Species Considerations—*Species selection for bioaccumulation testing*
  Needs include guidance on further identification or development of contaminant-specific receptors of choice, tissue residue values for terrestrial and avian wildlife, and additional information on amphibian and wetland species.

- Toxicology—*Dose-response relationships for bioaccumulative contaminants*
  Needs include determining the applicability of the critical body residue (CBR) approach to multiple classes of chemical mixtures, determining differential partitioning of bioaccumulative contaminants among tissues, and conducting further research on how to resolve or compensate for uncertainties related to the assessment of bioaccumulation of sediment-associated contaminants.

GLOSSARY

Note: Numbers in brackets refer to the source of the definition. The citations are provided in the list of references immediately following the glossary.

Acid-volatile sulfides (AVS) — The sulfides removed from sediment by cold acid extraction, consisting mainly of hydrogen sulfide (H_2S) and iron sulfide (FeS). AVS is a possible predictive tool for divalent metal sediment toxicity. [1]

Bioaccumulation — The accumulation of contaminants in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, pore water, or dredged material. [1]

Bioaccumulation factor (BAF) — The ratio of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. [2]

Bioaccumulative chemicals of concern (BCC) — Chemicals identified as a concern for sediment quality assessment because of their ability to accumulate in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, pore water, or dredged material. [1; modified]

Bioavailable — For chemicals, the state of being potentially available for biological uptake by an aquatic organism when that organism is processing or encountering a given environmental medium (e.g., the chemicals that can be extracted by the gills from the water as it passes through the respiratory cavity or the chemicals that are absorbed by internal membranes as the organism moves through or ingests sediment). In water, a chemical can exist in three different basic forms that affect availability to organisms: (1) dissolved, (2) sorbed to biotic or abiotic components and suspended in the water column or deposited on the bottom, and (3) incorporated (accumulated) into organisms. [3; paraphrased]

Bioconcentration — A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g., by gill or epithelial tissue) and elimination. [4]

Bioconcentration factor (BCF) — The ratio of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water, in situations where the organism is exposed through the water only and the ratio does not change substantially over time. [2]

Biomagnification — Result of the process of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels. The term implies an efficient transfer of chemical from food to consumer, so that residue concentrations increase systematically from one trophic level to the next. [4]

Biota-sediment accumulation factor (BSAF) — Relative concentration of a substance in the tissues of an organism compared to the concentration of the same substance in the sediment. [1]

Biotransformation — Enzyme-catalyzed conversion of one xenobiotic compound to another. [5]

Bioturbation — The act of resuspending contaminated fluid or sediment particles into the water column through turbulent activities of biota. [6]

Critical body residue (CBR) — The whole-body concentration of a chemical that is associated with a given adverse biological response. This assumes organisms consist of a single compartment rather than the multiple compartments of which they actually consist, but it has considerable utility as a first approximation of dose. [3]

Desorption — A process that involves the removal of a chemical from a solid to which it is attached or a liquid in which it is dissolved. [7]

Diffusion — (nonbiological) Nonadvective transport due to migration and mixing of dissolved suspended solutes (including particulates) in natural waters in response to concentration gradients. Diffusion can be at the molecular level, due to Brownian motion's producing random movements of the solute's molecules (molecular diffusion), or it can be movements of solutes (including particles) due to turbulent eddies, velocity shear, or bioturbation (turbulent diffusion). Both types of diffusion result in mixing and dispersal of dissolved and bound chemicals. [3]

Dissolved organic carbon (DOC) — The fraction of the organic carbon pool that is dissolved in water and that passes through a 0.45-µm glass fiber filter. DOC quantifies the chemically reactive organic fraction and is an accurate measure of the simple and complex organic molecules that make up the dissolved organic load. [3]

Eh — The measure of the electromotive force of a reaction. [8]

EROD — Ethoxyresorufin O-deethylase catalyzed by cytochrome P4501A (CYP1A proteins) and found in the liver. [9]

Food chain model — A mathematical model that estimates the quantitative transfer of chemicals through the different trophic levels of the food chain. These models vary in complexity, can contain many state variables and parameters, and consider the movement of a chemical through a food chain consisting of one or more trophic levels. These models are typically used with toxic, nonselective, and bioaccumulative chemicals that can affect the entire structure of an ecosystem. [10]

Food chain multiplier — A multiplier that is intended to be applied to the bioconcentration factor of a chemical to estimate the bioaccumulation factor, thereby taking into account accumulation of the chemical up the food chain due to predation. [11]

Food web transfer — Transfer of a chemical from food to consumer, so that residue concentrations increase systematically from one trophic level to the next. [11; paraphrased]

Half-life — Time required to reduce by one-half the concentration of a material in a medium (e.g., soil water) or organism (e.g., fish) by transport, degradation, transformation, or depuration. [4]

Hydrophobic (lipophilic) chemical — A chemical of low water solubility and correspondingly high solubility in lipids or nonpolar solvents. [12]

Hydrophobicity — Partitioning behavior between lipid and aqueous phases. [13]

In situ — In the natural or original position; the use of the field and natural conditions rather than the standardized conditions of laboratory experiments. [14]

Indicator species — A species that may be used as an indicator of changes in environmental quality or conditions. Measured endpoints include the presence, absence, or relative abundance; changes in growth; bioaccumulation of selected chemicals; and changes in reproductive status. [6; modified]

Interstitial water — Water occupying space between sediment or soil particles; also called pore water. [15]

Kinetic models — Models describing chemical reactions and physicochemical processes. [8; paraphrased]

Lethal concentration of 10 out of 100 organisms (LC10) — The concentration of a substance that kills 10 percent of the organisms tested in a laboratory toxicity test of specified duration. [1]

Lethal concentration of 50 out of 100 organisms (LC50) — The concentration of a substance that kills 50 percent of the organisms tested in a laboratory toxicity test of specified duration. [1]

Lipid-water equilibrium partition coefficient (K_l) — The ratio of the concentrations of a given chemical in lipid and in water. [16]

Molecular diffusion — A process of spontaneous intermixing of different substances attributable to molecular motion and tending to produce uniformity of concentration. [15; paraphrased]

Nonionic sorption — A process by which a solute becomes physically or chemically associated with a solid sorbent through nonionic mechanisms. [7; paraphrased]

Octanol-water partition coefficient (K_{ow}) — The ratio of the concentration of a substance in an n-octanol phase to its concentration in the aqueous phase in an equilibrated two-phase n-octanol-water system. The log K_{ow} of a substance represents its likelihood to complex or sorb to organic carbon. The log K_{ow} of a chemical is directly proportional to its n-octanol solubility. [2]

Particulate organic carbon coefficient (P_{oc}) — The fraction of the organic carbon pool that is not dissolved in water, but is retained on a 0.45-µm glass fiber filter. POC is identical to suspended organic carbon (SOC) and is composed of plant and animal organic carbon and organic coating on silt and clay. [3]

Partition coefficient — The ratio of chemical concentrations to two different compartments or phases under steady state conditions. [7]

Reference dose — The estimated dose at which a chemical would be expected to show no effects in a test organism. [11]

Pore water — Water occupying space between sediment or soil particles; also called interstitial water. [15]

Redox potential — The potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given electrolyte. [15]

Resident species — Native, indigenous organisms found at a particular site. [17; modified]

Reversible sediment/pore water partition coefficient (K_p) — Ratio of the concentration of sediment to the concentration of pore water. [18]

Sediment organic carbon-water partition coefficient (K_{soc}) — The ratio of the concentration of chemical in the organic carbon phase to the concentration in water. [3]

Semipermeable membrane devices (SPMD) — A thin film or narrow column of lipid (usually triolein) enclosed in lay-flat or capillary polymeric tubing. Only dissolved or bioavailable organic pollutants diffuse through polymeric films used in SPMDs. [19]

Simultaneously extracted metals (SEM) — divalent metals—commonly cadmium, copper, lead, mercury, nickel, and zinc—that form less soluble sulfides than does iron or manganese and are solubilized during the acidification step (0.5 M HCl for 1 hour) used in the determination of acid-volatile sulfides in sediments. [20]

Slope factors — The slope of the dose-response curve in the low-dose region. When low-dose linearity cannot be assumed, the slope factor is the slope of the straight line from zero dose (and zero excess risk) to the dose at 1 percent excess risk. An upper bound on this slope is usually used instead of the slope itself. The units of the slope factor are usually expressed as 1/(mg/kg-day). [21]

Sorption — A process by which a solute becomes physically or chemically associated with a solid sorbent regardless of the mechanism (e.g., chemisorption, adsorption, absorption). [7]

Steady state — The state in which fluxes of material moving bidirectionally across a membrane or boundary between compartments or phases have reached a balance. An equilibrium between phases is not necessarily achieved. [3]

Superhydrophobic chemicals — Chemicals that are not water-soluble; chemicals that have a strong affinity for lipids (fats). These chemicals are characterized by a log K_{ow} greater than 6. [3; paraphrased]

Theoretical bioaccumulation potential (TBP) — An approximation of the equilibrium concentration in tissue if the material in question were the only source of contaminants to the organisms. [1]

Tortuosity — The quality of having repeated turns or bends; something twisted. [22]

Trophic level — The different feeding relationships in an ecosystem that determine the route of energy flow and the pattern of chemical cycling. [11]

Trophic level transfer — Efficient transfer of chemical from food to consumer, so that residual concentrations increase systematically. [11]

Trophic transfer coefficient — The ratio at which efficient transfer of chemical from food to consumer occurs. [11]

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BIOACCUMULATION TESTING AND INTERPRETATION FOR THE PURPOSE OF SEDIMENT QUALITY ASSESSMENT: STATUS AND NEEDS

1. INTRODUCTION

1.1 Problem Statement

Many federal agencies, including the U.S. Environmental Protection Agency (EPA), U.S. Army Corps of Engineers (USACE), National Oceanic and Atmospheric Administration (NOAA), U.S. Fish and Wildlife Service (FWS), and U.S. Geological Survey (USGS), are tasked with environmental monitoring and assessment issues and are routinely making sediment management decisions using bioaccumulation data. Toxic persistent organic contaminants are distributed in sediments throughout the United States (USEPA, 1996), with sediments serving as both a sink and a reservoir for these chemicals. Decision-making processes predicated on bioaccumulation are complicated by numerous factors, including site-specific issues and the variability in chemical bioavailability due to seasonal, physicochemical conditions, or anthropogenic changes to the environment. It is no longer sufficient to know only whether chemicals accumulate because bioaccumulation itself is not an effect but a process. Regulatory managers must know whether the accumulation of chemicals is associated with or responsible for adverse effects to aquatic organisms and organisms that prey on them, including humans. Another complicating factor is that EPA programs have different mandates, often requiring different applications and uses of bioaccumulation data. This document represents a summary of existing knowledge on the use of bioaccumulation data as part of sediment quality assessments.

1.2 Purpose

A number of sediment assessment methods have been developed to determine the bioaccumulation potential of contaminants in sediments. EPA's Office of Science and Technology and Office of Solid Waste formed a "Bioaccumulation Analysis Workgroup" consisting of 40 headquarters and regional participants. This workgroup has overseen the production of the present "status and needs document," the purpose of which is to provide background information and report on the status of bioaccumulation testing and interpretation in various EPA programs. This document:

- Provides a comprehensive summary of existing knowledge on bioaccumulation.
- Compiles exposure and effects data for persistent, bioaccumulative chemicals.
- Discusses factors that affect the bioavailability of sediment-associated contaminants.
- Identifies how various programs currently use bioaccumulation data for sediment management decisions.
- Identifies issues and research needs for interpreting bioaccumulation data for the purpose of assessing sediment quality.

This document is not intended to provide all that is known on bioaccumulation, but rather is a comprehensive summary of current knowledge and limitations, issues, and needs. It is an attempt to

identify, categorize, and enumerate effects resulting from the accumulation of chemicals. The document is intended to be a synopsis of tools in the regulator's toolbox.

1.3 Scope of the Document

This document is organized into two parts - the main text, which provides a summary of existing knowledge, discusses bioaccumulation processes, and reviews EPA's uses of bioaccumulation data and issues associated in that process, and an appendix containing the exposure and effects data. The following specific elements are contained within the respective chapters:

- Chapter 2 discusses factors that affect the bioavailability of sediment-associated contaminants.
- Chapter 3 describes methods and techniques that have been developed for measuring and modeling bioaccumulation.
- Chapter 4 identifies important bioaccumulative chemicals, presents an overview of the information contained in the chemical-specific summary tables (Appendix), and describes how the data were obtained.
- Chapter 5 presents brief synopses of current research on and uses of bioaccumulation data in several EPA programs.
- Chapter 6 summarizes further research needs for interpreting the bioaccumulation of persistent organic pollutants to assist in protecting aquatic and terrestrial biota and humans from toxic effects of bioaccumulative chemicals in sediments.
- The Appendix is a compilation of chemical-specific summary tables that represent bioaccumulation research conducted during the past 12 years. The summary tables contain information associating the presence and quantity of potentially bioaccumulative chemicals in sediment with uptake in the tissues of aquatic and terrestrial organisms and with the effects of those chemicals on the organisms.

1.4 Regulatory Uses

A brief synopsis of possible uses of bioaccumulation data in EPA programs under a variety of statutes is presented below. More detailed information on how bioaccumulation data are used by various programs is provided in Chapter 5. Typical applications of bioaccumulation guidance might be the characterization of sediment contamination at Superfund sites, the verification of contaminants of concern in sediment for purposes of NPDES permitting, and the selection of disposal options for dredged material.

The Office of Enforcement and Compliance Assurance (OECA) is responsible for developing and implementing enforcement and compliance assurance strategies for the National Environmental Policy Act (NEPA) and other federal regulations. Consequently, it may use bioaccumulation data under a broad range of statutes to determine the environmental acceptability of proposed federal actions.

The Office of Prevention, Pesticides, and Toxic Substances (OPPTS) uses the results of bioaccumulation tests to support review of new and existing chemicals under the Toxic Substances Control Act (TSCA) and the registration/re-registration of chemicals under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). In addition bioaccumulation information may be used to provide guidance on the design of new chemicals to reduce bioavailability and partitioning of toxic chemicals to sediment.

The Office of Solid Waste and Emergency Response (OSWER) is responsible for controlling hazardous wastes and remediating hazardous waste sites under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Under CERCLA, the Office of Emergency and Remedial Response (OERR)—the Superfund Program—uses sediment assessment methods, including bioaccumulation data, as a standard part of initial sampling during the preliminary site assessment and the more in-depth Remedial Investigation/Feasibility Study for Superfund sites where sediment contamination might be present. Under RCRA, the Office of Solid Waste (OSW) has proposed the Hazardous Waste Identification Rule (HWIR; USEPA, 1999). The proposed rule addresses listed hazardous wastes, as well as mixtures of and residues derived from managing the hazardous wastes, that pose low risks to human health and the environment. The rule provides the framework for establishing chemical-specific concentrations in wastes that may not be exceeded to be eligible for a self-implementing exemption from the hazardous waste management system requirements under Subtitle C of RCRA. The framework includes a risk-based methodology that is being developed for use as the basis for the exit concentrations. The methodology considers the bioaccumulative potential of relevant chemicals in the evaluation of potential exposures from multiple pathways, in multiple media, and from a variety of waste management units.

In response to the Hazardous and Solid Waste Amendments of 1984 (HSWA), which amended RCRA, and the Pollution Prevention Act of 1990 (PPA), EPA released the Waste Minimization National Plan (WMNP) in November 1994. The WMNP focuses on reducing the generation and subsequent release to the environment of the most persistent, bioaccumulative, and toxic chemicals in hazardous wastes. One of the objectives of the WMNP was to develop a flexible risk-based screening tool that would assist stakeholders in identifying source reduction and recycling priorities. EPA committed to fulfill this objective by developing a tool that would prioritize chemicals based on their persistence, bioaccumulation potential, toxicity, and quantity. This screening tool, the Waste Minimization Prioritization Tool (WMPT), has been developed by OSW and the Office of Pollution Prevention and Toxics (within OPPTS). EPA used WMPT scores for thousands of chemicals to develop a RCRA PBT Chemical List, which includes chemicals of greatest concern to the RCRA program on a national basis (USEPA, 1998). EPA will use the RCRA PBT List to focus attention on actions that reduce the generation of these chemicals in RCRA hazardous waste by fifty percent by 2005.

The Office of Water (OW) is responsible for EPA's water quality activities, which represent a coordinated effort to restore the nation's waters. The functions of this program include developing national programs, technical policies, and regulations relating to drinking water, water and sediment (including dredged material) quality, and ground water; establishing environmental and pollution source standards; and providing for the protection of wetlands. In addition, this office furnishes technical direction, support, and evaluation of regional water activities; enforces standards; and develops programs for technical assistance and technology transfer. OW oversees the provision of training in the fields of water quality, economic and long-term environmental analysis, and marine and estuarine protection.

OW and the U.S. Army Corps of Engineers (USACE) developed joint technical guidance for evaluating the potential for contaminant-related impacts associated with the discharge of dredged material in the ocean under the Marine Protection, Research, and Sanctuaries Act (MPRSA) (USEPA and USACE, 1991). Similar updated guidance has been published for evaluating dredged material discharges in fresh, estuarine, and saline (near-coastal) waters under section 404 of the Clean Water Act (CWA) (USEPA and USACE, 1998). These documents employ a tiered testing protocol in which bioaccumulation data figure prominently.

Under sections 301, 304, 306, and 307 of the CWA, the Office of Science and Technology (OST) within OW promulgates technology-based national effluent limitations guidelines that control the discharge of toxic chemicals and other pollutants by categories of industrial dischargers. Bioaccumulation data and modeling are used in support of this effort.

In response to the Water Resources Development Act (WRDA) of 1992 requirement that EPA conduct a national survey of data regarding sediment quality in the United States, OST prepared *The National Sediment Quality Survey* (NSQS) (USEPA, 1997). For calculations related to bioaccumulation, the survey makes use of fish tissue residue data and models bioaccumulation from sediment using the theoretical bioaccumulation potential approach. A national database containing information in the NSQS, the National Sediment Inventory, will be maintained and updated on a regular basis so that it can be used to assess trends in both sediment quality and the effectiveness of existing regulatory programs at the federal, state, and local levels.

Section 403 of the CWA requires determination of the quantities of and potential for bioaccumulation of released chemicals, the potential for pollutant transport, potential harm to biological communities, and direct and indirect effects on humans. *CWA Section 403: Procedural and Monitoring Guidance* (USEPA, 1994), developed by the Office of Wetlands, Oceans and Watersheds (OWOW) within OW discusses the qualities of target species and methods for assessing bioaccumulation; monitoring program design, including sampling of caged or indigenous indicator species; the type of tissue to be analyzed in invertebrates and fishes; and techniques for extracting and analyzing chemical contaminants. USEPA (1995a) provides additional information on some of these topics.

EPA's National Estuary Program (NEP), authorized under CWA section 320, is a national demonstration program that uses a comprehensive watershed management approach to address water quality and habitat problems in designated estuaries on the Atlantic, Gulf, and Pacific coasts and in the Caribbean. OWOW developed guidance for this program (USEPA, 1992b), which is similar to that for section 403 (above) and which includes the design and conduct of bioaccumulation monitoring studies to link exposure and effects and to examine risks to target species and humans.

Section 402 of the CWA authorizes the National Pollutant Discharge Elimination System (NPDES) permitting program, administered by the Office of Wastewater Management (OWM) within OW, to regulate the discharge of pollutants from point sources into navigable waters. Bioaccumulation screening methods can be used to identify chemicals of potential concern in the sediments, followed by chemical-specific analysis for confirmatory purposes. Until the states adopt numeric criteria into their standards for sediment contaminants based on bioaccumulation, the NPDES program does not require permitting authorities to include, in their NPDES permits, sediment bioaccumulation-based numeric limits. However, states have the discretion to include such limits in permits based on an interpretation of their narrative standards for toxics. To establish such permit limits, it will be necessary for permitting authorities to develop Waste Load Allocations (WLAs) for the relevant sediment contaminants.

Section 118(c)(2) of the CWA (Public Law 92-500 as amended by the Great Lakes Critical Programs Act of 1990 [CPA], Public Law 101-596, November 16, 1990) required EPA to publish proposed and final water quality guidance on minimum water quality standards, antidegradation policies, and implementation procedures for the Great Lakes System. In response to these requirements, EPA developed the *Final Water Quality Guidance for the Great Lakes System* (USEPA, 1995b). The guidance incorporates bioaccumulation factors (BAFs) into the derivation of criteria and values to protect human health and wildlife.

Section 118(c)(3) established the Assessment and Remediation of Contaminated Sediments (ARCS) Program to assess the extent of sediment contamination in the Great Lakes and to demonstrate bench- and pilot-scale treatment technologies for contaminated sediment. Under the ARCS Program, the Great Lakes National Program Office (GLNPO) used bioaccumulation data and models to estimate comparative human health risks associated with direct and indirect exposures to contaminated sediments in the lower Buffalo River under selected remedial alternatives. It was shown that risks could be reduced under the different remedial alternatives compared to no action, particularly if dredging was the selected option.

Sediment Management Standards (SMS) for the state of Washington were promulgated by the Washington State Department of Ecology under Chapter 173-204 WAC in March 1991. The purpose of these standards is to "reduce and ultimately eliminate adverse effects on biological resources and significant human health threats" resulting from contaminated sediments. The state of Washington is developing human health sediment quality criteria for bioaccumulative compounds in Puget Sound sediments, which will be incorporated into the state's existing SMS. These criteria are based on standard risk assessment methodologies in conjunction with empirically derived biota-sediment accumulation factors (BSAFs).

1.5 Definitions

The terms *bioconcentration*, *bioaccumulation*, and *biomagnification* are sometimes used interchangeably in the literature, but they have distinct meanings in this document. The following definitions represent the most accepted usage of these terms. These definitions apply throughout this document.

- Bioconcentration is defined as the process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g., by gill or epithelial tissue) and elimination.
- Bioaccumulation is defined as the accumulation of chemicals in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, and pore water in the sediment.
- Biomagnification is the result of the process of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels. The term implies an efficient transfer of chemical from food to consumer, so that residue concentrations increase systematically from one trophic level to the next.

Another important concept is *trophic transfer*. Trophic transfer is simply the movement of contaminants from one trophic level, i.e., prey, to another trophic level, i.e., predators (Schwarz and Lee, 1980). Trophic transfer can result in either bioaccumulation or biomagnification. A chemical's capacity for trophic transfer can be measured in terms of the trophic transfer coefficient (TTC), which is determined by dividing the concentration of a contaminant in a predator's tissue by the concentration of that contaminant in its prey (Suedal et al., 1994). Trophic transfer has been noted as a significant source of chemicals to predator species such as fish, and fish tissue levels are dependent primarily on the ability of the organism to excrete or store the contaminant (Bryan, 1979). Biomagnification is said to occur when a TTC is greater than one. TTCs below one indicate contaminants that do not biomagnify, although bioaccumulation is still possible for these substances.

Biomagnification is of concern to those tasked with assessing sediment quality because of the potential for apparently low, no-effects concentrations of chemicals in abiotic media to elicit adverse effects in higher-trophic-level species. The fact that some higher-trophic-level species can biomagnify certain chemicals makes it crucial that the pathways and mechanisms of transfer be understood. A great deal of information and numerous measurements are involved in determining biomagnification, including information regarding an organism's position in a complex food web, predator-prey relationships, feeding habits, age and sex of the sampled organisms, tissue chemistry data, lipid composition, and gut content analyses. In many cases, studies attempting to assess biomagnification have been plagued by poor experimental design, resulting in a high degree of variability (Suedel et al., 1994). These results have limited the ability to determine whether trophic transfer and biomagnification were occurring.

Bioconcentration, biomagnification (Connell, 1989), and bioaccumulation operate with most aquatic organisms, with bioaccumulation and biomagnification the most likely processes by which air-breathing aquatic animals (e.g., seals, whales, and dolphins) and semiaquatic species (e.g., aquatic birds) acquire chemicals. These higher-trophic-level species lack an organism-to-water exchange interface, making it difficult for the bioconcentration mechanism to operate (Connell, 1989). Bioconcentration may be the sole process for organisms that draw their food and oxygen requirements from dissolved components in the water mass (i.e., phytoplankton and some bacteria) (Connell, 1989). For many bioaccumulative compounds, the principal route of movement into and through aquatic food webs appears to be dietary ingestion rather than bioconcentration from water because these compounds generally exhibit low water solubility and tend to concentrate in the lipid fractions of biological tissues (Suedel et al., 1994). Therefore, the principal pool of these compounds available to upper-trophic-level consumers is from dietary items rather than from abiotic media (Suedel et al., 1994). Biomagnification is most likely to occur with persistent compounds having log K_{ow}s greater than 5, and with organisms that have long lives and probably are among the top predators (Connell, 1989; Suedel et al., 1994). Organisms that cannot excrete or otherwise regulate contaminants can readily biomagnify these materials with age (Bryan, 1979).

Many metals show a potential for trophic transfer via uptake from food, but not in sufficient quantities to result in biomagnification. Those metals which show a propensity to biomagnify include arsenic, methylmercury, and perhaps inorganic mercury (Suedel et al., 1994). Biomagnification of methylmercury, relative to inorganic mercury, has been attributed to higher lipid solubility and an ability to transfer across membranes, long biological half-life, and long life span of top predators, such as aquatic birds (Bryan and Langston, 1992; Huckabee et al., 1979). For organic compounds, PCBs, DDT, DDE, and toxaphene have shown the greatest potential to biomagnify in aquatic ecosystems (Suedel et al., 1994).

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2. FACTORS AFFECTING BIOAVAILABILITY

2.1 Overview

A wide range of physical, chemical, and biological factors have the potential to influence the bioavailability of sediment contaminants. This chapter presents a brief summary of some of the more important of those factors. The distinction between these categories is somewhat artificial. In reality, complex interactions between physical, chemical, and biological factors result in changes in contaminant bioavailability. A summary of important factors is given in Table 2.1. This discussion is not intended to be a definitive review of all factors that potentially affect contaminant bioavailability. Several reviews have outlined the major factors affecting the bioavailability of sediment contaminants, including Landrum and Robbins (1990), Hamelink et al. (1992), and others.

2.2 Routes of Exposure

The observed bioavailability of sediment contaminants is the result of the chemical and environmental speciation of the contaminant as well as the behavior and physiology of the organism. The two basic routes of exposure for organisms are transport across biological membranes exposed to dissolved contaminants in sediment pore water and the ingestion of contaminated sediment particles. Exposure to dissolved contaminant concentrations in sediment pore water appears to be the predominant route of exposure for most benthic organisms (Muir et al., 1985; Oliver, 1987; Shaw and Connell, 1987). However, exposure due to sediment ingestion might be a significant route of exposure for some species (Landrum, 1989; Harkey et al., 1994a; Meador et al., 1995; and others) and appears to be the predominant pathway for some benthic species, such as the oligochaete *Lumbriculus variegatus* (Leppanen and Kukkonen, 1998).

For upper-trophic-level species, ingestion is clearly the predominant route of exposure, especially to hydrophobic chemicals, although uptake through water and sediment ingestion or exposure can also be important depending on the trophic level of the organism and the physical-chemical characteristics of the contaminant.

2.3 Physical Factors

Sediments are dynamic environments characterized by a wide range of competing processes with variable rates. The rate of mixing in surficial sediment layers by physical processes such as turbulence and bioturbation competes with the rate of sedimentation to determine the depth to which contaminated sediment will be buried. The net effect of these processes can be modeled in a variety of fate and transport models, such as those developed by the USEPA-Athens laboratory, (e.g., WASP5). The concentration profile within the sediment is very important to bioavailability and subsequent potential for bioaccumulation because it determines the chemical environment of the contaminated sediment and the physical availability of the contaminant to biological organisms (i.e., whether organisms will be in contact with the contaminant).

Diffusion processes also affect the mobility and bioavailability of sediment-associated contaminants. Diffusion processes are driven by concentration gradients that can be established within sediment pore waters as well as between sediment pore waters and the overlying water column. Diffusion in sediments is limited by the twisted path among sediment particles (tortuosity), as well as molecular diffusion limits.

Table 2-1. Summary of Factors Influencing Bioavailability of Sediment-associated Chemicals

Physical Factors	Chemical Factors	Biological Factors
• Rate of mixing • Rate of sedimentation • Diffusion • Resuspension	• AVS concentrations for Cu, Cd, Pb, Ni, Zn • Redox conditions • pH • Interstitial water hardness • Sediment organic carbon content • Dissolved organic carbon content • Organic-water equilibration constants for organic compounds • Organic matter characteristics • Equilibration time with sediment	• Biotransformation • Bioturbation • Organism size/age • Lipid content • Gender • Organism behavior • Diet, including sediment ingestion, feeding mechanism • Organism response to physicochemical conditions

Resuspension can also have a large impact on the bioavailability of sediment-associated contaminants by either reexposing epibenthic filter feeders to contaminated particulates or increasing the aqueous concentration of a contaminant through desorption from the particulates within the water column (Landrum et al.,1994).

2.4 Chemical Factors

Chemical conditions determine to a large extent the degree of association with particles (e.g., sorption, desorption, precipitation, dissolution). This association is important because the potential bioavailability of sediment-associated chemicals such as divalent metals and nonionic organic compounds is primarily related to the amount of chemical freely available in the interstitial (pore) water of the sediment.

In general, chemical characteristics, such as molecular size and polarity, have a large influence on bioavailability. Large, nonpolar chemicals such as highly chlorinated PCBs have low aqueous solubilities and a strong tendency to be associated with dissolved and particulate organic matter and thus are less bioavailable (at least to non-sediment ingestors). In contrast, small, ionic species such as certain metals, especially alkali or alkaline earth metals like sodium (Na^+) and calcium (Ca^{2+}), have high aqueous solubilities and therefore tend to be more bioavailable. Even between these extremes, chemical characteristics of contaminants have a large influence on bioavailability. In the following subsections, the specific chemical factors important in controlling the pore water concentrations of divalent metals and nonionic organic compounds are discussed.

2.4.1 Metals

Key factors that affect the partitioning and speciation, and thus the bioavailability, of sediment metals include the redox conditions (i.e., whether the conditions are oxic or anoxic), pH, interstitial water hardness, organic carbon content of the sediment, and pore water concentration of dissolved organic carbon. The redox conditions and pH influence the oxidation state and the dissolved speciation of the metal. Metals exhibit a range of reactivities with respect to complexation with both organic and inorganic phases present in the sediment, resulting in varying concentrations of dissolved versus particulate metals.

Total sediment metals concentrations are usually not predictive of the bioavailability of these trace elements. However, metals concentrations in interstitial water (pore water) have been correlated with biological effects (Swartz et al, 1985; Kemp and Swartz, 1988; and others). For several divalent metals, a key partitioning phase controlling cationic metal activity and toxicity in sediments appears to be acid-volatile sulfide (AVS), which is an operationally defined fraction of sulfide minerals of which iron sulfide (FeS) predominates (Di Toro et al. 1990; Carlson et al. 1991; Di Toro et al. 1992; and others). Simultaneously extracted metals (SEM) and AVS measurements can be made to assess the potential bioavailability of SEM metals (Cd, Cu, Pb, Ni, and Zn). The SEM/AVS theory assumes that the concentration of metals dissolved in pore water within the sediment (to which benthic species would be exposed) is related to the abundance of a "controlling phase" in the sediment (i.e., AVS). SEM are theoretically defined as metals that form more stable minerals with sulfide than does Fe (e.g., Cd, Cu, Ni, Zn, Pb).

The SEM/AVS model states that if the AVS concentration is less than the concentration of SEM, toxicity will be observed (Di Toro et al., 1990). In other words, if the SEM/AVS ratio is greater than 1, sufficient AVS is not available to bind all the SEM and benthic organisms *might* be exposed to toxic concentrations of metals. In contrast, if the ratio is less than 1, sufficient AVS exists to bind all SEM and adverse effects in benthic species are not expected. Another way of expressing this relationship is through a difference (i.e., SEM – AVS). This approach gives a quantitative measure of the metal available, in excess of AVS, instead of just a ratio that can be high even in lightly contaminated sediment if the AVS levels are low (Hansen et al. 1996; Ankley et al. 1996).

While SEM/AVS theory has successfully predicted the toxicity of sediment contaminated with Cd and Ni (Ankley et al., 1991; Carlson et al., 1991) and zinc and lead (Casas and Crecelius, 1994), success predicting the toxicity of Cu-contaminated sediments has been mixed (Ankley et al., 1993).

There are at least two possible explanations for the mixed results of the AVS theory: (1) other solid phases (e.g., iron and manganese oxides) and complexing ligands (e.g., natural organic matter) might successfully compete for dissolved metals in sediments or (2) organisms might alter the condition of their immediate environment, thereby exposing themselves to conditions different from those measured in the bulk sediment (e.g., different AVS concentrations or pH).

The bioavailability of mercury, although theoretically mercury is a SEM metal, appears to be controlled more by methylation than by AVS concentrations. Mercury commonly occurs in three chemical forms in the environment—elemental mercury (Hg^0), inorganic mercury (Hg^{+1}, Hg^{+2}), and organic mercury (e.g., methylmercury, phenylmercury). Methylmercury compounds are extremely toxic and are efficiently bioaccumulated through aquatic food chains. Methylmercury is formed in aquatic sediments due to microbial methylation of inorganic mercury. Sulfate-reducing bacteria appear to be particularly efficient methylators in sediment systems. The relationship between total mercury and methylmercury concentrations in water appears to be quite variable. In a recent study of aqueous samples collected

from several streams, an experimentally flooded wetland, and peat pore water, no obvious relationships between total mercury and methylmercury concentrations were observed. Methylmercury as a percent of the total mercury concentration ranged from less than 1 percent to over 90 percent (Kelly et al., 1995). Therefore, direct measurement of methylmercury concentrations might be necessary to determine the bioavailability of mercury.

2.4.2 Nonionic organic compounds

The most important factor determining the bioavailability of nonionic organic chemicals is sorption to dissolved and particulate organic matter. Sediment-pore water partitioning of nonionic organic compounds is influenced by the organic carbon content of the sediment; thus, $K_p = K_{oc} \times f_{oc}$, where K_p represents the reversible sediment/pore water partition coefficient, K_{oc} is the particle organic carbon coefficient, and f_{oc} is the fraction of organic carbon in the sediment (kg organic carbon/kg dry weight of the sediment).

Octanol-water partitioning has become a common method for evaluating the potential of a contaminant to bioaccumulate (Donkin, 1994). Hydrophobicity is the most important chemical characteristic determining the bioaccumulation behavior of organic chemicals in aquatic systems, although some have suggested that activity coefficients in water are a better estimator (Nagel, 1991). Octanol is not a perfect model for biological lipids. A major disadvantage of octanol-water partitioning is that experimental determination can be subject to very large measurement errors. The octanol-water partition coefficient (K_{ow}) is the ratio of a chemical's solubility in n-octanol and water at equilibrium. A key parameter in determining K_{ow} values, water solubility, is subject to large experimental errors, particularly for the very hydrophobic molecules of greatest environmental interest (Donkin, 1994). An EPA workgroup is developing standardized log K_{ow} values for selected chemicals based on a review of available laboratory measurement and modeling data.

Connell (1991) has shown that bioaccumulation can be predicted from octanol-water partitioning when the log K_{ow} lies between 2 and 6. Chemicals with a log K_{ow} less than 2 usually bioconcentrate more than would be expected from their K_{ow} values; chemicals with a log K_{ow} greater than 6 tend to bioconcentrate less than expected (Connell, 1991).

Thomann (1989) extensively evaluated the relationship between the K_{ow} of a chemical and its potential for biomagnification. Uptake efficiency increases with increasing log K_{ow}, reaching a maximum when log K_{ow} is between 3 and 6 (depending on an organism’s size). For compounds with a log K_{ow} greater than 6, uptake efficiency begins to decrease. Thomann also concluded that biomagnification through the food chain is unlikely to occur for chemicals with a log K_{ow} less than 5, but is likely for chemicals with log K_{ow} between 5 and 6.5. Biomagnification remains important for chemicals with log K_{ow} values up to 8, although other factors, such as top predator growth rates and bioconcentration by phytoplankton, take on greater significance (Thomann, 1989). It is important to note that the predictive relationships between K_{ow} and bioaccumulation or biomagnification potentials assume that the compound is not metabolized. If metabolism occurs, these correlations are not applicable.

The nature of the sediment organic matter also appears to affect the observed sediment-pore water partitioning of nonpolar organic contaminants. Enhanced partitioning has been observed in heavily contaminated sediments relative to uncontaminated sediments (Boyd and Sun, 1990; Chin and Gschwend, 1992). The high anthropogenic organic content of these sediments appeared to provide a more effective sorbent for nonpolar organic compounds than did natural sediment organic matter. Studies of differences in partition coefficients between soil and sediment organic matter suggest that

higher partition coefficients measured for sediment organic matter relative to soil organic matter were due to the relative polarity of soil organic matter relative to the sediment organic matter (Grathwohl, 1990; Kile et al. 1995).

Finally, the results of several laboratory studies suggest that increased equilibration time between contaminants and sediments results in decreased bioavailability of organic contaminants to benthic organisms (McElroy and Means, 1988; Landrum, 1989). Several mechanisms have been proposed to explain the observed decreases in bioavailability including contaminant diffusion into less bioavailable sediment compartments and removal of ingestible particles through packaging into fecal pellets (Landrum, 1989).

2.5 Biological Factors

The degree of bioavailability of the contaminant under various exposure scenarios determines the *potential* for bioaccumulation and toxicity. Toxicity ultimately is determined by the exposure of an animal to bioavailable contaminants in concert with the animal's sensitivity to the contaminant. Bioaccumulation is a function of the bioavailability of contaminants in combination with species-specific uptake and elimination processes. These processes have been shown to be a function of the organism's lipid content (Landrum, 1988), size (Landrum et al., 1992), growth rate, gender, diet, and ability to metabolize or transform a given contaminant, as well as the chemical conditions of the surrounding medium. For example, conditions such as temperature and dissolved oxygen concentrations can affect the observed contaminant uptake rate by influencing an organism's metabolic rate and thus the respiration and ventilation rate. Spigarelli et al. (1983) found that ambient temperature affected PCB bioaccumulation in brown trout by affecting food consumption, growth, and lipid content. Connell and Miller (1984) reported that low dissolved oxygen concentrations can increase the ventilation rate of aquatic organisms, which may result in increased uptake rates.

Bioturbation of sediments by benthic organisms can alter the physical and chemical characteristics of the sediment. A recent study of the effects of bioturbation on the bioavailability of cationic metals showed that bioturbation can enhance the bioavailability of some cationic metals in surficial sediments. Burrowing activity of the oligochaete *Lumbriculus variegatus* significantly reduced AVS concentrations in surficial sediments and resulted in elevated interstitial water concentrations of cadmium (Peterson et al., 1996).

The physical reworking of sediment in laboratory microcosms by oligochaetes has been shown to result in enhanced contaminant concentrations (i.e., hexachlorobenzene, pentachlorobenzene, and trifluralin) in the surface sediments (Karickhoff and Morris, 1985). This reverse "conveyor belt" type of bioturbation occurs when fine sediments are ingested at depth and egested as fecal material in the sediment surface. The rate of contaminant transport as a result of bioturbation is independent of the chemical characteristics of the sorbed contaminants and is much more rapid than the chemical transport of these compounds through diffusion and sorption processes. However, the release of the reworked contaminants to the overlying water was less than that predicted due to slow contaminant desorption from fecal pellets (Karickhoff and Morris, 1985).

The degree of biotransformation or biodegradation of a contaminant may be strongly influenced by the degree to which the compound is associated with sediment particles. Shimp et al. (1990) stated that modeling chemical residence time in sediments is more difficult than modeling biodegradation in other media because of the influence of partitioning (which determines the proportion of a discharged mass that reaches the sediments), the rate at which sediment particles settle to the bottom, the rate at which particles can be buried, and the extent to which particles are resuspended and transported downstream.

They also noted that biodegradation of a chemical mass adsorbed to sediment particles can change when the particle is buried and the environment becomes anoxic or anaerobic. Boethling et al. (1995) found that contaminant adsorption to sediment particles resulted in enhanced biodegradability.

Other biological factors that can affect contaminant bioavailability include the burrowing and feeding behavior of the individual organism or species. The depth to which an organism burrows, the type of feeding mechanism it uses (e.g., filter feeding, particle ingestion), the size range of the sediment particles it consumes (Harkey et al., 1994b), and its diet all have a large influence on the concentration of contaminant to which the organism will be exposed.

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3. METHODS FOR ASSESSING BIOACCUMULATION

3.1 Introduction

The factors controlling the partitioning of a contaminant in the environment and its movement through the food chain are as complex as the factors controlling its toxicity once it has been taken up by an organism. This chapter describes a number of approaches that are potentially useful tools for assessing bioaccumulation. It has been divided into two main sections, with the first describing methods to measure bioaccumulation directly and the second describing methods to model bioaccumulation. The selection of the appropriate approach is dependent on what questions are being asked, the type of environment, the species, and the contaminants of concern.

Because of the uncertainties associated with the use of predictive bioaccumulation and biomagnification models, EPA prefers that the bioaccumulation potential of a chemical be determined by direct field measurements, although the Agency recognizes that in many cases direct measurements are not possible (USEPA, 1996a). As part of the Great Lakes Water Quality Initiative (USEPA, 1993a; 1995a), EPA listed three possible approaches for determining bioaccumulation factors (BAFs), in order of the Agency's preference:

1. A field-measured BAF, using animals living at or near the top of the food chain.

2. A laboratory-measured BCF, multiplied by an appropriate factor (food chain multiplier, or FCM), reflecting the difference between the laboratory organisms and the field organisms.

3. A BCF modeled from a chemical's octanol-water partitioning coefficient, multiplied by an appropriate FCM.

The following questions, as presented in Boese and Lee (1992), are useful in determining the most appropriate approach for evaluating bioaccumulation. Although this list of questions was developed for bedded sediment tests, the questions are generally applicable to any type of direct measurement of bioaccumulation.

- *Is the goal to monitor existing bioaccumulation or to predict bioaccumulation under future exposure conditions?*

Direct measurement of bioaccumulation will give a snapshot of the tissue residues at the time and location of sampling. Direct measurement can be accomplished either by measuring tissue concentrations in field-collected organisms or by conducting laboratory bioaccumulation tests using field-collected sediments. On the other hand, predictive modeling can also be used to estimate the extent and/or pattern of bioaccumulation of specific substances under specified exposure conditions. Predictive models can be used when it is not practical to directly measure tissue concentrations (i.e., to determine how tissue concentrations will change over time following a change in exposure conditions). Predictive models can also be used as a screening tool to determine whether it is appropriate to make direct measures of bioaccumulation.

- *Is the test or model being used as a screening tool or as an accurate predictor?*

It is important to clearly identify the data quality objectives before a bioaccumulation study is conducted because the types of questions answered will be dependent on the data collected or generated. Predictive models can cost less and can be run without site-specific data, but the more generic the model, the more the predictions will be subject to high uncertainty. On the other hand, site-specific measurements of contaminant concentrations in sediment and tissue can be highly accurate and precise, but they generally have more limited predictive capacity; i.e., they are not useful for prediction of the impacts of changing environmental conditions or for cross-species extrapolation of results.

- *Is the goal to qualitatively identify which sediment compounds will bioaccumulate or to develop quantitative estimates of tissue concentrations for these compounds?*

If the ultimate goal of an investigation is to determine whether chemicals that bioaccumulate are present in a sediment sample, relatively simple and inexpensive short-term tests can be used. However, the duration of such tests is generally insufficient to allow tissue concentrations in test organisms to reach steady state with sediment or water concentrations. If quantitative estimates of tissue concentrations in exposed organisms are required, longer-term tests, (i.e., a minimum of 28 days) are required. Boese and Lee (1992) list a number of studies using different organisms and exposures, along with estimates of the percentages of steady-state tissue concentrations reached after 10- and 28-day exposures.

- *Will conditions required to reach steady state be met?*

Bioaccumulation is typically measured at steady state (Spacie and Hamelink, 1984). Four factors might prevent steady-state conditions from being achieved in an exposure study: (1) sediment contaminant concentration or bioavailability changes during the course of the study, (2) the exposure period is insufficient to reach steady state, (3) an animal's ability to bioaccumulate the chemical is altered during the course of the exposure period, and (4) additional uptake routes that have not been accounted for exist.

- *Are uptake routes in addition to sediment exposure likely to be important?*

A number of potential exposure routes might be present, depending on the test species and chemical of concern. It is important to identify each of these routes prior to test initiation to prevent substantial underestimations of bioaccumulation.

- *Is a goal to determine or predict the time course of uptake and/or elimination?*

A kinetic model will be more useful than a partitioning model to predict how tissue concentrations will change over time. Kinetic models are very useful for determining how long it will take for tissue concentrations to reach a desired level, for example, how long it will take to decrease to a no-effect level after cleanup has occurred.

- *Is it required that local species be used in the assessment?*

Either standard testing species or indigenous organisms can be used in a bioaccumulation study. The use of indigenous species is desirable since the results of a study using such species would have greater ecological significance as well as relevance to the site under investigation. Standard testing species have the obvious advantage of being easier to maintain in the laboratory because the requirements for their

survival in the laboratory have been well studied. Results of studies using standard test species are also directly applicable to other studies using the same species. On the other hand, a number of problems are associated with the use of standard, nonindigenous species, particularly the potential inability to extrapolate results to indigenous species.

- *Is more than one species to be tested?*

A single species might be adequate for survey work and most research studies. For regulatory testing, however, two species from different taxa are often required. Bivalve species have been identified as good candidates for testing the bioaccumulation potential of PAHs (USEPA and USACE, 1991).

- *Will field or experimentally spiked sediments be used?*

Field sediments are used when a particular site is being evaluated or when dredged material is being tested. Spiked sediments are typically used when a new compound is being evaluated. There are inherent problems in both approaches. With field sediments, collection, handling, and transportation can result in chemical alterations, and the presence of multiple contaminants can confound results. Although spiked test sediments, using artificially prepared sediments or sediments taken from a "clean" reference area, can avoid some of the problems associated with field-collected sediments, they may not be fully representative of natural conditions found at the site of concern.

3.2 Laboratory and Field Methods for Assessing Bioaccumulation

Direct or empirical determination is the simplest approach to measure bioaccumulation in aquatic organisms. Direct determination can be conducted using either laboratory-exposed or field-collected organisms, and generally this approach minimizes or eliminates many of the problems associated with modeling (see below). However, the costs associated with empirical determinations of bioaccumulation can be high, and the results of these determinations typically have only site-specific or study-specific applicability. It must also be recognized that bioaccumulation testing may only deal with the first step in a bioaccumulation chain in which higher levels are typically of interest.

For compounds with a log K_{ow} greater than 6.5, there is a loss of linearity between K_{ow} and bioaccumulation, resulting in considerable uncertainty in modeled predictions of biological uptake. Thus, for these compounds, direct determination is generally the most reliable method for assessing bioaccumulation.

3.2.1 Laboratory Determination of Bioaccumulation

Important issues in laboratory determinations of bioaccumulation of chemicals from sediments include selection of an appropriate test species, sediment sampling and handling methods, conditions during exposure to the sediment, exposure duration, and statistical analyses.

3.2.1.1 Test Species Selection

Ankley et al. (1992) list a number of key factors to consider when selecting appropriate test organisms for standardized sediment bioaccumulation tests, including the following:

- The ability to reflect the ecological position of the species of concern in the field to ensure a realistic exposure scenario.

- A healthy condition and capability to remain healthy during the course of the laboratory exposure.
- Availability throughout the year.
- A relatively well defined exposure history.
- The ability to be reared in a laboratory.
- Adequate biomass for chemical analyses.
- The ability to withstand the long-term exposure periods necessary to reach equilibrium.

For bioaccumulation tests with whole sediment, Boese and Lee (1992) have identified a number of additional factors that are important to consider when selecting an invertebrate test species. Species that provide the most meaningful results for sediment bioaccumulation tests are (1) those in which ingested sediment is the major uptake route for higher-K_{ow} compounds (Landrum, 1989), (2) those which are sufficiently pollution-tolerant and can survive relatively long exposure times, (3) infaunal species tolerant to a wide range of sediment and water quality characteristics, and (4) those which have a low potential for metabolizing contaminants of concern.

Based on the factors listed above, Ankley et al. (1992) believe that the oligochaete *Lumbriculus variegatus* is an appropriate freshwater test species for most situations. They prefer this species because it is relatively easy to culture and handle; it is tolerant to a relatively wide range of sediment characteristics, including particle size and organic carbon content; and it is adaptable to long-term test exposures. Other freshwater oligochaete species that appear to satisfy the criteria are *Stylodrilus heringianus, Limnodrilus hoffmeisteri, Tubifex tubifex,* and *Pristina leidyi*. Using essentially the same criteria, Ingersoll et al. (1995) recommended the use of the amphipod *Hyalella azteca* and the midge *Chironomus tentans* for testing freshwater sediments, although Ingersoll et al. (1998) noted that amphipods may not be suitable test species because of their small tissue mass and sensitivity, while the midge's life cycle may be too short.

Lee et al. (1993) recommended five bioaccumulation test species for marine evaluations based on their feeding type, biomass, salinity tolerance, pollution tolerance, culture potential, bioaccumulation toxicity information, commercial availability, and historical use in a substantial number of experimental bioaccumulation studies and regulatory monitoring programs. The five species are the polychaetes *Nereis diversicolor* and *Neanthes (Nereis) virens* and the bivalves *Macoma nasuta, Macoma balthica*, and *Yoldia limatula*. Lee et al. (1993) recommended that at least one of these species be used in all testing situations, and USEPA and USACE (1991) recommend that bioaccumulation tests include a deposit-feeding bivalve mollusk and a burrowing polychaete. Eight secondary taxa were also recommended by Lee et al. (1993) if certain site-specific requirements are important such as large organism size (arenicolid worms), additional phylogenetic groups (i.e., crustaceans), adaptability to culturing (e.g., *Neanthes arenaceodentata*), and high pollution tolerance (*Capitella* spp.).

Mac and Schmitt (1992) argue that bioaccumulation testing with fish has a number of advantages over testing with invertebrates. Certain fish species resuspend sediments, increasing contaminant bioavailability. Fish can provide adequate tissue mass for chemical analysis, and because they have higher lipid mass than invertebrates, tissue mass requirements for organic contaminant analyses are further reduced. Fish can also receive sediment-associated contaminant exposure from several routes, including direct ingestion and accumulation through gills and skin, and their gills may act as a substrate for the dissociation of hydrophobic chemicals from sediment particles. Finally, fish can be used in

laboratory exposure experiments, as well as in *in situ* studies with caged or free-ranging animals, and they are often of more direct concern regarding biomagnification and human health.

Although fish have the potential to be good laboratory models for bioaccumulation studies, to date only one standardized testing protocol has been published (Mac et al., 1990). This test, using the fathead minnow (*Pimephales promelas*), measures the bioavailability of contaminants in sediments from freshwater systems. No similar test for marine species has achieved wide acceptance, although several species have been used successfully in laboratory studies on bioaccumulation. These species include spot *(Leiostomus xanthurus*), sheepshead minnow (*Cyprinodon variegatus*), and Atlantic silverside (*Menidia menidia*) (Rubinstein et al., 1984a,b).

3.2.1.2 Sediment Sampling and Exposure Conditions

Laboratory testing can eliminate a number of the problems associated with field testing, particularly the spatial and temporal variability associated with natural exposure. However, laboratory testing can create a number of additional problems that are important to consider when designing a study. For example, proper handling of sediment samples and test animals is critical, as is maintaining optimal conditions for animal survival throughout the test period.

Either field-collected or experimentally manipulated (spiked) sediments can be used in laboratory tests. In both cases, however, handling, transport, and manipulation of test sediments can result in the loss of fine sediments, interstitial water, and water-soluble compounds. Cross contamination with metals and organic compounds can occur, as can changes in grain size distribution, chemical concentrations, and sorption equilibria. Details on methods for sediment collection, laboratory setup, and design and conduct of tests can be found in Lee et al. (1993), ASTM (1988, 1992, 1996), and USEPA (In prep.).

3.2.1.3 Exposure Duration

Exposure duration is a critical aspect of experimental design in bioaccumulation testing. If the goal of a test is simply to determine whether contaminants are bioavailable or the potential for bioaccumulation exists, short-term (10- to 28-day) tests can be used, although USEPA and USACE (1998) recommend 28-day tests. However, even data from 28-day exposures should not be assumed to represent steady-state conditions (Mac and Schmitt, 1992). Boese et al. (1997) conducted 28-day bioaccumulation tests with *Macoma nasuta* and both PCB-spiked sediment and DDT-contaminated sediment. Compared to steady-state BAFs measured under similar laboratory conditions, BAFs (C_t/C_s) measured after 28 days ranged from 10 percent to 155 percent of steady-state BAFs, with only 5 of 22 PCB congeners or DDT family compounds within 80 percent of steady state. Four of these five congeners were the most hydrophobic congeners measured (i.e., PCB 170, 180, 194, and 209). This is particularly true of chemicals with log K_{ow} greater than 4, for which bioaccumulation through the food chain becomes more important.

Ankley et al. (1992) compared bioaccumulation of PCBs by laboratory-exposed *L. variegatus* and field-collected oligochaetes. They found good agreement between both groups in terms of uptake of PCB homologues with six or fewer chlorines, but field-collected oligochaetes tended to have higher concentrations of the heptachloro through decachloro congeners. The authors concluded that the field-collected oligochaetes were at equilibrium, suggesting that laboratory exposures of greater than 30 days would be required to achieve steady state for compounds having log K_{ow} values greater than 7.0 to 8.0. Similar results were obtained by Rathbun et al. (1987, cited in Mac and Schmitt, 1992) when comparing PCB uptake by caged and resident fish in a confined disposal facility.

As a general goal, ASTM (1996) recommends that bioaccumulation tests be of sufficient duration to reach 80 percent of steady state. For a variety of reasons, this is not always possible. However, methods have been developed to extrapolate results of 28-day bioaccumulation tests to derive steady-state tissue concentration. For example, the log K_{ow} of a neutral organic compound of concern can be compared with the log K_{ow} in Figure 3-1 to indicate the proportion of steady-state concentration (Css) expected in 28 days. This will allow estimation of the steady-state value from the 28-day laboratory exposure data through the use of a steady-state correction factor. The correction factor is the reciprocal of the decimal fraction indicating the proportion of Css expected in 28 days (USEPA and USACE 1998). For example, if the 28-day uptake is one-third of steady state, the correction factor is 1/0.33 or 3. Correction factors can be obtained from previous laboratory studies (e.g., Boese and Lee, 1992, cited in Lee et al., 1993).

3.2.2 Field Determination of Bioaccumulation

Measuring bioaccumulation at a particular site requires consideration of which test species to use, whether to examine natural populations or use transplanted populations, and how to compare bioaccumulation occurring under conditions at a potentially contaminated site with that occurring at a reference site.

3.2.2.1 Caged vs. Natural Populations

For field determinations of bioaccumulation, test animals can be taken from resident populations at the site of concern or can be transplanted from other locations and maintained at the site of concern in cages or other holding systems. The advantages and disadvantages of each approach are discussed in this subsection.

The use of transplanted test animals confined to cages can simplify field assessment of bioaccumulation in a number of ways. Test animals can often be obtained from commercial vendors in large quantities or from uncontaminated reference locations. Because of this, variability associated with exposure conditions and times for individual test animals can be eliminated. All test organisms can begin the exposure period with the same, or similar, background contaminant concentrations in their tissues, and they will receive essentially the same exposure during the test period. Test animals can be selected based on size and age, as well as sex. Studies can also be designed so that water column and sediment exposures can be differentiated and uptake kinetics can be studied *in situ*. Finally, and perhaps most importantly, exposure concentrations or conditions can be accurately determined because the animals will be confined to a small, well-defined area. The exposure period is controlled by the investigator, permitting time to steady state and other issues to be considered when designing a transplant study with caged animals. Transplant studies provide a balance between experimental control and environmental realism not usually attained with either standard laboratory bioassays or assessment of resident populations.

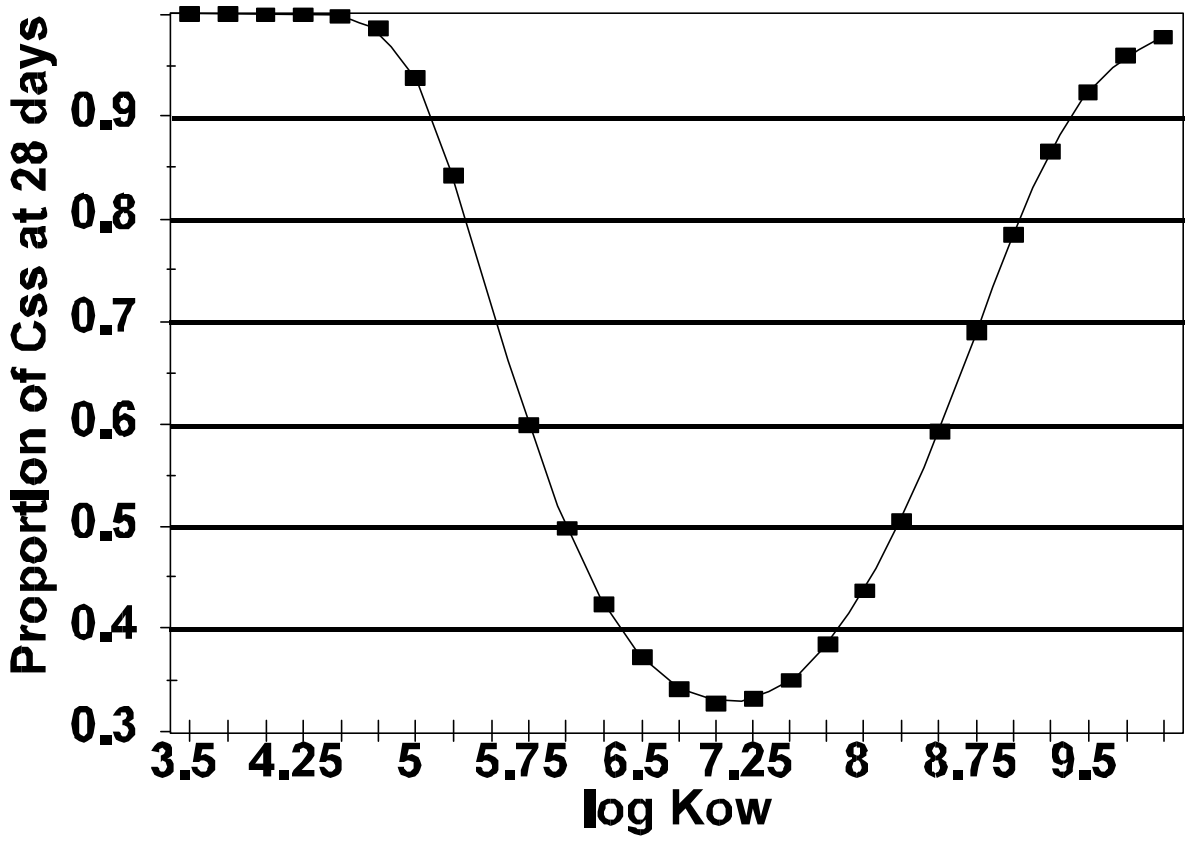

Figure 3-1. Expected Proportion of Steady-state Concentration (Css) of Neutral Organic Compounds Reached in 28-day Laboratory Exposures. The proportion is a function of the log K_{ow} of the compound of interest. Figure adapted from McFarland (1994).)

Transplant studies with caged animals are usually conducted with sedentary species (i.e., bivalves) or mobile species with very limited home ranges, so that accurate exposures can be determined. For the most part, this requirement limits test species to lower-trophic-level (i.e., prey) organisms. If larger, more mobile species such as fish are used, exposure might not be realistic because these animals might have difficulty feeding properly and food chain transfer might not be adequately assessed, thus introducing large uncertainty into estimates of bioaccumulation. Furthermore, stresses associated with handling and crowding could have important effects on the physiology of larger, mobile species.

The greatest advantage to assessing native, free-ranging populations is the potential to evaluate bioaccumulation from all routes of exposure *in situ*. Unfortunately, it is difficult to determine exposure concentrations for all but the most sedentary wild animals. Free-ranging animals might experience a wide range of exposures throughout their home ranges, and for predatory species these home ranges can be quite large. Exposure concentrations can be averaged throughout an animal's home range, although this approach might underestimate the contribution of contaminant hot spots to the animal's total loading, resulting in an overestimation of bioaccumulation factors. Another common approach is to use an upper confidence limit on the range of exposures. This latter approach provides a more conservative estimate of the actual exposure concentration an animal receives, although it might result in an underestimation of

bioaccumulation factors.

In addition to problems associated with estimating exposure concentrations, it is also difficult to estimate exposure duration in native, free-ranging populations. Animals might have been in the sampling area for a considerable length of time or only briefly. Without some means of tracking a free-ranging animal's movements prior to capture, the duration of its exposure becomes an unknown variable. Also, collection of adequate sample sizes can be difficult, particularly when data quality objectives require the use of single species, sexes, and age classes.

3.2.2.2 Species Selection

Selection of test species for field determinations of bioaccumulation is somewhat simplified compared to species selection for laboratory testing. If resident species are used, the choice of species will obviously be limited to whatever species are available at the site of concern. If one is attempting to accurately determine the relationship between tissue concentrations in a species and sediment exposure point concentrations, it is critical that test animals be closely matched according to age, sex, and size. Otherwise, variability in a population of animals will be too great. Animals that are experiencing major physiological changes, e.g., female fish producing vitellogenin prior to spawning, might not be at steady state and, therefore would be inappropriate for bioaccumulation studies. Although it might be desirable to evaluate bioaccumulation in higher-trophic-level organisms, such as predatory birds and fish, these species typically have large home ranges, introducing considerable uncertainty into estimates of exposure concentrations. Furthermore, these species integrate exposures over relatively long time frames, and their tissue concentrations are generally not reflective of short-term changes in exposure concentrations. Thus, if the goal of a study is to evaluate changes in bioaccumulation over short time frames (e.g., during the course of a dredging or remediation project), sedentary or lower-trophic-level species can be used.

A variety of species can be used in transplant studies, with the preferred species for a particular site a function of natural occurrence. In general, it is preferred to use species that already inhabit the area of concern, but surrogate species can be used with permission from state regulatory officials. The use of surrogate or closely related species is often a desired approach because it provides flexibility in the number of species under consideration and available sources. The primary concerns with transplanted species are introduction of unwanted or exotic species and introduction of disease or parasites.

Another approach that might have some utility in field investigations involves the deployment of semipermeable membrane devices (SPMDs), which use thin-walled, lay-flat polyethylene tubing filled with a thin film of a large-molecular-mass, neutral lipid, such as triolein. Huckins et al. (1990, 1993, 1994) have described the theory and use of SPMDs in detail. Although compounds associated with particles, DOC, or colloids cannot pass through the membranes of SPMDs, and therefore are not accumulated by them, SPMDs can be used to estimate the concentration of superhydrophobic compounds in the freely dissolved state. Since bioaccumulation of compounds that are both freely dissolved and associated with dissolved or particulate matter can occur, concentrations measured by SPMDs may likely underestimate uptake by organisms.

3.2.2.3 Reference Sediment Selection

When assessing bioaccumulation at a given site, it is often desirable to use an appropriate reference site to obtain sediment for comparison. A reference sediment is collected near an area of concern and is used to assess sediment conditions exclusive of material(s) of interest (ASTM, 1994). Because reference sediment is not "control" sediment, the reference sediment may have some level of contamination. A control sediment is a well-characterized sediment that provides a measure of test conditions and acceptability by providing information on the health and relative quality of the test organisms. Control sediment is not necessarily collected near the site of concern. Testing a reference sediment, therefore, provides a site-specific basis for evaluating toxicity.

Ideally, reference sites should reflect ambient conditions. Selection of a reference site should avoid areas in the immediate vicinity of, including depositional zones of, spills, outfalls, or other significant sources of contaminants, in addition to areas that are subject to sediment migration of previous dredge material discharges (Federal Register, 1995). In addition to reference site selection based on contaminant concentrations, it is also critical to select reference locations based on their similarity to the test site in terms of habitat type, flow characteristics, physical characteristics of the sediment, and aquatic communities present.

3.2.3 Statistical Design Considerations

Although uncertainty and bias are to a certain degree unavoidable in field- or laboratory-based bioaccumulation studies, it is critical that they be minimized as much as possible. It would be beyond the scope of this document to provide detailed information on how to design statistically sound sampling or testing programs; however, some key statistical design considerations are discussed below. More detailed information on this subject has been summarized elsewhere (EVS, 1995; Baudo, 1990).

According to EVS (1995), bias and uncertainty can be reduced by carefully defining the population(s) of interest. This can be accomplished in a number of ways, including the following:

- Dividing the population to be sampled into logical strata, e.g., substrate type for sediments; sex, age, and weight for biota samples.
- Using adequate replication and sampling over spatial and temporal scales relevant to the sample types; i.e., the size of an area to be characterized is based on the size of the test species' home range.
- Conducting synoptic sampling; i.e., sampling all media types over the same spatial and temporal scales
- Ensuring that samples being collected are representative of the population being evaluated; i.e., if the study is being conducted to evaluate bioaccumulation in an entire population of organisms, sampling should not be biased to include only one segment of that population.

Compositing of samples can also be used to reduce costs and increase statistical power. The main drawback of compositing sediment samples is that, unless taken into full consideration in the sampling design, information regarding the concentrations of contaminants at hot spots can be lost by mixing these sediments with other less contaminated sediment. On the other hand, if one is attempting to establish the relationship between contaminant concentrations in sediment and contaminant concentrations in the tissues of a fish species with a large home range, compositing sediment samples might be appropriate since the composite concentration might provide a more accurate representation of

the animal's exposure. When dealing with sedentary organisms or organisms with limited home ranges, it is more appropriate to relate tissue concentrations to single exposure point concentrations.

By using the widest range of exposure point concentrations, site-specific relationships can be developed between contaminant exposures and biological uptake, particularly if existing information on contaminant gradients at the site is available. A wide range of exposure point concentrations make it possible to perform regression analyses. The collection of organisms from hot spots and the chemical analysis of their tissues might not be representative of their population as a whole and might bias the site-specific relationship. Similarly, it might be inappropriate to chemically analyze tissues of test animals from laboratory bioassays characterized by significant mortality among test species (i.e., sediments from hot spots) because of the strong potential for bias due to unrepresentative accumulation by the test organisms.

While investigators frequently attempt to make predictions at one site based on relationships observed at another, such predictions are valid only within the ranges of the variables measured. Attempts to extrapolate outside these ranges will introduce unquantifiable uncertainty into the predictions.

Detailed information on appropriate methods for stratified sampling can be found in Snedecor and Cochran (1980) and Gilbert (1987). USEPA (1994a) provides a discussion on spatial averaging, and Gilbert (1987) discusses factors to consider when deciding whether to composite samples.

3.3 Approaches for Modeling Bioaccumulation

USEPA currently believes that both mechanistic and empirical modeling approaches are needed to improve bioaccumulation predictions (USEPA, 1996a). Empirically derived bioaccumulation indicators appear to be more accurate, but properly validated models can be used to predict biomagnification and bioaccumulation in some cases (USEPA, 1996a).

3.3.1 Introduction

There are two main approaches to model development: (1) an empirical approach in which laboratory or field data are interpreted to calculate parameters such as bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) and (2) a mathematical approach that employs kinetic or equilibrium models, generally referred to as food web models, in which the mechanistic aspects of bioaccumulation are considered. These two approaches are not mutually exclusive since quality field data are normally used to calibrate and confirm mathematical-approach models, and in turn these models provide useful insight regarding field study design and key parameters to measure. The validity and utility of any model is largely dependent on the quality of input parameters used and the level of uncertainty acceptable in model outputs. The type of model chosen is dependent on the goals of the study, exposure scenario, required accuracy and precision, availability of data, and available resources (Boese and Lee, 1992), as discussed in Section 3.1.

The different approaches for modeling are described in this section to provide a basis for understanding the link between concentrations of contaminants in sediment and bioaccumulation by aquatic and terrestrial biota, including humans.

3.3.2 Empirical Models

Direct or empirical determination is the simplest approach to monitoring or assessing bioaccumulation in aquatic organisms and is the recommended approach when the highest degree of accuracy is required (e.g., in support of regulatory actions) (USEPA, 1996a). Methods for bioaccumulation testing are discussed in Section 3.2. For field-measured bioaccumulation estimates to be reliable and useful, the field study design and data interpretation components must be carefully considered and standardized. Several studies have shown that field-measured BAFs and BSAFs can vary as a function of location and time and among species, even at similar trophic levels (Connolly and Glaser, 1998; Hydroqual, Inc., 1995). This section discusses the different quantitative measures of bioaccumulation processes currently in use.

3.3.2.1 Bioconcentration Factors

Bioconcentration is the uptake of a contaminant from water by aquatic organisms where water is the only pathway. Bioconcentration factors (BCFs, expressed as L/kg of tissue), as defined in Equation 1, are based on laboratory studies of organisms exposed to water containing a chemical of concern, where C_t is the concentration of a contaminant in the tissue of the organism (mg/kg, preferably dry weight, but moisture content should also be reported) and C_w is the concentration in water (mg/L) defined in terms of whether it is the total, dissolved, or truly dissolved (noncomplexed) concentration. (The last is preferred.)

$$BCF = C_t/C_w \qquad (1)$$

BCFs are most useful for small, low-trophic-level organisms such as phytoplankton, which are in rapid equilibrium with substances in water, for chemicals with log K_{ow}s up to 5 (Spacie et al., 1995). BCFs do not account for biomagnification of chemicals in the food web (USEPA, 1996a). Hence, for larger, higher-trophic-level organisms, BCFs have been shown to underestimate bioaccumulation potential for hydrophobic compounds that have log K_{ow} values greater than or equal to 4.5 and are resistant to metabolism and degradation.

3.3.2.2 Bioaccumulation Factors

In USEPA (1995b), the bioaccumulation factor (BAF) is defined as “the ratio of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time.” BAFs have been used successfully to predict tissue residues of polar organic compounds, neutral organic compounds, and metals.

Data from laboratory or field bioaccumulation studies can be used to generate BAFs, which are the ratios between contaminant concentrations in organisms and environmental media. BAFs can be calculated as the product of BCFs and food chain multipliers (FCMs) or they can be measured empirically. EPA prefers the latter (USEPA, 1995b, 1996a). Empirical BAFs are most useful since they integrate all environmental routes of exposure and take into account bioavailability considerations for the system under study. Field-measured BAFs are especially important for compounds with log K_{ow} values greater than 6 since prediction of bioaccumulation of these compounds is overestimated if based on their hydrophobicity alone (Spacie et al., 1995). Note that for compounds with very low solubility, which makes their analytical detection in water challenging (e.g., certain PCB congeners, dibenzo-*p*-dioxins,

dibenzofurans), BSAF-corrected BAFs are also recommended (USEPA, 1995b). See Cook et al. (1993) and USEPA (1995b) for methods.

Two empirical BAFs have been reported in the literature, where they are defined as the concentration of contaminant in tissue divided by either the concentration of contaminant measured in water (USEPA, 1995b) or the concentration of contaminant measured in sediment (Lee, 1992; Boese and Lee, 1992) (Equations 2 and 3, respectively). Note that BAFs can be converted to less variable BSAFs if lipid and total organic carbon (TOC) contents are known, as discussed in the next section. As with BCFs, the type of water concentration (whether it be freely dissolved [uncomplexed], dissolved [filtered], and total [unfiltered]) in the BAF expression must be clearly defined. Guidance is available to calculate the BAF in terms of freely dissolved concentration in the water when data regarding total concentrations in the water, particulate organic carbon (POC), and dissolved organic carbon (DOC) measurements are available (USEPA, 1995b).

$$BAF_w = C_t/C_w \qquad (2)$$

$$BAF_S = C_t/C_s \qquad (3)$$

Where BAF is the BAF calculated using empirical data (L/kg of tissue, or kg of sediment/kg of tissue); C_t is the concentration of a contaminant in the tissues of an organism (mg/kg, preferably dry weight, but moisture content should also be reported); C_s is the concentration of contaminant in the sediment (mg/kg, preferably dry weight); and C_w is the concentration of the contaminant in the water (mg/L).

Empirical BAFs are general and do not discriminate among exposure routes, rates of uptake or elimination, or species' physiology. However, the BAFs can be calculated correctly only if the field design accounts for the exposure scenarios for the species of interest, including migration, spatial and temporal patterns in contaminant concentrations, and life history considerations of the organism (age, gender) (USEPA, 1994a; EVS, 1995). These factors are typically derived on a site- or study-specific basis, and they can vary considerably with water body, sediment type, and species (Rubinstein et al., 1983).

BAFs can also vary with time if the concentrations are changing as a function of time in water or organisms. As environmental conditions change, the predictive capacity of BAF diminishes considerably since the BAF is operationally defined for only those conditions during which the measurements were made. For situations with varying contaminant exposure, kinetic models, described in Section 3.3.3.1, are more appropriate.

3.3.2.3 Biota-Sediment Accumulation Factors

In USEPA (1995b), BSAFs are defined as

> the ratio of a substance's lipid-normalized concentration in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment, in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism.

Site-specific BSAFs (kg of organic carbon/kg of lipid) are calculated for nonpolar organic compounds using the formula

$$BSAF = (C_t/f_1) / (C_s/f_{oc}) \qquad (4)$$

where C_t is the contaminant concentration in the organism (both wet and dry weight are commonly used, so moisture content should be provided whichever is used, as well as a clear delineation of which is selected), f_1 is the lipid fraction in tissue, C_s is the contaminant concentration in sediment (generally dry weight), and f_{oc} is the organic carbon fraction in sediment. This lipid-normalized relationship was developed for neutral (nonionic) organic compounds and is not appropriate for inorganic substances (e.g., metals), although it has been applied to tributyltin (Eisler, 1989). This relationship is not applicable to methylmercury because methylmercury binds tightly to tissue macromolecules (Spacie et al., 1995; Bridges et al. 1996).

One of the basic premises of equilibrium-based modeling as related to sediments is the equilibrium partitioning theory (Di Toro et al., 1991). This theory is being used to propose sediment quality guidelines for two nonionic organic compounds (e.g., USEPA, 1994b), as well as for PAH mixtures and metals mixtures. The essence of the theory is that concentrations of hydrophobic chemicals in sediments are more predictive of biological effects when they are normalized to sedimentary organic carbon. Through this normalization, the concentration of these compounds in the pore water can be predicted based on Equation 5. Evidence to date indicates that chemicals that are freely dissolved in the pore water are more bioavailable than chemicals sorbed to sediments. Thus the pore water concentration, as measured or as predicted through equilibrium partitioning, is a better predictor of bioaccumulation than concentrations of chemicals on a dry weight basis in the sediment (Di Toro et al., 1991).

$$C_w = C_s/f_{oc}K_{oc} \qquad (5)$$

where C_w is the freely dissolved concentration of nonionic chemical compound in pore water, C_s is the concentration of the chemical in the sediment, f_{oc} is the fraction of sedimentary organic carbon, and K_{oc} is the organic carbon-water partition coefficient (which can be related to K_{ow}).

As with BAFs, BSAFs are typically derived on a site- and species-specific basis, using empirical data (USEPA, 1992a). Therefore, they incorporate the effects of metabolism, biomagnification, growth, and bioavailability. BSAFs can also be used to estimate BAF_{fd}, as described in Cook et al. (1993) and USEPA (1995b), where BAF_{fd} is defined as follows, where C_{fd} is the freely dissolved concentration of a contaminant in water:

$$BAF_{fd} = C_t/C_{fd} \qquad (6)$$

Accurate information on organism lipid content and sediment TOC content is required to calculate a BSAF. Lipid content can vary considerably within a single species, based on life stage, sex, and season, so caution is necessary when attempting to use site- or species-specific BSAFs as predictors of tissue burdens in different systems. As with BAFs, proper calculation requires a reasoned approach regarding species exposure, including movement and life history as well as spatial and temporal trends.

BSAFs are most directly applied to infaunal organisms with known home range. For example, Lake et al. (1990) found that analysis of PCBs in mollusks and polychaetes at field sites representing a range of TOC and contaminant concentrations showed that BSAF calculations (i.e., lipid- and TOC-normalized concentrations) significantly reduced the variability in the raw tissue-sediment data relative to non-

normalized data. Work by Hydroqual, Inc. (1995), however, has shown that lipid normalization does not always decrease the variability in BAFs (or BSAFs) and that the decision to lipid normalize and the method by which lipid normalization is achieved depend on species-specific factors as well as lipid contents.

Since ecosystems are rarely in equilibrium, BSAFs include an inherent measure of disequilibrium of the system, which can be quantified as described in USEPA (1995b). Disequilibrium is caused by kinetic limitations for chemical transfer from sediment to water, sediment to biota, or water to the food chain, as well as biological processes such as growth or biotransformation (USEPA, 1995b). Theoretically, at equilibrium BSAFs range from 1 to 4 since the ratio of K_l to (K_l/K_{soc}) is thought to range from 1 to 4, where K_l is defined as the lipid-water equilibrium partition coefficient and K_{soc} is defined as the sediment organic carbon-water equilibrium partition coefficient (USEPA, 1995b). However, since most systems are not at equilibrium, a wider range of BSAFs is reported. This wider range of BSAFs measured in the field does not invalidate the concept. On the contrary, it underlines the need for a field-measured BSAF that is able to incorporate disequilibrium processes (as well as exposure conditions). Several compilations of BSAFs are available, including Lee (1992), Boese and Lee (1992), and Parkerton et al. (1993), as well as a USACE Contaminants Database accessible via the Internet (McFarland and Fergusen, 1994a).

The use of site-specific BSAFs using techniques described in USEPA (1994a) is preferred. However, if literature values are used, available options include selecting a given percentile of the BSAF distribution (as in the TBP method, which uses the 94th percentile) (McFarland and Ferguson, 1994a) or using a regression equation as in the proposed Washington State guidance for sediment quality criteria for human health (PTI, 1995).

BSAFs are most useful for systems that are in steady state, which is technically defined as concentrations in sediment, water, and organisms that do not change as a function of time even though they may not reflect a thermodynamic equilibrium distribution between sediment, water, and organisms. In a practical sense, systems are often considered steady state if the concentrations do not change within the period of study. Therefore, the use of BSAFs to predict tissue concentrations might not be reliable in situations in which the chemical of interest is rapidly degraded or inputs of the chemical to the system vary. In these instances, kinetic models might be more appropriate (see Section 3.3.3.1).

Hydroqual, Inc. (1995) has developed a database of field-measured bioaccumulation factors for a variety of superhydrophobic compounds. Part of this effort involved development of a procedure whereby BAFs or BSAFs could be predicted for previously unstudied chemicals, species, or water bodies. Hydroqual concluded that within a homogeneous group of compounds (e.g., PCB congeners) BAFs and BSAFs can be predicted only within a factor of 10. The uncertainty arises from site- and species-specific differences in food web structure, partitioning at the base of the food web, and the physiology of the organisms, as well as measurement error (Hydroqual Inc., 1995). Predicting BAFs and BSAFs for chemicals outside the “homogeneous group” results in even greater uncertainty. However, results of chemical class-specific analyses in Tracey and Hansen (1996) revealed a similarity of BSAF values among species and habitat types.

The biota-suspended solids accumulation factor (BSSAF) has also been proposed for some studies. It is identical to the BSAF approach, with the exception that contaminant uptake by fish is from suspended solids, rather than in-place sediments (USEPA, 1994a). Its use has been limited.

3.3.2.4 Food Chain Multiplier

As discussed in Section 3.3.2.2, a BAF can be estimated from a BCF if the BCF is multiplied by a factor to account for food web transfer. This factor is referred to as a food chain multiplier (FCM) (USEPA, 1993a, 1995b).

$$BAF = (BCF)(FCM) \qquad (7)$$

The FCM is defined as the ratio of a BAF to an appropriate BCF (USEPA, 1995b). It has been calculated in a variety of different ways, two of which are discussed briefly below. In both approaches, FCMs are calculated assuming metabolism is negligible.

USEPA (1993a) calculates FCMs using a model of the stepwise increase in the concentration of an organic chemical from phytoplankton (trophic level 1) through the top predatory fish level of a food chain (trophic level 4) (Thomann, 1989). Thomann's model was used to generate BCFs and BAFs for trophic level 2 species (e.g., zooplankton) and BAFs for trophic level 3 and 4 species (small fish and top predator fish, respectively) over a range of chemicals with log K_{ow} values from 3.5 to 6.5. At each log K_{ow} value, FCMs were calculated as follows:

$$FCM2 = BAF2/BCF2 \quad (8)$$

$$FCM3 = BAF3/BCF2 \quad (9)$$

$$FCM4 = BAF4/BCF2 \quad (10)$$

where FCM2, FCM3, and FCM4 are the food chain multipliers for trophic level 2, 3, and 4 species, respectively; BCF2 is the BCF for trophic level 2 organisms; and BAF2, BAF3, and BAF4 are the BAFs for trophic level 2, 3, and 4 species, respectively. Field-measured BAFs from the Great Lakes for trophic level 4 were found to be within an order of magnitude of those predicted using this approach (Thomann, 1989; USEPA, 1993a). At log K_{ow} values of 6.5 and greater, the relationship was less certain.

The FCM is defined below as given in USEPA (1995b), where BAF_{fd} is predicted using the Gobas (1993) bioaccumulation model. In the Gobas (1993) model disequilibrium, as discussed relative to BSAFs in the last section, is included in BAF predictions to some extent by inputting the measured concentrations of the chemical in the sediment and in the water column into the model (USEPA, 1995b). This disequilibrium is then propagated through the food web model.

$$FCM = BAF_{fd}/K_{ow} \qquad (11)$$

The trophic level of an organism is needed when applying FCMs to determine BAFs. Trophic levels have traditionally been described in discrete terms as primary producers, primary consumers, secondary consumers, and top predators. Using this approach, trophic levels are symbolized by whole numbers. However, organisms have clearly defined or uniform food sources only in very rare circumstances. Typically, any organism higher in the food chain than primary consumers is likely at an intermediate trophic level, feeding on multiple trophic levels. As a result, attempting to model trophic transfer using linear food chain models introduces considerable variability into predictions of top predator tissue burdens.

Some methodologies have been developed to address trophic level issues. For example, Broman et al. (1992) have described a method to quantitatively estimate *in situ* biomagnification of organic contaminants that uses ratios of stable isotopes of nitrogen to classify trophic levels of organisms. Carbon and nitrogen isotopes are useful in characterizing an organism's trophic level because animals' metabolic processes tend to enrich the heavy isotopes of these elements, ^{13}C and ^{15}N (Peterson and Fry, 1987). Using this approach, significant enrichment of ^{15}N in tissue relative to ^{15}N in unmetabolized reference samples (i.e., in air) is indicative of increasing trophic levels.

Broman et al. (1992) have used the stable isotope approach to classify trophic levels in a littoral and a pelagic food web in the Baltic, as part of an attempt to study trophic transfer of dioxins and furans in that ecosystem. Based on their results, the authors have concluded that the isotopic method is a powerful tool for quantitatively estimating trophic biomagnification of a contaminant from field data at steady state. However, to evaluate non-steady-state conditions and the relative contributions of various exposure pathways, a more mechanistic approach, such as that described by Thomann (1989), is required. Stable isotope ratios can then be used in conjunction with a more mechanistic approach to provide more refined information on trophic pathways and consumption patterns.

3.3.2.5 Theoretical Bioaccumulation Potential

The theoretical bioaccumulation potential (TBP) has been used to evaluate the environmental impacts of bioaccumulative nonpolar organic compounds associated with dredged material (USEPA and USACE, 1991; 1998). It is defined in USEPA and USACE (1998) as "an approximation of the equilibrium concentration in tissues if the dredged material in question were the only source of contaminant to the organism." It is a "coarse screen" and is applicable only to nonpolar organic compounds at present.

The TBP can be calculated relative to the BSAF as follows (USEPA and USACE, 1998):

$$TBP = BSAF\ (C_s/f_{oc})\ fl \quad (12)$$

where TBP is expressed on a whole-body wet-weight basis in the same concentration units as C_s, C_s is the concentration of the chemical in the dredged material or reference sediment, BSAF is set equal to 4, f_{oc} is the total organic carbon content of the dredged material expressed as a decimal fraction, and fl is the organism lipid content expressed as a decimal fraction of whole-body wet weight. Since the use of the default value of 4 can lead to inaccurate estimates (McFarland and Ferguson, 1994a, 1994b), the USACE Contaminants Database, as documented in Lutz and McFarland (1995), has been compiled to provide empirically measured BSAFs for use in TBP calculations.

Although the TBP approach has been commonly applied as a screening tool in the evaluation of dredged material, it has not been extensively used in risk assessments or in the development of sediment quality thresholds. Using the TBP method with the default BSAF value of 4 (as well as the recommended use of geometric means for all parameters) tended to overestimate the body burden of PCBs in carp and walleye at the Manistique, Michigan, site by factors of 2.9 and 18, respectively (Pelka, 1998). This result is consistent with the intended use of 4 as a default value, which is to be protective but not necessarily predictive, since a BSAF of 4 is at the 94th percentile of the USACE Contaminants Database and is a factor of 12 greater than the median BSAF in the database (McFarland, 1998).

3.3.3 Mechanistic Models

In general, mechanistic models or food web models can be grouped into two categories—equilibrium-based and kinetic approaches (Lee, 1992). Equilibrium and kinetic models have been successfully used to describe bioaccumulation of nonpolar organic compounds (i.e., dioxins, furans, and PCBs). The models have not been so successfully applied in describing bioaccumulation of metals or organic compounds subject to metabolism or degradation, such as PAHs.

3.3.3.1 Modeling Within Aquatic Food Chains

Equilibrium Models. Equilibrium models can incorporate uptake of contaminants from the water column, from contaminated sediments, and via the food chain (Lee, 1992). These models are usually referred to as "dynamic" because absolute thermodynamic equilibrium between contaminant concentrations in biota, water, and sediments is rarely reached in a natural setting. Thus, the equilibrium-based models assume steady-state conditions between organisms and the environment. Even steady-state conditions, where the concentrations do not change significantly as a function of time, are not always satisfied in natural settings, which might indicate the need for kinetic modeling as discussed in the Kinetic Models section below.

Equilibrium models also assume a closed system, reversibility of reactions, and sufficient time for the substance to distribute throughout the system. This time requirement to reach full distribution is highly variable. For example, the time required for equilibration of a substance between small organic particles and water might be seconds, days, or years depending on the particle size and the K_{ow} of the substance (Spacie et al., 1995). Equilibrium through a food chain is likely to have an even higher time requirement to reach steady state, depending on the complexity of the food chain and myriad other factors (Gobas and Z'Graggen, 1994).

In general, equilibrium models are applicable to compounds with log K_{ow} values of 3.5 to 6.0 that do not degrade or transform at rapid rates. Field validation of these models has been limited primarily to large lake systems. EPA is interested in including terms for degradation and transformation in the models, expanding the validation efforts, and characterizing the uncertainty in food web models (USEPA, 1996a).

More complex models have been developed to predict the steady-state concentration of contaminants throughout the food web. The Thomann et al. (1992) model (referred to as the Thomann model) and the Gobas (1993) model have been used in recent regulatory efforts, so they are discussed in more detail below as examples of complex equilibrium-based food web models that incorporate interactions with sediment.

The Thomann model, an extension of a previous model (Thomann [1989] model), is a five-compartment steady state model that includes four exposure routes in the description of accumulation by benthic species. This model predicts the accumulation of hydrophobic chemicals in pelagic aquatic systems. In the Thomann model, ingestion of particulate contaminants is considered associated with (1) sediment organic carbon, (2) overlying phytoplankton and ventilation of free dissolved contaminant, (3) interstitial water, and (4) overlying water. The five compartments in the model are phytoplankton/detritus, zooplankton, forage fish, piscivorus fish, and benthic invertebrates. In Thomann et al. (1992), the benthic model is applied to an amphipod-sculpin food web in Lake Ontario to assess the relative importance of different exposure routes for each species.

The equations in the Thomann model include rates for uptake, growth, and excretion, but since it is a steady-state model, the change in concentration in tissues as a function of time is assumed to be zero. Two broad classes of parameters are identified: (1) chemical-specific parameters, including uptake and excretion rates and assimilation efficiency, and (2) organism physiology-specific parameters, including growth and respiration rates and feeding preferences.

Thomann et al. (1992) conclude that with respect to the Lake Ontario food web, (1) the amphipod accumulates most of its body burden from the sediment and not from phytoplankton that make up approximately 80 percent of its diet, and (2) the sculpin accumulates virtually all of its body burden through uptake via the food chain for chemicals with log K_{ow} greater than 5.0.

The Gobas (1993) model is also a steady-state model that has been applied to a Lake Ontario food web. This model provides estimates of site-specific concentrations of hydrophobic organic chemicals in aquatic macrophytes, phytoplankton, zooplankton, benthic invertebrates, and fish from few measured input data including chemical concentrations in water and sediments. Similar to the Thomann model, this model combines the toxicokinetics of individual organisms (e.g., uptake, elimination) as well as the trophodynamics of food webs.

No significant differences were observed between predicted or observed concentrations in the four fish species and two benthic invertebrates modeled. However, the observed concentrations in phytoplankton and zooplankton were higher than predicted, possibly due to small sample sizes and sampling difficulties (Gobas, 1993). One of the key conclusions was that Lake Ontario fish are more sensitive to changes in sediment concentration than to changes in water concentrations. This result and the conclusions of Thomann et al. (1992) emphasize the importance of sediment interactions when modeling aquatic food chains in equilibrium-based steady-state models.

Kinetic Models. In contrast to equilibrium-based models, kinetic models describe bioaccumulation as the net effect of rate processes (uptake and loss of contaminant). Kinetic models have primarily focused on bioconcentration of contaminants from the water column, although more recently they have been applied to uptake from sediment as well (e.g, Boese et al. 1997). Incorporation of bioaccumulation through the food chain in kinetic models requires substantial amounts of data on uptake and loss kinetics in fish. Kinetic models have the benefit that they can be used to predict tissue concentrations with time under non-steady-state conditions (Lee, 1992). General assumptions of kinetic models include constant uptake rate(s), instantaneous mixing within the compartment(s), and a negative exponential depuration process for all compartments (Spacie et al., 1995). Under field conditions, violations of these assumptions are likely to occur. For example, the uptake rate of a substance can vary due to changes in behavior, food type, food availability, and other environmental factors (Spacie et al., 1995).

In general, two types of kinetic models are used—simple first-order kinetic models and bioenergetics-based bioaccumulation models. In the first-order model, all uptake routes are aggregated into a single uptake and a single elimination rate constant as shown below (Spacie and Hamelink, 1982; Davies and Dobbs, 1984). In this model, the organism is considered to be a single, homogeneous, membrane-bound compartment placed in water containing an infinite supply of the substance at a given concentration (Spacie et al., 1995). Slow desorption kinetics from sediment can violate this assumption in natural systems.

$$dCt/dt = k1 * C_w - k2 * Ct \qquad (13)$$

where dCt/dt is the rate of change of the chemical concentration in tissue over time (mg/kg/t), C_w is the chemical concentration in the water (µg/L), k1 is the uptake rate constant (L water/kg tissue * t), k2 is the elimination rate constant (1/t), and t is time. This equation can be modified for bioaccumulation from sediments by substituting k_s (sediment uptake rate coefficient) for k1, and C_s for C_w. Good estimates of k_s and k2 are required for this model to successfully predict the time to steady state and the steady state body burden (Boese and Lee, 1992). In this model, the concentration in the tissue increases over time at a rate that is highest initially. This rate then gradually decreases over time until some asymptotic concentration is reached (Spacie et al., 1995; Boese et al., 1997). These models are most useful to model nonequilibrium processes in open systems that approach or achieve a steady state.

Complex kinetic models, sometimes called bioenergetics-based toxicokinetic bioaccumulation models, allow uptake to occur from multiple routes including overlying water, interstitial water, and ingested sediment, as well as elimination via multiple routes. Uptake from each route is assumed to be independent and additive. The uptake from each route is based on the flux from that medium (e.g., ingestion rate of sediment), its contaminant concentration, and the appropriate assimilation efficiency associated with that route (gill or gut). Loss from the organism is due to elimination or metabolism. Metabolism can be difficult to predict since it is poorly correlated with chemical hydrophobicity and appears to vary widely across species (Hydroqual, 1995).

These complex kinetic models consider the chemical and biological processes that occur in the water column and biota, and each step is modeled using first-order kinetics, second-order kinetics, or steady-state kinetics. These models can be used for non-steady-state exposures, in separating the importance of different uptake routes, and with organisms undergoing substantial growth (Boese and Lee, 1992). However, extensive data are required to correctly apply the models, which makes them in general better suited as a research tool.

As an example of this approach, Landrum and Robbins (1990) and Landrum et al. (1992) extensively modeled the kinetics of PAH uptake and elimination by the freshwater amphipod *Diporea* sp. to show the relative importance of sediment, pore water, and overlying water sources. They found that ingestion or desorption kinetics from sediments appear to control the bioavailability of PAHs to the organisms, and that the rate of desorption was a function of the season as well as the aging of the sediments. Landrum and Robbins (1990) concluded that instantaneous equilibrium (as is assumed in the equilibrium models) is not appropriate for estimating the amount of contaminant that is bioavailable or for predicting the amount of bioaccumulation directly from sediment.

As with equilibrium-based models, application of kinetic models to extremely hydrophobic chemicals (log K_{ow} greater than 6) can be problematic due to the very long uptake times required to reach steady state with the water (one or more years) (Spacie et al., 1995). Since many organisms do not live this long, steady state is never reached. In addition, uptake of these chemicals might be difficult to predict due to the breakdown in relationships between various rates of uptake and depuration for these chemicals (Hawker and Connell, 1988; Gobas et al., 1989, cited in Spacie et al., 1995) or due to growth dilution effects (Niimi and Cho, 1981; Sijm et al., 1992, cited in Spacie et al., 1995).

3.3.3.2 Modeling from Aquatic to Terrestrial Systems

Aquatic organisms provide a direct link for exposure of contaminants to terrestrial species that have an aquatic diet, such as kingfishers, herons, and muskrats, or have a large aquatic component in their diet, such as bald eagles and mink. As discussed in the previous sections, numerous models exist to predict the transfer of contaminants from sediment and surface water through the aquatic food chain. In the

terrestrial environment, a food web modeling approach is used to predict the transfer of contaminants from the aquatic to the terrestrial food chain. Food web modeling is used to calculate a total daily dose of a chemical consumed by a terrestrial species. Therefore, all food web models include terrestrial species, with the exposure parameters and assumptions compiled or derived, and bioavailability of the contaminants determined.

Terrestrial species that represent important components of the ecosystem and are exposed to chemical contamination are used in the food web model. The receptors can be important or rare species or surrogate species that represent major functional groups at the area of concern. The following factors are considered when selecting ecological receptor species:

- Importance to the ecological community, including such factors as high abundance and biomass and importance as a prey species.
- Sensitivity to the contaminants.
- Potential for exposure.
- Relevance to human beneficial uses (i.e., bird watching, hunting, fishing).
- Availability of information.

Once terrestrial species have been selected, exposure parameters and assumptions related to the chemicals of concern are compiled for model development. Exposure parameters include total daily ingestion of food and water, important aquatic dietary components (e.g, fish, crayfish, benthic macroinvertebrates), and feeding territory. Depending on the terrestrial species, exposure parameters can be compiled from the primary literature and USEPA (1993b, 1993c). However, in many cases ingestion rates are not available and are thus calculated using allometric equations (Opresko et al., 1993).

Chemicals are rarely 100 percent bioavailable from the diet, especially when consumed from the field diet. In many cases the chemicals administered to the test species are in a more bioavailable form because they are generally dissolved in a carrier (e.g., acetone, corn oil) before being mixed with the test diet. Therefore, it is important to determine what the relative bioavailability of the chemical is in the diet and to select an appropriate bioavailability factor for each receptor group (e.g., bird or mammal) and contaminant. Information on the bioavailability of chemicals from the diets of birds and mammals is available from a number of sources such as texts by Hrudley et al. (1996) and Ammerman et al. (1995).

The structure of a generic food web model is

$$IR_T = SUM\ [(C * I * BF)_i * EF]/BW \qquad (14)$$

where IR_T is the total rate of contaminant ingestion (mg/kg bw-day wet weight); C_i is the concentration of the chemical in medium i (mg/kg wet weight); I_i is the rate of ingestion of medium i (mg/day wet weight); BF_i is the relative bioavailability factor of the chemical from media i (unitless); EF is the proportion of study area relative to entire home range of terrestrial species (exposure fraction, unitless); and BW is the body weight of terrestrial species (kg).

3.3.3.3 Modeling from Aquatic and Terrestrial Systems to Humans

Exposure to humans is modeled using an approach similar to that described above for terrestrial species. The link between sediment contamination and human health is primarily assessed through the direct

consumption of sediment-dwelling invertebrates (such as clams and crabs) or less frequently through indirect consumption of fish that are contaminated through trophic transfer from a sediment source (Boese and Lee, 1992). In theory, humans could also be exposed through consumption of terrestrial species that ingest aquatic species, although this pathway is limited since the eating preferences of humans do not typically include any terrestrial wildlife species with large aquatic diets.

Important considerations in modeling exposure to humans include the correct determination of fish or shellfish consumption rates (which differ widely across the United States) and a proper definition of the portion of the fish or shellfish actually consumed by humans in terms of both its chemical concentration and its lipid content. As discussed in the previous sections, numerous models exist to link the concentration in fish or shellfish to the concentration in sediment through the aquatic food chain.

As an example, exposure to humans through fish consumption was recently modeled as part of the Great Lakes Water Quality Initiative (GLWQI) (USEPA, 1993a; 1995a). Humans typically eat fish fillets, which usually have lower lipid content than the whole fish generally consumed by wildlife. Therefore, lower standard lipid values have been developed for humans (5 percent) than for wildlife (7.9 percent) (USEPA, 1993a). As part of the GLWQI process, percent lipid data for edible tissues (mostly skin-on fillets) were gathered from the fish contaminant monitoring programs in Michigan, Wisconsin, Ohio, Indiana, New York, and Minnesota. In the proposed guidance, when BAFs for human health are derived from BCFs through the application of an FCM, the appropriate FCM based on the chemical's log K_{ow} is selected from the trophic level 4 (top carnivore) fish species (USEPA, 1993a). These BAFs are based on the Gobas (1993) model, as described in Section 3.3.2.4. Additional guidance is available in USEPA (1997) regarding human health risk assessment and seafood consumption limits.

3.4 Use of Critical Body Residue Approach

The previous sections have focused on the ability to predict or measure the body burden of a chemical in biota. Although the bioaccumulation of a contaminant is an important consideration, bioaccumulation in and of itself is not a hazard. The critical question becomes at what point does bioaccumulation result in body burdens that result in adverse effects on individual organisms (prey and predator species) and ultimately on populations or whole ecosystems, although extensions beyond the individual organism are not well developed at this time.

One increasingly popular approach that links body burdens in an individual organism to toxicological effects in that organism is the critical body residue (CBR) approach. This approach effectively shifts the focus from measuring concentrations in water or sediment to predict toxicity to measuring concentrations in tissues. The CBR approach has several advantages over more commonplace approaches that measure concentrations in water and sediment, as discussed in McCarty and MacKay (1993):

- Bioavailability and exposure from all routes is integrated by the organism.
- Assumptions regarding steady state, equilibrium or uptake kinetics are not required.
- Effects of metabolism are explicitly considered (though the approach is not readily amenable to compounds that are rapidly metabolized).
- Mixture toxicity can be assessed.

The basis of CBR is the assumption that whole body residues are a useful surrogate measurement of the amount of chemical at the site(s) of toxic action and that toxic responses can be predicted from these whole body concentrations. Several researchers, including Ferguson (1939), McGowan (1952), and

McCarty et al. (1992), have shown that for neutral organic compounds, the body residue level which causes narcotic toxicity is relatively constant across a wide variety of organisms.

There are several approaches for estimating screening level CBRs. Many CBRs can be estimated from acute and chronic studies from any exposure-based endpoint, whether it be an LC10 or an LC50, by establishing relationships between exposure-based and residue-based dose estimates (McCarty and MacKay, 1993). In particular, a great deal of work has been done with the fathead minnow (McCarty et al., 1985, 1992; McCarty, 1986, 1990; Mayer et al., 1986, 1992), and this work has been used to form the basis for guidance on the interpretation of bioaccumulation test results (Dillon et al., 1992). Ambient water quality criteria and BCFs have been proposed to calculate body burdens associated with toxicity (Cook et al., 1992; Shephard 1997). Bridges et al. (1996) note that potential body residues could be calculated using chronic water concentrations associated with effects (e.g., Final Chronic Values for Water Quality Criteria or Great Lakes water quality criteria from the GLWQI) and BCFs, for comparison to bioaccumulation test data. Additionally, the range of sediment quality assessment values, including proposed EPA equilibrium partitioning sediment guidelines, has been suggested as a possible basis to extrapolate body residues from BAFs determined in the bioaccumulation test (Bridges et al., 1996), although this approach has yet to be tested. Additivity of toxicants would have to be addressed.

Although the CBR approach has great potential, it is not readily amenable to many carcinogens or mutagens with short half-lives, to chemicals that are rapidly metabolized, or to chemicals such as metals that when present in aqueous media elicit organism responses such as excess mucus excretion that results in suffocation of the organism (McCarty and MacKay, 1993). Therefore, knowledge of the mode of toxic action is an important prerequisite to applying the CBR approach.

Several groups have developed databases to assess the link between body burden and toxic effects. Among these is the group at EPA-Duluth (Jarvinen and Ankley, 1999). The U.S. Army Corps of Engineers and EPA have jointly developed the Environmental Residue-Effects Database (ERED), a compilation of literature data where tissue contaminant concentrations and biological effects were simultaneously measured in the same organism (USACE, 1997).

3.5 Application of Approaches in Deriving Tissue Residue-linked Sediment Chemical Levels

Considerable interest exists today in using the approaches or tools discussed above to identify sediment concentrations associated with threshold tissue concentrations that are protective of aquatic organisms or their predators, including humans. Acute sediment toxicity is relatively easy to evaluate through the use of standardized laboratory bioassays, but the effects of chronic, low-level exposure can be much more difficult to assess or predict, particularly when these effects are the result of exposure to bioaccumulative compounds. As noted in the next chapter, a key aspect of developing tissue residue-linked sediment chemical levels for evaluating the potential for chronic toxicity is to understand the relationships between concentrations of chemicals in sediment and corresponding concentrations of these chemicals in the tissues of exposed organisms along with their associated effects.

The development of tissue residue-linked sediment chemical levels may focus on the protection of benthic species or higher-trophic-level organisms. Several approaches to develop tissue residue-linked sediment chemical levels for species other than benthic organisms were discussed in Cook et al. (1992). These approaches were based on linking sediment concentrations to tissue residues associated with toxicity to those organisms analyzed or projected toxicity to organisms up the food chain.

The comparison of exposure and effects forms the basis of ecological and human health risk assessment, for which guidance is available (USEPA, 1989, 1992b, 1996b). The development of tissue residue-linked sediment chemical levels for the protection of human health requires consideration of several important parameters. These include identification of the target human population to be protected, the species and portions of the fish that are consumed, and the rate of fish consumption. Guidance on the collection and evaluation of this information is provided in USEPA (1997). Many risk assessments have been conducted to establish tissue residue-linked sediment chemical levels on a site-specific basis. A few key examples include concentrations of tetrachlorodibenzo-*p*-dioxin (TCDD) in sediment associated with impacts on fish and birds as well as ongoing development of sediment quality criteria for human health by Washington State.

For TCDD, an interim risk assessment was conducted to relate concentrations of TCDD in water, sediment, and fish tissue to a low or high likelihood of population failure in aquatic life and wildlife (USEPA, 1993d). The report discussed the TCDD exposure, bioaccumulation, and toxic effects data used to estimate sediment concentrations that may be of concern. BSAFs were among the techniques used. Although the approach was qualified as a simple demonstration and not a definitive characterization of TCDD risk, sediment concentrations were presented, on a pg/g dry weight basis, that are believed to be associated with low and high risk to sensitive fish, mammalian wildlife, and avian wildlife species.

In another example, the state of Washington is developing human health criteria for bioaccumulative compounds in Puget Sound sediments. The criteria will be incorporated into the state's existing Sediment Management Standards (Chapter 173-204 WAC). Human health sediment quality criteria (HHSQC) are based on standard risk assessment methodologies in conjunction with empirically derived biota-sediment accumulation factors (BSAFs). The formulas used to calculate the criteria are outlined in more detail below.

For carcinogenic compounds:

$$HHSQC = \frac{R * BW * AT * UCF}{CPF * ED * IR * BSAF * FL}$$

For noncarcinogens:

$$HHSQC = \frac{RfD * BW * UCF}{IR * BSAF * FL}$$

where

R = risk level (unitless);
BW = average human adult body weight (kg);
AT = time period over which exposure is averaged (years);
UCF = unit conversion factor (mg/g);
CPF = chemical-specific cancer potency factor as defined by EPA (IRIS);
RfD = reference dose (mg chemical/kg body weight/day);
ED = exposure duration (years);
IR = fish ingestion rate (grams/day);
BSAF = chemical-specific biota-sediment accumulation factor (mg chemical/kg lipid per mg chemical/kg organic carbon); and
FL = percent fish lipid (g lipid/g tissue).

Washington State Department of Ecology's (Ecology) proposed construct for human health criteria relies on a tiered approach, with "Tier I" representing an initial evaluation to determine if sediment chemical concentrations pose a significant human health risk. Additional, site-specific analysis would then be available ("Tier II") to verify the results of the Tier I analysis.

Ecology has focused its efforts on developing HHSQC for a short list of nonpolar organic compounds. The focus is on chemicals for which confidence in the toxicity and bioaccumulation is the highest:

DDD	benzo(a)pyrene
DDE	benzo(a)anthracene
DDT	benzo(b)fluoranthene
hexachlorobenzene	benzo(k)fluoranthene
hexachlorobutadiene	chrysene
PCBs	dibenzo(a,h)anthracene
dioxins/furans	indeno(1,2,3-cd)pyrene

A database of more than 1,200 chemical-specific BSAF values for finfish and shellfish was compiled by Washington State Department of Health (WDOH) and used to develop recommended BSAFs for HHSQC (WDOH, 1995). Analyses of these data showed highly significant regressions of BSAF on K_{ow} for PCBs and dioxins in finfish and for PAH and PCBs in shellfish (PTI, 1995).

For several chemicals (PAHs, PCBs, and dioxins/furans), sediment criteria are calculated based on a summing of chemicals within each group. For PAHs and dioxins/furans, Ecology is proposing the use of toxicity equivalence factors (TEFs), which allows scientific evidence about the cancer potency of individual compounds to be taken into account in the calculation of human health risk. For PCBs, a criterion is proposed for total PCBs (although congener-specific analysis might be considered for Tier II analysis). Ecology is currently investigating the cost and liability implications of the HHSQC through "case studies" (Weiss, 1998).

Other approaches that have been used include whole river sediment strategies, in which concentrations of contaminants in fish, for example, are predicted as a function of different sediment remediation scenarios. One example of this approach was applied in the Fox River (Paulson, 1998). In this example, PCB transport models were used to predict PCB residues in fish in different stretches of the Fox River over an extended period of time. Again, BSAFs were used in the modeling effort, so although the results were presented as PCB concentrations in fish (as fish consumption advisories), PCB concentrations in sediments associated with these tissue residues could also be calculated for different portions of the river.

In summary, developing tissue residue-linked sediment chemical levels involves an explicit assessment of both exposure and effects. The link between these two considerations is most clear for species in direct contact with sediment, such as benthic invertebrates, but even that link can be obscured through multi contaminant exposures. For higher trophic level organisms (e.g., fish, humans and avian species), models have been developed to establish the link.

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4. IMPORTANT BIOACCUMULATIVE CHEMICALS

4.1 Overview

Knowledge of the relationship between quantities of chemicals in sediments and the toxicological effects of those chemicals in the tissues of organisms has gradually evolved, and the relationship is better understood for some chemicals than for others. As noted by Adams et al. (1992), current efforts to develop a tissue residue approach for evaluating sediment quality require linking toxic effects to organism residues, as well as linking the chemical residues in those organisms to concentrations of chemicals in the sediment. This approach could lead to the identification of sediment concentrations associated with threshold tissue concentrations that are protective of aquatic organisms or their predators, including humans. However, as was discussed in Chapter 2, a number of physical, chemical, and biological variables can affect bioaccumulation and must be considered when establishing such "tissue residue-linked sediment chemical levels".

To assist in understanding both the importance of bioaccumulation in the interpretation of sediment quality and the status of our knowledge of the bioaccumulation of potentially toxic chemical contaminants, information associating the presence and quantity of potentially bioaccumulative chemicals in sediment with uptake in the tissues of aquatic and terrestrial organisms and with the effects of those chemicals on the organisms was collected and reviewed. An attempt was made to include only data from literature published since 1986. In limited cases, however, it was necessary to use literature from 1985 or earlier. Initially, only studies reporting exposure (including sediment or water/pore water concentrations), tissue concentrations, *and* toxic effects were examined; later, data from studies linking exposure concentrations with tissue concentrations *or* tissue concentrations with toxic effects were also included.

Toxicity and chemistry data for the chemicals reviewed in this document were obtained from various sources, including local and EPA libraries. Keyword searches were conducted in WAT-TOX (University of Waterloo) and other on-line databases such as DIALOG and the Chemical Information System (CIS), retrieving chemical-specific citations from the Environmental Protection Agency's AQUIRE (AQUatic Toxicity Information REtrieval), ECOTOX, and ASTER databases (Office of Research and Development, Duluth, Minnesota); "Screening Benchmarks for Ecological Risk Assessment" database, Oak Ridge National Laboratory, Oak Ridge, Tennessee; Chemical Evaluation Search and Retrieval System (CESAR, developed by the National Institutes of Health and EPA); ENVIROFATE (Environmental Fate) database (sponsored by EPA's Office of Toxic Substances); IRIS (Integrated Risk Information System), HSDB (Hazardous Substances Data Bank), and HEAST (Health Effects Assessment Summary Tables, National Institutes of Health and EPA); ERED (Environmental Residue-Effects Database, U.S. Army Corps of Engineers and EPA); and other sources. Information was compiled from peer-reviewed publications and reports, as well as federal and state agencies' documents and reports (gray literature), including the Agency for Toxic Substances and Disease Registry (ATSDR) toxicity profiles, a series of synoptic reviews of chemical hazards to biota (Fish and Wildlife Service), *Environmental Science and Technology*, *Environmental Chemistry and Toxicology*, *Water Research*, and *Aquatic Toxicology.* Searches were conducted at different times and by different people, depending on the chemical; thus, although every effort was made to be as comprehensive as possible, variations in search strategies and data interpretation might have affected the completeness of the data presented. Tables summarizing these findings are presented in a separate appendix to this document (EPA-823-R-00-002). Additional information on tissue residue and effects is also available in *Linkage of Effects to Tissue Residues: Development of a Comprehensive Database for Aquatic Organisms Exposed to Inorganic and Organic Chemicals* (Jarvinen and Ankley, 1999).

4.2 Rationale for Choice of Chemicals

A list of bioaccumulative compounds of potential concern was identified based on input from the Bioaccumulation Analysis Workgroup and a review of various agency documents. These chemicals are known to be found in the sediment and in animal tissues at levels associated with toxic effects and are referenced in one (usually more) of the literature items in Table 4-1. Seventeen pesticides on the list (Table 4-2) were included based on having a half-life of greater than 30 days, BCF greater than 1000, LC50 (acute fish) less than 1 ppm, and log K_{ow} greater than 4.2. Chemicals with a log K_{ow} greater than 3.5 are considered to be bioaccumulative, that is, they are likely to partition into organic materials, including the lipids of organisms and predicted and measured BAFs are correlated within the range of log K_{ow} 3.5 to 6.5 (Thomann, 1989). Of the chemicals in Table 4-2, information is reviewed for 11 metals, 1 chlorinated phenol, 10 polycyclic aromatic hydrocarbons (PAHs), 13 pesticides, selected dioxins and furans, selected Aroclors and congeners of the polychlorinated biphenyls (PCBs) group, and total PCBs (Appendix). These chemicals are marked with an asterisk in Table 4-2.

Criteria for selecting the chemicals to be researched included the following: (1) information was readily available; (2) the chemical was of immediate concern and known to bioaccumulate; (3) the chemical was representative of a group or class of compounds; and (4) the chemical was considered to be important in one or more EPA programs.

Table 4-1. Sources of Information for Selection of Important Bioaccumulative Compounds

1997 Listing of Fish and Wildlife Consumption Advisories (USEPA, 1997a).
Regional Ambient Fish Tissue Monitoring Program (RAFT) contaminants of concern (provided by EPA Region 7).
Great Lakes Water Quality Initiative Bioaccumulative Chemicals of Concern (BCCs).
Persistent Organic Pollutants (POPs) listed in "Substantiation report of the Task Force on POP," 4th meeting, Den Haag (the Netherlands), February 21-25, 1994.
Table 9-5 in USEPA and USACE (1998) *Inland Testing Manual* (which is the same as Table 10 in USEPA and USACE (1995), *QA Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations.* Chemical evaluations. EPA 823-B-95-001): Octanol/water partition coefficients (K_{ow}) for organic priority pollutants and 301(h) pesticides.
Recommended target analytes in USEPA (1995a), *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories.* Volume 1. *Fish sampling and analysis.* Second edition, EPA 823-R-95-007.
List of target analytes in USEPA (1992), *National Study of Chemical Residues in Fish.* Volume 1. EPA 823-R-92-008a.
USEPA National Sediment Quality Survey (USEPA, 1997b).

Table 4-2. Important Bioaccumulative Compounds

Class	Compound	CASRN
Metals and Metallic Compounds	arsenic*[1]	7440-38-2
	cadmium*	7440-43-9
	chromium VI*	7440-47-3
	copper*	7440-50-8
	lead*	7439-92-1
	methylmercury*	22967-92-6
	nickel*	7440-02-0
	selenium*	7782-49-2
	silver*	7440-22-4
	tributyltin (oxide)*	56-35-9
	zinc*	7440-66-6
Substituted Phenols	pentachlorophenol*	87-86-5
	pentachloroanisole	1825-21-4
Low-Molecular-Weight Aromatics	acenapthylene	208-96-8
	acenaphthene*	83-32-9
	anthracene	120-12-7
	fluorene	86-73-7
	phenanthrene*	85-01-8
High-Molecular-Weight PAHs	benzo(a)anthracene*	56-55-3
	benzo(a)pyrene*	50-32-8
	benzo(b)fluoranthene*	205-99-2
	benzo(k)fluoranthene*	207-08-9
	benzo(g,h,i)perylene*	191-24-2
	chrysene*	218-01-9
	dibenzo(a,h)anthracene	53-70-3
	fluoranthene*	206-44-0
	indeno(1,2,3-c,d)pyrene	193-39-5
	pyrene*	129-00-0
Chlorinated Aromatic Hydrocarbons	1,2-dichlorobenzene	95-50-1
	1,3-dichlorobenzene	541-73-1
	1,4-dichlorobenzene	106-46-7
	hexachlorobenzene (HCB)	118-74-1
	hexachloroethane	67-72-1
	hexachlorobutadiene	87-68-3
	hexachlorocyclopentadiene	77-47-4
	octachlorostyrene	29082-74-4
	pentachlorobenzene	608-93-5
	1,2,4,5-tetrachlorobenzene	95-94-3
	1,2,3,4-tetrachlorobenzene	634-66-2
	tetrachloroethane	25322-20-7
	1,2,4-trichlorobenzene (TCB)	120-82-1
Halogenated Ethers	4-chlorophenyl phenyl ether	7005-72-3
	4-bromophenyl phenyl ether	101-55-3

Table 4-2. Continued

Class	Compound	CASRN
Pesticides	aldrin*[2]	309-00-2
	chlordane*[2]	57-74-9
	chlorpyrifos*[2]	2921-88-2
	*p,p*N-DDD*	72-54-8
	*p,p*N-DDE*	72-55-9
	*p,p*N-DDT*[2]	50-29-3
	diazinon*	333-41-5
	dicofol*[2]	115-32-2
	dieldrin*[2]	60-57-1
	disulfoton*	298-04-4
	alpha-endosulfan[2]	959-98-8
	beta-endosulfan	33213-65-9
	endrin[2]	72-20-8
	ethion[2]	563-12-2
	ethalfluralin[2]	55283-68-6
	heptachlor*[2]	76-44-8
	heptachlor epoxide	1024-57-3
	alpha-hexachlorocyclohexane ("-BHC)	319-84-6
	beta-hexachlorocyclohexane ($-BHC)	319-85-7
	delta-hexachlorocyclohexane (*-BHC)	319-86-8
	gamma-hexachlorocyclohexane ((-BHC, lindane)	58-89-9
	methoxychlor[2]	72-43-5
	mirex[2]	2385-85-5
	nitrofen (no longer in use)	1836-75-5
	oxyfluorfen*[2]	42874-03-3
	pentachloronitrobenzene (PCNB)	82-68-8
	permethrin[2]	52645-53-1
	S-fenvalerate[2]	66230-04-4
	terbufos*	13071-79-9
	toxaphene*	8001-35-2
	trifluralin[2]	1582-09-8
Dioxins/Furans	2,3,7,8-tetrachlorodibenzo-*p*-dioxin*	1746-01-6
	2,3,7,8-tetrachlorodibenzofuran*	51207-31-9
	1,2,3,7,8-pentachlorodibenzo-*p*-dioxin*	40321-76-4
	2,3,4,7,8-pentachlordibenzofuran*	57117-31-4
	1,2,3,7,8-pentachlorodibenzofuran*	57117-41-6
	1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin*	39227-28-6
	1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin*	57653-85-7
	1,2,3,4,7,8-hexachlorodibenzofuran*	70648-26-9
	1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin*	35822-46-9
PCBs (Aroclors)	Aroclor 1016*	12674-11-2
	Aroclor 1221	11104-28-2
	Aroclor 1232	11141-16-5
	Aroclor 1242*	53469-21-9
	Aroclor 1248*	12672-29-6
	Aroclor 1254*	11097-69-1
	Aroclor 1260*	11096-82-5
	Aroclor 1268	11100-14-4

Table 4-2. Continued

Class	Compound		CASRN
PCBs (Congeners)[3]	PCB 8	2,4N-dichlorobiphenyl	34883-43-7
	PCB 18	2,2N,5-trichlorobiphenyl	37680-65-2
	PCB 28	2,4,4N-trichlorobiphenyl*	7012-37-5
	PCB 44	2,2N,3,5N-tetrachlorobiphenyl	41464-39-5
	PCB 52	2,2N,5,5N-tetrachlorobiphenyl	35693-99-3
	PCB 66	2,3N,4,4N-tetrachlorobiphenyl	32598-10-0
	PCB 77	3,3N4,4N-tetrachlorobiphenyl*	32598-13-3
	PCB 81	3,4,4N,5-tetrachlorobiphenyl*	70362-50-4
	PCB 101	2,2N,4,5,5N-pentachlorobiphenyl	37680-73-2
	PCB 105	2,3,3N,4,4N-pentachlorobiphenyl*	32598-14-4
	PCB 118	2,3N,4,4N,5,-pentachlorobiphenyl*	31508-00-6
	PCB 126	3,3N,4,4N,5-pentachlorobiphenyl*	57465-28-8
	PCB 128	2,2N,3,3N,4,4N-hexachlorobiphenyl	38380-07-7
	PCB 138	2,2N,3,4,4N,5N-hexachlorobiphenyl	35065-28-2
	PCB 153	2,2N,4,4N,5,5N-hexachlorobiphenyl	35065-27-1
	PCB 156	2,3,3N,4,4N,5-hexachlorobiphenyl*	38380-08-4
	PCB 169	3,3N4,4N,5,5N-hexachlorobiphenyl*	32774-16-6
	PCB 170	2,2N,3,3N,4,4N,5-heptachlorobiphenyl	35065-30-6
	PCB 180	2,2N,3,4,4N5,5N-heptachlorobiphenyl	35065-29-3
	PCB 187	2,2N,3,4N,5,5N,6-heptachlorobiphenyl	52663-68-0
	PCB 195	2,2N,3,3N,4,4N,5,6-octachlorobiphenyl	52663-78-2
	PCB 206	2,2N,3,3N,4,4N,5,5N,6-nonachlorobiphenyl	40186-72-9
	PCB 209	2,2N,3,3N,4,4N,5,5N,6,6N-decachlorobiphenyl	2051-24-3

[1] Chemicals with asterisk have been researched for bioaccumulation information, which is contained in chemical-specific information tables in the Appendix.
[2] These pesticides were noted by EPA's Office of Pesticide Programs to have BCF >1000, $t_{1/2}$ (hydrolysis) > 30 days, LC50 (acute fish) <1 ppm and log K_{ow} >4.2.
[3] PCB congeners marked with an asterisk were recommended by Philip Cook, USEPA, Office of Research and Development, Duluth, Minnesota, and Richard Pruell, USEPA, Office of Research and Development, Narragansett, Rhode Island. Unmarked congeners are additional congeners measured by NOAA's National Status and Trends Program.

EPA and other agency programs have identified different bioaccumulative chemicals for different purposes. For example, the Great Lakes Water Quality Initiative limited its list of bioaccumulative chemicals of concern (BCCs) to any chemical "which, upon entering the surface waters, by itself or as its toxic transformation product, bioaccumulates in aquatic organisms by a human health bioaccumulation factor greater than 1,000, after considering metabolism and other physicochemical properties that might enhance or inhibit bioaccumulation...." (Final Water Quality Guidance for the Great Lakes System; Final Rule, 40 CFR Parts 9, 122 et al.; *Federal Register*, Thursday, March 23, 1995; pages 15387-15388, and Table 6A, page 15393). The BAF of 1,000 (log BAF = 3.00) was used to determine a limited number of chemicals for which regulatory criteria would be developed; if a lower BAF had been used, more potentially bioaccumulative chemicals would have been included on the list.

Using different criteria, other programs have identified potentially bioaccumulative chemicals not included in the Great Lakes Initiative list. EPA's Office of Pollution Prevention and Toxics developed a preliminary list of potentially persistent, bioaccumulative chemicals based on a half-life greater than 30 days, estimated BCF value exceeding 250 (log BCF = 2.40) (log K_{ow} of 3.5), molecular weight greater than 600, and production volume greater than 10,000 pounds per year (see Chapter 5 for additional information). Canada's government proposed using persistence criteria of half-life in air $ 2 days, water

$ 6 months, soil $ 6 months, or sediment $ 1 year; and bioaccumulative criteria of BCF or BAF $ 5,000 (log BCF or BAF $ 3.70) applied to freshwater fish (data for nonfish species to be used with judgment) or log K_{ow} $ 5 to screen chemicals for possible "virtual elimination" under the Canadian Environmental Policy Act Priority Substances List. (See *Toxic Substances Management Policy: Persistence and Bioaccumulation Criteria*, Final Report of the ad hoc Science Group on Criteria, Government of Canada, Environment Canada, June 1995.)

Thus, the same chemical might be of concern for one program, or within one region or state or site, and not be of concern for another because of specific program mandate(s), levels present in sediment, sources and loadings, or presence of sensitive organisms. Information was compiled on the selected chemicals to help identify gaps in our understanding of the nature of bioaccumulation and toxicity of these chemicals and to justify the inclusion of certain chemicals as bioaccumulative compounds.

4.3 Summary Data in Tables

The tables in the Appendix contain information and data on each persistent and potentially bioaccumulative organic compound or metal, including (1) chemical characteristics, human health concerns, wildlife and aquatic organism partitioning factors, and food chain multipliers, if known, and (2) a profile of the chemical's toxicity, mode of action, and potential for bioaccumulation. Data and references from laboratory and field studies on the toxicity and bioaccumulation of the chemical in invertebrates, fishes, wildlife, and humans are also presented. References are numbered and cited in full at the end of each table.

No attempt was made to screen reports to determine whether the methods used and the results obtained met some preselected level of quality or whether particular quality assurance and quality control procedures had been specified for the collection of particular types of data and for the accurate measurement of chemical concentrations in sediment, pore water, or tissues. Some data are from field studies that involved the assessment of multiple contaminants. No attempt was made to partition the reported effects among the various chemicals evaluated in these field studies. Because a variety of methods and techniques have been used to measure the bioaccumulation of different chemicals in the tissues of organisms, it is the reader's responsibility to evaluate each study carefully to determine its quality, limitations, and uncertainties in relation to the purpose for which that study might be used in interpreting sediment quality.

The chemical characteristics in the summary tables indicate the hydrophobic nature and persistence of each compound. Water solubilities were taken from the Hazardous Substances Data Bank (USEPA, 1995b). Half-lives for the chemicals were derived from data compiled in USEPA (1989; also published as Howard et al., 1991). When possible, the half-life was determined by sediment grab sample or aerobic soil die-away test data, but more often it was based on estimated unacclimated aqueous aerobic biodegradation. The latter information provides only a relative assessment of the persistence of the compound in the environment since degradation rates can be influenced by a variety of physical, chemical, and biological factors (reviewed in Rand, 1995). Shimp et al. (1990) stated that adsorption to sediment particles could rapidly remove most of a chemical from the water column compartment to the sediment compartment, but modeling chemical residence time in sediments is more difficult than modeling biodegradation in other media. Factors such as the partitioning coefficient of the chemical (which determines the proportion of a discharged mass that reaches the sediments), the rate at which sediment particles settle to the bottom, the rate at which particles can be buried, and the extent to which particles are resuspended and transported downstream can have either positive or negative effects on a chemical's biodegradation rate. Shimp et al. also noted that biodegradation of a chemical mass adsorbed

to sediment particles can change when the particle is buried and the environment becomes anoxic or anaerobic. Boethling et al. (1995) examined data for many chemicals and found that in nearly all cases incorporation into sediment enhanced biodegradability.

The log K_{ow} value provided for each nonionic organic chemical is the log of its octanol/water partition coefficient, which represents the relative ability of the chemical to dissolve in water versus octanol, as well as the likelihood of the chemical to complex or sorb to organic carbon. For most chemicals, this value is the one recommended in a draft report (Karickhoff and Long, 1995) that was based on an extensive literature review of measured and modeled data for pure compounds. The draft report is under review by an interagency committee to standardize the log K_{ow} values. Log K_{ow}s for some of the PCB congeners and dioxins and furans were obtained from Mackay et al. (1992).

Log K_{oc} was calculated from the equation:

$$\log K_{oc} = 0.00028 + 0.983(\log K_{ow}).$$

This equation was derived by Di Toro (1985) by regressing K_{oc} to K_{ow}, which demonstrated that the particle organic carbon coefficient was approximately equal to its octanol/water partition coefficient (kg/L). The higher the log K_{ow} and log K_{oc} values, the more likely the chemical will bind to sediment, especially sediment containing high concentrations of organic carbon, and to accumulate in the fatty tissues of aquatic and terrestrial biota. The accumulated chemicals can also biomagnify through the trophic levels of a food chain, as the contaminants in the consumed prey are concentrated in tissues of the predator. Thomann (1989) developed a model for predicting BAFs by using food chain multipliers generated on the basis of the log K_{ow}. For log K_{ow} values in the range of 3.5 to 6.5, model-predicted BAFs compared favorably with measured ones. Uncertainty in predicting bioaccumulation for nonpolar ionic chemicals with log K_{ow}s greater than 6.5 (e.g., superhydrophobic chemicals) increases, probably as the result of rapid metabolism, reduced bioavailability, very low water solubilities, and inhibition of transport due to the large size of the molecule (USEPA, 1991).

Daily intake levels of concern for the protection of human health were compiled from USEPA (1995c, 1995d), including estimated values for carcinogenic endpoints (slope factors) and noncarcinogenic endpoints (reference doses) for the oral ingestion exposure pathway. The carcinogenic classifications of these chemicals are the weight-of-evidence categories established by EPA's Human Health Assessment Group. The categories are defined as follows (USEPA, 1995c):

A	=	Human carcinogen
B1	=	Probable human carcinogen; limited evidence in humans but sufficient evidence of carcinogenicity in animals
B2	=	Probable human carcinogen; inadequate or lack of evidence in humans but sufficient evidence in animals
C	=	Possible human carcinogen; inadequate data for humans and limited evidence of carcinogenicity in animals
D	=	Not classifiable as to human carcinogenicity because of inadequate or no evidence
E	=	Not a human carcinogen, based on no evidence of carcinogenicity in adequate studies

Factors affecting partitioning of the chemical in relation to wildlife and aquatic organisms, food chain multipliers (biomagnification factors), toxic effects and mode of action, and other information were compiled from various sources, as referenced in the bioaccumulation summary tables.

4.4 Insights from the Chemical Summary Tables

Examination of the data compiled for the bioaccumulative chemicals included in the Appendix provides information that might be useful in addressing a number of issues pertaining to bioaccumulation. It is important to note that it is not enough to simply understand bioaccumulation and the factors that control it. Rather, one must understand that certain chemicals, when sufficiently bioavailable, can produce toxic effects in aquatic organisms and terrestrial wildlife and can pose risks to higher trophic levels (including humans) feeding on those organisms. Interpretation of the effect levels also requires consideration of the lipid levels (percent lipid) measured in the organisms. Lipid measurements can vary depending on the methodology used to extract and analyze the lipids. To facilitate comparison among results, it is necessary to convert all the values to the same units. The data in the Appendix tables were usually not converted in order to allow the end user to refer back to the original study, if necessary. However, molar unit conversions were made for three chemicals that have a nonpolar narcotic mode of toxic action—acenapthene, phenanthrene, and pyrene—because narcosis is believed to occur as the result of the presence of toxicant molecules in the organism rather than because of the absolute character of the molecules (reviewed in Rand, 1995). This conversion allows direct comparisons of the tissue residue and effects data for these chemicals.

The compilation of data for the bioaccumulative chemicals revealed that most studies only compared sediment or water concentrations to tissue levels and few studies have measured concentrations in sediment or water *and* concentrations in tissue *and* effects on the organism. No data were found for disulfoton, oxyfluorfen, and Aroclor 1248. Numerous studies did report tissue residue *and* effect concentrations (see last paragraph in this section). BCFs were obtained for various species for 24 chemicals, BAFs for 25 chemicals, BMFs for wildlife for 11 chemicals, and BSAFs for 43 chemicals. (The most BSAF values were reported for PCB congeners, chlordane, *p,p*N-DDE, *p,p*N-DDT, and dieldrin.) For some chemicals appropriate data were sparse (Aroclor 1016, Aroclor 1242, benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chromium, chrysene, 1,2,3,7,8-pentachlorodibenzofuran, 2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin, 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin,1,2,3,4,7,8-hexachlorodibenzofuran, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, and dicofol).

Examination of the chemical summary tables might help to shed light on the following bioaccumulation issues:

- *What species are potentially available for use in testing?*

A variety of organisms have been used to determine bioaccumulation in field and laboratory situations, but not consistently among chemicals. Organisms for which data were found in the tables included those species commonly used in bioaccumulation testing (e.g., *Macoma balthica, Nereis diversicolor, Neanthes arenaceodentata, Chironomus* spp., *Pimephales promelas*) and others that had been obtained in field studies (e.g., stoneflies, caddisflies, freshwater and marine mussels, tubificid worms, carp, sole, sculpin, three-spined stickleback), including some endemic species. Further discussion of issues related to bioaccumulation testing was presented in Chapter 3.

- *How should we account for differential partitioning of bioaccumulative contaminants among tissues?*

Studies compiled in the Appendix reveal that different tissues can contain different amounts of bioaccumulative contaminants. Tissue residue measurement methodology varied greatly with the study,

from using the whole organism to obtain residues (usually invertebrates and small fishes) to examining uptake in specific organs (hepatopancreas, liver, gill, gall bladder, kidney) or in muscle. Potentially the best way to account for this partitioning is normalization to lipid, as was done in some studies. Knowledge of the "site of action" is essential for some chemicals to interpret the data. For example, nerve tissue needs to be examined in the case of some metals.

- *How can bioaccumulation methods be used to assess population-level effects?*

Evaluating endpoints that relate to the survival and success of populations in the wild could reduce uncertainties about the impacts that might occur from exposure to bioaccumulative contaminants in sediment. Percent survival or mortality was the most frequently reported effect. Other endpoints that have been examined include changes in shell thickness and tissue weight or shell deformations (bivalves), scope for growth or growth rates, impacts on reproduction (imposex, breeding impairment, deformed larvae), behavioral changes (feeding rates), immune system dysfunction, metabolic changes or enzyme induction, and histopathological changes.

Extrapolation of subcellular (e.g., enzyme induction, immune system dysfunction) and individual (e.g., growth rates, tissue weight, behavioral changes) effects to population-level effects has proven difficult. Population-level effects might be examined by analyzing the bioaccumulation of chemical contaminants of several species at different trophic levels, as well as by assessing those species' abundances, reproduction success (gonad development, viability of eggs and larvae, recruitment), and age class distributions over a period of time. Histopathological changes can be monitored to provide information on why abundances, reproduction, and age class distribution might change in relation to contaminant uptake. This information can also be incorporated into population modeling efforts to improve our ability to predict population-level effects (discussed in Chapter 3). For example, one study on fathead minnows exposed to sediment containing Aroclor 1254 reported that reproduction was inhibited and frequency and fecundity were 5 to 30 percent of values observed in unexposed fish (Melancon et al., 1989).

- *How can tissue-specific residue levels be coupled with chronic toxicity response data to develop dose-response relationships for bioaccumulative contaminants?*

The most striking lack of information concerned effects. Where sediment *and/or* water *and* tissue concentrations were found, no associated effects data were reported for organisms exposed to acenaphthene, phenanthrene, benzo(a)anthracene (invertebrates), benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dicofol, 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin, 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin, 2,3,7,8-tetrachlorodibenzofuran (invertebrates and fishes), silver, toxaphene, PCB 28, PCB 105, PCB 126, and PCB 156 (invertebrates and fishes). However, many of the studies found for dioxins and furans and PCB congeners reported tissue residues as the result of food exposure in association with effects on wildlife (e.g., eagle, heron, falcon, duck, and mink). References in which effects data were reported also contained tissue residue data, except for two studies in which cladocerans and amphipods were exposed to arsenic (sediment *and* water *and* effects data only). Sediment concentrations *and* tissue residues *and* effects data were reported for only nine cases. Of the metals examined, tributyltin had the most references to studies that included tissue residue *and* effects data from research on amphipods, polychaetes, mollusks, and fishes. More tissue residue *and* effects data for more species were found for 2,3,7,8-TCDD, *p,p*′-DDE, *p,p*′-DDT, and total PCBs than the other organic chemicals examined. Limited effects data (one to a few references) were found for arsenic, cadmium, chromium, lead, methylmercury, nickel, selenium, zinc, pentachlorophenol, benzo(a)pyrene, benzo(g,h,i,)perylene, fluoranthene, pyrene, *p,p*′-DDD, *p,p*′-DDE, *p,p*′-DDT, diazinon, dieldrin, heptachlor, congeners of dioxins and furans besides 2,3,7,8-TCDD, total PCBs, and Aroclors 1016,

1242, 1254, and 1260. Tissue residue concentrations and effects data for 2,3,7,8-TCDD included several fish species and birds, and for 2,3,7,8-TCDF included rainbow trout, birds, and mink.

The studies reporting sediment *and* tissue residue *and* effects data included Janssens De Bisthoven et al. (1992), which linked deformed antennae in larvae of the midge *Chironomus thummi* to tissue *and* sediment metal concentrations (copper, zinc, lead). Waite et al. (1991) found changes in shell thickness and tissue weight in relation to sediment *and* water *and* tissue concentrations of tributyltin in the oyster *Crassostrea gigas.* Sediment *and* tissue concentrations with survival data were collected for amphipods exposed to fluoranthene and pyrene (Landrum et al., 1994; Harkey et al., 1997). Whole animal wet weights were reduced in freshwater mussels exposed to a higher methylmercury sediment concentration relative to those obtained from mussels exposed to a lower sediment concentration at the least contaminated station (Salazar et al., 1995).

Tissue residues *and* effects were reported for 48 of the chemicals researched; however, for 12 of the chemicals, tissue residue and effects data were observed only for wildlife species. Mortality was a frequently reported effect for many aquatic invertebrates and fishes. Tissue concentrations of 300 µg/kg ww in muscle or liver of rainbow trout were associated with elevated EROD activity after 70 days' exposure to Aroclor 1254 (Toxscan, Inc., 1990), and eggshell thinning was associated with tissue residues of DDD, DDE, and DDT in birds. The development of dose-response relationships for bioaccumulative chemicals will require a better understanding of chronic toxicity responses and, in some cases, the internal dose or tissue residue level at the site(s) of toxic action (see review in Rand, 1995).

It is important to note that, although some chemicals have records for many species—including sediment/water *and* tissue, and tissue *and* effects—in most cases these data are for different species. For example, for benzo(a)pyrene, of 23 invertebrate species, only 1 (*Chironomus riparius*) has both types of data, and these were obtained from different studies. Though it may be possible to infer similar partitioning relationships (e.g., BSAFs) between closely related species in similar environments, data limitations clearly remain an obstacle for developing tissue residue-linked sediment chemical levels. One case in which a single species contains numerous concentration values for both categories of data (but no *single* study that reported sediment/water concentrations *and* tissue concentrations *and* effects data) is tributyltin. The mussel *Mytilus edulis* has been used in several studies to examine sediment contaminant bioaccumulation and effects of this metal. However, when trying to interpret these data, they need to be scrutinized carefully to determine, at a minimum, whether the form of tributyltin reported is consistent across the studies and whether procedures for estimating body burdens are comparable in the field and laboratory studies.

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5. SUMMARY OF AGENCY INFORMATION ON BIOACCUMULATION DATA COLLECTION AND INTERPRETATION

Bioaccumulation of toxic persistent organic contaminants by aquatic organisms is an ongoing concern for several federal agencies, including the U.S. Environmental Protection Agency (EPA), U.S. Army Corps of Engineers (USACE), National Oceanic and Atmospheric Administration (NOAA), U.S. Fish and Wildlife Service (FWS), and U.S. Geological Survey (USGS). These agencies have conducted research related to the issues presented in Chapter 1 and are involved in the development of policies and procedures pertaining to bioaccumulative chemicals. This chapter presents brief synopses of activities related to bioaccumulation data collection and interpretation in various EPA programs and in other federal agencies. Table 5-1 provides a summary of the information contained in this section.

5.1 EPA Headquarters Programs

USEPA has developed a comprehensive, multimedia Contaminated Sediment Management Strategy (59(167) FR 44879-44882, August 30, 1994; USEPA, 1994a, 1998a) describing the implementation of policies to consistently assess, prevent, and remediate contaminated sediment under existing statutory and regulatory authority. Components of the strategy address assessment, prevention, remediation, research, and outreach activities conducted to accomplish four strategic goals:

- Prevent further sediment contamination that may cause unacceptable ecological or human health risks.
- When practical, clean up existing sediment contamination that adversely affects the Nation's water bodies or their uses, or that causes other significant effects on human health or the environment.
- Ensure that sediment dredging and dredged material disposal continue to be managed in an environmentally sound manner.
- Develop and consistently apply methodologies for analyzing contaminated sediments.

EPA is using information and data on bioaccumulation in support of this strategy in its various programs. The ultimate goal of the Agency is to develop an approach to bioaccumulation assessment that will allow consistent, uniform, and robust decision making among the various Agency programs. In April 1994, the Agency participated in a consultation with the Science Advisory Board's (SAB) Bioaccumulation Subcommittee, consisting of representatives from the SAB's Ecological Processes and Effects Committee and Drinking Water Committee, to discuss approaches to estimating the bioaccumulation potential of chemicals and various mass balance/food web models. The SAB provided recommendations for modifying existing approaches for using mass balance/food web models and for prioritizing research needs related to these tools, particularly the collection of field and laboratory data that would help reduce uncertainties in these models (USEPA, 1995a). EPA has also formed a Bioaccumulation Analysis Workgroup, consisting of representatives from program and regional offices, to discuss cross-program issues in the interpretation of bioaccumulation information for the purpose of sediment quality assessment. The following subsections describe activities undertaken within EPA's program offices and regions that are related

Table 5-1. Summary of EPA Uses of Bioaccumulation Data for the Interpretation of Sediment Quality

Agency Mission and Mandates		Components of Contaminated Sediment Management					
Program	**Relevant Statutes[1]**	**Research**	**Assessment**	**Remediation**	**Dredged Material Management**	**Prevention**	**Outreach**
Office of Prevention, Pesticides, and Toxic Substances							
Office of Pesticide Programs	FIFRA		O				
Office of Pollution Prevention and Toxics	TSCA, PPA	O	O			O	O
Office of Air and Radiation	CAA		O				
Office of Research and Development							
National Health and Environmental Effects Research Laboratory		O	O				O
National Exposure Research Laboratory		O	O				
Office of Solid Waste and Emergency Response							
Office of Emergency and Remedial Response (Superfund)	CERCLA, SARA	O	O	O			
Office of Solid Waste	RCRA, HSWA, PPA	O	O	O		O	
Office of Water							
Office of Science and Technology	CWA, WRDA, GLCPA	O	O			O	O
Office of Wetlands, Oceans, and Watersheds	CWA, MPRSA, WRDA	O	O	O	O	O	O

Agency Mission and Mandates		Components of Contaminated Sediment Management					
Program	**Relevant Statutes[1]**	**Research**	**Assessment**	**Remediation**	**Dredged Material Management**	**Prevention**	**Outreach**
Office of Wastewater Management	CWA					**O**	

Table 5-1. Continued

Agency Mission and Mandates		Components of Contaminated Sediment Management					
Program	**Relevant Statutes[1]**	**Research**	**Assessment**	**Remediation**	**Dredged Material Management**	**Prevention**	**Outreach**
Region 1				**O**	**O**		
Region 2				**O**	**O**		
Region 3/Chesapeake Bay Program	CWA	**O**	**O**	**O**	**O**	**O**	**O**
Region 4					**O**		
Region 5		**O**	**O**	**O**	**O**		**O**
Great Lakes National Program Office	CWA as amended by GLCPA		**O**	**O**	**O**		
Region 6			**O**		**O**		
Region 7			**O**		**O**		
Region 8					**O**		
Region 9			**O**	**O**	**O**		
Region 10		**O**	**O**	**O**	**O**		
International Efforts			**O**			**O**	

[1]Acronyms: CAA = Clean Air Act; CERCLA = Comprehensive Environmental Response Compensation and Liability Act; CWA = Clean Water Act; FIFRA = Federal Insecticide, Fungicide, and Rodenticide Act; GLCPA = Great Lakes Critical Programs Act; HSWA = Hazardous and Solid Waste Amendments; MPRSA = Marine Protection, Research, and Sanctuaries Act; PPA = Pollution Prevention Act; RCRA = Resource Conservation and Recovery Act; TSCA = Toxic Substances Control Act; WRDA = Water Resources Development Act. Statutes are listed only for headquarters and program offices.

to research on bioaccumulative chemicals, assessment of such chemicals in the environment and potential risks from exposure, remediation and dredged material management of bioaccumulative chemicals, prevention of the manufacture or release of persistent organic pollutants, and outreach to inform and educate the public on the topic of bioaccumulative chemicals.

5.1.1 Office of Prevention, Pesticides, and Toxic Substances (OPPTS)

OPPTS develops national strategies for toxic substance control. It is responsible for the promotion of pollution prevention (P2) as the principle of first choice, as well as assessment of risk to human health and the environment from exposure to pesticides (Office of Pesticide Programs) and industrial chemicals (Office of Pollution Prevention and Toxics). Important activities of the office are to establish procedures and criteria for assessing chemical substances and to develop guidelines for chemical testing. OPPTS also develops rules and procedures for industry reporting, and develops and enforces regulations for controlling industrial chemicals and pesticides deemed hazardous to humans or the environment. Interest continues in the development of new sediment test methods for determining the environmental fate, ecotoxicity, and bioaccumulation of pesticides and industrial chemicals in sediment.

An important role of bioaccumulation test data is to support review of new and existing chemicals under the Toxic Substances Control Act (TSCA) and the registration/reregistration of pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). In addition, bioaccumulation information may be used to provide guidance on the design of new chemicals to reduce bioavailability and partitioning to sediment.

OPPTS is in the process of harmonizing its own (OPPT and OPP) test guidelines with those of the OECD (Organization for Economic Cooperation and Development) to create a single set of guidelines that minimizes variability and unnecessary testing. The office prepared “public draft” sediment toxicity test guidelines employing chironomids (including tissue residue analysis) and amphipods (freshwater, estuarine, and marine). These have been published in the *OPPTS Test Guidelines, Series 850 Ecological Effects,* Volume I (USEPA, 1996a). These 850 guidelines are in the process of being finalized. OPPTS is also involved in developing new OECD sediment toxicity test guidelines for chironomids. An environmental fate test guideline, “Sediment/Water Microcosm Biodegradation Test” (OPPTS 835.3180), has gone final and is publicly available. Also, the office is near final approval of an OECD guideline (“Aerobic and Anaerobic Transformation in Aquatic Sediment”) that has a similar purpose.

5.1.1.1 Office of Pesticide Programs (OPP)

The mission of OPP is to safeguard public health and the environment from unreasonable pesticide risks, while ensuring that pesticides are regulated fairly and efficiently. In carrying out its responsibilities under FIFRA, OPP must consider both the risks posed by pesticides and the benefits that pesticides offer to society. State and tribal agencies and many other organizations, both public and private, are vital partners in this effort.

Assessment

Bioconcentration studies are currently required by two divisions of OPP under FIFRA for the registration of pesticides. The Environmental Fate and Effects Division requires bioconcentration testing as prescribed in 40 CFR, Part 158 under guidelines 72-6 and 165-4, -5; the Health Effects Division requires a bioconcentration test under test guideline 171-4. The purpose of these studies is to determine

if pesticide residues accumulate in fish used as human food sources, to determine the edible portions of such fish, and to characterize the fate of pesticides within the various tissue compartments of an organism.

The Environmental Fate and Effects Division of OPP requires bioaccumulation tests to support the registration of formulated end-use products intended for outdoor use (except domestic outdoor), or aquatic impact uses resulting in direct discharge into aquatic environments. Bioaccumulation testing is required when the active ingredient or its principal degradation products have a water solubility less than 0.5 mg/L, the octanol/water partition coefficient is greater than 1,000 (log K_{ow} = 3), it is persistent in water (e.g., half-life greater than 30 days), or it accumulates in organs and tissues of mammals or birds.

The studies are flow-through, preferably using radioisotopic analytical techniques, and the exposure system must maintain constant concentrations of chemical in true aqueous solution not to exceed 1/10th the 96-hour LC50 for the test species. The preferred test species is the channel catfish or the bluegill sunfish. The studies require 28 days of exposure with a depuration of 14 days. Extractable residues of 0.05 mg/L or greater must be identified in two samples of edible tissue and two samples of viscera. If pesticides are shown to bioaccumulate in fish tissue, the Environmental Fate and Effects Division may require accumulation testing with nontarget organisms.

The accumulation study required by the Health Effects Division (171-4) is a metabolism study designed to determine the magnitude of residues in fish following exposure to a pesticide. The studies are required when fish may be exposed to the pesticide or its degradation products. The test uses carbon-14 and may be static or flow-through depending on the aquatic system under consideration. Fish residue data are required for bottom feeding species (e.g., catfish), predators (e.g., bass), and shellfish (both mollusks [e.g., clams, oysters] and crustaceans [e.g., shrimp, crabs]). For pesticides used in estuarine areas, data on whole fish protein concentrate and on smoked, canned, or other processed fish products are needed to determine whether a Food Additive Regulation is necessary.

5.1.1.2 Office of Pollution Prevention and Toxics (OPPT)

The mission of OPPT is (1) to protect and improve human health and the environment, to achieve risk reduction, sustainability, and environmental justice, and to enhance the quality of life; (2) to promote safer designs and wiser use of materials, products, processes, practices, technologies, and disposal methods, using pollution prevention as the principle of first choice; and (3) to provide information, education, and technical assistance to empower the public to make informed decisions on the risks associated with toxic substances.

Prevention/Assessment/Outreach

Draft Multimedia Strategy for PBT Pollutants

EPA recently released a draft strategy to further reduce risks to human health and the environment from existing and future exposure to priority persistent, bioaccumulative, and toxic (PBT) pollutants. The strategy, available on the Internet at www.epa.gov/pbt/strategy.htm, reinforces and builds on existing EPA commitments related to priority PBTs, such as the 1997 Canada-U.S. Binational Toxics Strategy, the North American Agreement on Environmental Cooperation, and the recently released Clean Water Action Plan. EPA is forging a new approach to reduce risks from and exposures to priority PBT pollutants through increased coordination among EPA national and regional programs. This approach

also requires the significant involvement of stakeholders, including international, state, local, and tribal organizations, the regulated community, environmental groups, and private citizens.

The four main elements of the PBT Strategy are

- Develop and implement national action plans for priority PBT pollutants
- Screen and select more priority PBT pollutants for action
- Prevent introduction of new PBT pollutants
- Measure progress

To date, EPA actions to reduce emissions of PBT pollutants have been largely separate regulatory activities aimed at different environmental media. Such actions will now be better coordinated to ensure, for example, that regulations removing the PBT from air do not inadvertently result in transferring the pollution to the ecosystem. Developing an Agency-wide strategy enables EPA to harness all of its tools—voluntary, regulatory, international, enforcement, compliance, and research—and direct them at a set of priority pollutants of common concern to all EPA program offices. EPA's first 12 priority PBT pollutants, from the Canada-U.S. Binational Toxics Strategy, are aldrin/dieldrin, benzo(a)pyrene, chlordane, DDT (+ DDD + DDE), hexachlorobenzene, alkyl-lead, mercury and compounds, mirex, octachlorostyrene, PCBs, PCDD (dioxins) and PCDF (furans), and toxaphene.

The strategy outlines a number of actions that EPA will take to reduce exposures to and uses of PBT chemicals. Some of the near-term actions include the following:

- Preventing the introduction of new PBT chemicals in commerce
- Encouraging voluntary reductions of priority PBT chemicals in hazardous waste
- Giving the public information on mercury emissions from utilities
- Increasing the public's right to know about local sources of PBT pollutant emissions
- Evaluating fish in U.S. water bodies for PBT chemical contamination

Research/Prevention/Assessment

Screening the TSCA Inventory

In the early 1990s OPPT screened discrete organic chemicals on the TSCA Chemical Substances Inventory to provide a preliminary list of potentially persistent and bioaccumulative chemicals for further evaluation. This activity identified approximately 80 chemicals with estimated half-lives exceeding 30 days, estimated BCFs greater than 250, molecular weights greater than 600, and production volumes greater than 10,000 pounds per year. Substances having such physical properties often partition significantly to the sediment compartment in the aquatic environment. This list is being used by the Canadian government (joint project of Health Canada/Environment Canada) in activities aimed at prioritizing Canada's Domestic Substances List (DSL), the Canadian equivalent of the TSCA inventory, and identifying PBT chemicals.

Waste Minimization Prioritization Tool (WMPT)

The goal of the Waste Minimization National Plan (WMNP), developed by EPA's Office of Solid Waste (OSW) and mandated by the U.S. Congress, is to reduce the volume of the most persistent, bioaccumulative, and toxic chemicals in the nation's hazardous wastes at least 25 percent by the year 2000 (50 percent by 2005). In pursuing this goal, source reduction is preferred over recycling and a central purpose is to avoid cross-media transfers of constituents. The Waste Minimization Prioritization

Tool (WMPT) was developed jointly by OSW and OPPT to assist in the implementation of the WMNP. The WMPT ranks chemicals based on persistence, bioaccumulation, and toxicity potential ("PBTness"). To accomplish this, it classifies (bins) chemicals as high, medium, or low for persistence and bioaccumulation potential. As noted above, substances having such properties often demonstrate a marked tendency to accumulate in aquatic sediments, in addition to fatty tissue of exposed organisms. The WMPT is flexible, Windows-based software designed for screening only.

Toxics Release Inventory (TRI): PBT Rulemaking

OPPT maintains the Toxics Release Inventory (TRI) under the Emergency Planning and Community Right-to-Know Act (EPCRA). Proposed rulemaking that specifically targets PBTs was published in the *Federal Register* on January 5, 1999 (64 FR 687). As noted above, substances having such properties often demonstrate a marked tendency to accumulate in aquatic sediments, in addition to fatty tissue of exposed organisms. The rulemaking proposes to:

- Set persistence and bioaccumulation criteria for reporting on chemicals under EPCRA section 313.
- Add some chemicals that meet toxicity criteria for listing and are also persistent and bioaccumulative.
- Lower reporting thresholds for PBTs that are already on the TRI.

In so doing the rule provides general technical guidance on the types of persistence and bioaccumulation data needed to determine "PBTness." It also sets half-life criteria of 2 months for water/sediment and soil and 2 days for air, as well as a bioaccumulation factor/bioconcentration factor (BAF/BCF) of 1,000, for purposes of defining which substances are and which are not persistent and bioaccumulative under the rule. Further, although compartment-specific half-life criteria are the primary means of determining persistence, the rule indicates that multimedia fate modeling will be used to confirm findings based on compartment-specific half-lives, and it may override compartment-specific data if key model inputs are judged reliable.

TSCA: Proposed PBT Policy for Premanufacture Review Chemicals

Under TSCA, a Premanufacture Notice (PMN) must be submitted 90 days prior to manufacture of any new industrial chemical. For many years OPPT has used chemical "categories," based on toxicity, to streamline regulatory review, and until now categories (of which there are now more than 45) have been defined by structure/activity relationships (SARs). Taking a new approach, OPPT recently developed and proposed a category for persistent, bioaccumulative, and toxic (PBT) substances for purposes of PMN review. As noted above, substances having such properties often demonstrate a marked tendency to accumulate in aquatic sediments, in addition to fatty tissues of exposed organisms.

Proposed half-life criteria for persistence and bioaccumulation are tiered to reflect level of concern:

Criterion	Possible Actions
Persistence: > 2 mo for water/sed or soil; Bioaccumulation: fish BCF $ 1,000	Exposure/release controls; triggered testing
Persistence: > 6 mo for water/sed or soil; Bioaccumulation: fish BCF $ 5,000	More stringent controls; ban pending testing

To determine potential risk, EPA may use multimedia models to account for all loadings, transformation processes, and intermedia transfer in an integrated fashion. Implementation of the new PBT policy might also lead to testing to fill critical data gaps if EPA is unable to adequately determine the potential for persistence and bioaccumulation using existing information. The proposed testing strategy is tiered and includes sediment/water persistence test guidelines of increasing complexity in tiers 2 and 3. Analogously, laboratory testing for bioaccumulation potential would be conducted if tier 1 testing (Ready Biodegradability testing and measured log K_{ow}) confirms suspicion that a substance is potentially persistent and bioaccumulative. Standard fish bioconcentration testing is conducted in tier 2, and, potentially, bioaccumulation testing using sediment-dwelling aquatic organisms in tier 3.

Development of this TSCA new PBT chemicals policy has occurred in coordination with US national, US/Canada binational, and international efforts to identify and control the environmental release of persistent organic pollutants (POPs). The PBT category description, in the form of an October 5, 1998 proposed *Federal Register* policy statement (63 FR 53417), was provided to the United Nations Environment Program (UNEP) Governing Council's Criteria Expert Group (CEG) for POPs, established at the first session of the Intergovernmental Negotiating Committee (INC). The final policy statement on this PBT category responded to comments received on the proposed policy and was published in the Federal Register on November 4, 1999 (64 FR 60194). This final notice represents the first formal statement of US national policy regarding new chemical POPs. Under our domestic TSCA program, the policy statement provides guidance criteria for persistence, bioaccumulation and toxicity for new chemicals and advises the industry about our regulatory approach for chemicals meeting the criteria. Internationally, the October 5, 1998 proposed policy statement alerted the parties involved in negotiation of the POPs Convention to the need for inclusion of a new chemicals provision in the Convention. The issuance of the final policy statement reaffirms US leadership on this issue and serves as a model for other countries in taking steps to discourage the introduction of POPs as new chemicals and pesticides.

5.1.2 Office of Air and Radiation (OAR)

OAR incorporates information on bioaccumulation of air toxics in certain analyses when such information is available. For example, in the Urban Air Toxics Strategy, finalized in July 1999, OAR ranked air toxics to derive a list of the pollutants posing the greatest risk to public health in urban areas. As one part of this analysis, OAR ranked air toxics by relative potential for oral toxicity and food-chain bioaccumulation. Using estimated national emissions, in tons per year, OAR adjusted the emissions by multiplying a bioconcentration factor (BCF) and dividing it by the oral risk-based dose (RBD) for chronic effects. RBDs for chronic oral exposure were expressed as a milligram of an air toxic per kilogram of body mass per day. Measured and estimated BCFs for air toxics were obtained from EPA's draft Waste Management Prioritization Tool (WMPT). The WMPT is intended to allow EPA to rank relative hazards from the list of hazardous substances regulated under the Resource Conservation and Recovery Act, and it has been judged to be a reasonably comprehensive resource for the purpose of ranking air toxics. The BCF is an estimate of the proportion of a substance that will partition into aquatic

organisms relative to ambient water, at equilibrium. Well-developed BCFs consider both relative solubility in water and lipid and the ability of biological systems to metabolically alter the contaminant.

In addition, in March 1999 OAR released a Report to Congress presenting its methodology for conducting "residual risk" assessments. After setting technology-based standards for major industrial sources of air toxics, OAR must evaluate the remaining health and environmental risks (i.e., the residual risks) and set more stringent regulations, if necessary. For each of these assessments, OAR will identify the exposure pathways of concern, taking into consideration the environmental persistence and bioaccumulation potential of certain air toxics. For a limited subset of air toxics, assessments may include noninhalation exposure (e.g., food chain, other environmental media).

5.1.3. Office of Research and Development (ORD)

ORD provides scientific and technological expertise to remediate environmental and human health problems. Its three headquarters' offices, three national research laboratories, and two national centers work with other EPA program and regional offices, the states, and tribes. ORD conducts basic, peer-reviewed research and implements cost-effective, common-sense technology, including providing extramural research grants and fellowships to develop the sound environmental research necessary to ensure effective policy and regulatory decisions.

5.1.3.1 National Health and Environmental Effects Research Laboratory (NHEERL)

NHEERL in Research Triangle Park, North Carolina, is responsible for investigating the effects of environmental pollutants and other anthropogenic stressors on human health and ecosystems, using toxicological, clinical, epidemiological, ecological, and biogeographic research methods. Long-term research at NHEERL is defining and characterizing toxicological hazards, quantifying dose-response and other important cause-effect relationships, and assessing the integrity and sustainability of ecosystems. The Atlantic Ecology Division (AED) in Narragansett, Rhode Island; Mid-Continent Ecology Division (MCED) in Duluth, Minnesota; Gulf Ecology Division (GED) in Gulf Breeze, Florida; and Western Ecology Division (WED) in Corvallis, Oregon, are charged with developing methods and techniques for examining bioaccumulation of persistent organic chemicals and metals, evaluating bioaccumulation under field and laboratory conditions, developing models and other analytical procedures for assessing risks to biota from bioaccumulative chemicals, and assisting in the preparation of guidance for interpreting bioaccumulation data.

Research/Assessment

NHEERL has conducted numerous studies of bioaccumulation in marine biota. Examples include comparisons of field data to the 28-day bioaccumulation test for uptake of the pesticides DDT and dieldrin in the clam *Macoma nasuta* (WED) and measurement of the accumulation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), 2,3,7,8-tetrachlorodibenzofuran (TCDF), and polychlorinated biphenyls (PCBs) from Passaic River, New Jersey, sediment samples by sandworms, clams, and grass shrimp (AED) (Pruell et al., 1993). Another project involves the bioaccumulation and trophic transfer of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), PCBs, and other compounds in a laboratory food chain consisting of sediments, polychaetes, and lobster (AED). A second area of research involves the use of surrogate materials mixed into sediment to determine the bioavailability of sediment-associated contaminants. The ability of equilibrium-based and kinetic approach bioaccumulation models to predict tissue residues as a

cost-effective alternative to direct measurement of tissue residues has also been evaluated (WED) (Lee, 1992).

MCED is conducting research on assessing bioaccumulative chemicals found in freshwater sediments, as well as improving methods for evaluating the effects of such compounds on aquatic and terrestrial biota and developing tissue residue criteria for a variety of contaminants. Because relationships between complex mixtures of sediment contaminants and bioaccumulation and toxicity in benthic organisms are often uncertain, the Division is conducting controlled toxicity and bioaccumulation tests. Current research includes further investigation of the effects of pore water chemistry on bioavailability and toxicity identification evaluation (TIE) methods development.

The Great Lakes Water Quality Initiative (GLWQI) required bioaccumulation factors (BAFs) for fish that incorporated site-specific bioavailability, biomagnification/food chain effects, and metabolism. Additional complications were the need for BAFs for chemicals such as TCDD, which currently do not have measured concentrations in water, and a concern for variation over time and space, and in the chemical properties of the sediment-water distribution coefficient. Most of the potential variability was eliminated by basing BAFs on trophic level, lipid-normalized concentrations in tissues, and concentrations of freely dissolved chemicals in water. Freely dissolved concentrations in water are based on octanol-water partition coefficient (K_{ow})-correlated partitioning to particulate and colloidal organic carbon in the water. The ability of biota-sediment accumulation factor (BSAF) ratios to measure bioaccumulation and metabolism differences between chemicals was incorporated into a procedure for estimating BAFs for chemicals below analytical detection limits. Food chain models that incorporate benthic food chain linkages to pelagic fish were also evaluated and included in the GLWQI bioaccumulation methods. These methods need to be evaluated further in other aquatic ecosystems.

At MCED, laboratory methods for toxicity and bioaccumulation tests for a variety of freshwater benthic invertebrate species have been developed and validated. These include toxicity test methods for the amphipod *Hyalella azteca* and the midge *Chironomus tentans*, and a 28-day bioaccumulation test method for the oligochaete *Lumbriculus variegatus* (USEPA, 1994g). Field validations of bioaccumulation predictions have been accomplished (e.g. Ankley et al., 1992). Nonchemical factors that increase sediment contaminant toxicity, such as activation of PAHs in organisms by ultraviolet radiation, have been documented and incorporated into toxicity predictions.

MCED is also working on sediment-based ecological risk assessment methods. Fish early life stage toxicity from exposure to complex mixtures of PCDDs, PCDFs, PCBs, and other polyhalogenated aromatic chemicals that share an aryl hydrocarbon receptor-mediated mode of action has been related to sediment contamination in the Great Lakes through use of chemical-specific BSAFs, TCDD toxicity equivalence factors (TEFs), and dose-response relationships based on concentrations of these chemicals in fish eggs. Through retrospective analysis and correlation with epidemiological data, this work provides an initial validation of the integrated application of sediment-based bioaccumulation models for pelagic fish, chemical concentration in tissue-based dosimetry, and an additive toxicity equivalence model. The same methods may be applied to wildlife. Staff scientists from MCED also prepared an “interim report on data and methods for assessment of TCDD risks to aquatic life and associated wildlife” (USEPA, 1993). The report reviewed and evaluated data and models available for analyzing the effects of exposure to and bioaccumulation of TCDD in aquatic life and wildlife, and it addressed areas of uncertainty that limit how well risks can be characterized.

Scientists at MCED are participating in the Lake Michigan Bioaccumulation and Toxic Effects Characterization Study (LMBTECS), the purpose of which is to incorporate all of the data, models, and

methods of the Division's projects into the interpretation of a high-quality bioaccumulation data set obtained in conjunction with the ongoing Lake Michigan Mass Balance Study for the chemicals PCBs, *trans*-nonachlor, and atrazine. Besides the collection of sediment, plankton, benthos, fish, and water samples to evaluate bioaccumulation and toxic effects models, LMBTECS is unique because of the extensive list of analytes (approximately 1,000 chemicals) and the use of high-resolution gas chromatography/high-resolution mass spectrometry with stable isotope standards and maximum instrument sensitivity. This sensitivity, coupled with large-volume water samples (1,000 L) extracted by three different techniques, will maximize detection of hydrophobic organic chemicals in water. Much of the study involves interpretation of chemical concentrations in sediments and suspended solids. Core analyses, BSAFs, tissue dosimetry-effects relationships, and toxicity equivalence models for complex mixtures of chemicals with the same mode of action will provide a basis for retrospective analysis of exposures and associated toxicity risks.

GED's Estuarine Assessment program is working to develop, improve, and validate realistic diagnostic procedures to determine the ecological condition of Gulf of Mexico estuaries. Research related to bioconcentration/bioaccumulation is part of this program. Some biota are transplanted and exposed in cages for periods of 21 to 42 days, after which tissues are analyzed for metals, pesticides, PAHs, and PCBs. The exposures are conducted at many stations and seasonally to determine the spatial and temporal variability in the bioresidues. In other cases, indigenous species are analyzed from the same locations to determine the relative difference in tissue quality using the two assessment techniques. The types of biota that have been analyzed include freshwater bivalves, oysters, blue crabs, fishes, sea grasses, rooted vascular plants, algal mats, and periphyton. The study areas are those associated with Superfund sites, wastewater, urban and storm water runoff, agricultural runoff, dredging activities, and golf course runoff.

The residue concentrations have been compared to enzyme content, blood proteins, pigment content, biomass, and community structure for several of the biota to determine the impact of the residues. The chemical quality of the surface water and sediment has been determined during the analyses and compared to the tissue burdens to determine the bioconcentration factors from these different media. In addition, the effect of salinity on the magnitude of the residues has also been investigated. Currently, several GED personnel are developing a data set describing the tissue quality in several biota inhabiting reference coastal areas. The data from this study will be used to determine the relative impact of the anthropogenic activities on tissue quality determined in previous studies.

Outreach/Technical Guidance

The Pacific Ecosystems Branch in Newport, Oregon, produced a guide to the methods used for assessing pollutant bioaccumulation from bedded sediment in sediment-dwelling organisms (Boese and Lee, 1992). The guide assists researchers in selecting the best laboratory or field assessment method or bioaccumulation model based on the available data and the goals of the project.

AED developed a Standard Operating Procedure for the extraction of lipids from marine tissues (Pruell, 1995). Contaminant concentrations normalized to lipids measured using this SOP have been shown to correlate well with toxicity and contaminant depuration rate. The technique is also relatively simple and produces precise data.

Outreach/Database Development

MCED has developed databases to assist in the interpretation of bioaccumulation data. ECOTOX version 1.0 is now available for government users (Russom, 1996). Developed at MCED with support by the Department of Defense's Strategic Environmental Research and Development Program, ECOTOX allows users to search across three existing EPA databases—AQUIRE, PHYTOTOX, and TERRETOX—which contain ecotoxicological effects information for aquatic life, plants, and terrestrial wildlife, respectively. Version 1.0 also provides access to the Office of Pesticide Programs' Ecological Effects Database of aquatic and terrestrial effects data reviewed and categorized as acceptable for pesticide registration and reregistration guideline requirements explained under FIFRA Subdivision E, Parts 158.145 and 158.150. ECOTOX user's manuals can be obtained from the Scientific Outreach Program by phone, (218) 720-5602; fax, (218) 720-5539; or e-mail, outreach@du4500.dul.epa.gov. Data are grouped in the AQUIRE database according to chemical, aquatic organism, exposure conditions, and effect endpoint, and include BCF test results. TERRETOX is a terrestrial wildlife toxicity database that provides data linking quantified chemical exposures with observed toxic effects, providing data to quantify the relationships between chemical concentrations in environmental media or wildlife foods and residues in wildlife tissues. This database identifies sources of alternative data (domestic or laboratory animal toxicity and bioaccumulation information) when there is a lack of information on wildlife species.

MCED is currently developing a database of toxic effects to aquatic life associated with concentrations of bioaccumulative chemicals in tissues. To date, approximately 450 references from the scientific literature have provided data on 180 chemicals for freshwater and saltwater invertebrates and vertebrates, including amphibians. The data will allow prediction of toxicity risks or establishment of tissue residue-linked sediment chemical levels for single chemicals when concentrations of sediment contaminants in tissues of susceptible organisms can be determined through use of equilibrium partitioning, BSAFs, site-specific exposure models, or direct measurement. Tissue chemical concentrations associated with no observable effects, mortality, or reduction in growth or reproduction are most commonly noted.

5.1.3.2 National Exposure Research Laboratory (NERL)

NERL is responsible for characterizing the sources of environmental stressors and the compartments of the environment in which they reside or move, studying the pathways through compartments that lead to exposure of receptors to stressors, investigating intra- and intercompartmental stressor transfers and their transformations, and studying and characterizing receptors to predict or measure stressor exposure. The Ecological Exposure Research Division in Cincinnati, Ohio, and the Ecosystems Research Division, in Athens, Georgia, have been involved in research to develop and implement models to provide risk assessors with better and more refined estimates of exposure and dose.

Research/Assessment

Scientists at the Athens laboratory developed a model to analyze the bioaccumulation of PCBs in Lake Ontario alewife (*Alosa pseudoharengus*), coho salmon (*Oncorhynchus kisutch*), rainbow trout (*Oncorhynchus mykiss*), brown trout (*Salmo trutta*), and lake trout (*Salvelinus namaycush*) (USEPA, 1991a). The model addresses fish gill morphometry; feeding and growth rate; fractional aqueous, lipid, and nonlipid organic composition; and chemical properties used to estimate aqueous diffusivity and partitioning to fish lipid and nonlipid organic fractions such as molar volume and – octanol/water partition coefficient (K_{ow}).

5.1.4 Office of Solid Waste and Emergency Response (OSWER)

OSWER is responsible for controlling hazardous wastes and remediating hazardous waste sites under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), including ash, mining wastes, medical wastes, underground petroleum storage tanks, oil spills, municipal solid wastes, industrial solid wastes, and household hazardous wastes.

5.1.4.1 Office of Emergency and Remedial Response (Superfund/Oil Programs) (OERR)

OERR manages the Superfund program, which was created to protect citizens from the dangers posed by abandoned or uncontrolled hazardous waste sites. Congress established Superfund in 1980 by passing CERCLA, which gives the federal government the authority to respond to hazardous substance emergencies and to develop long-term solutions for the nation's most serious hazardous waste problems.

Research/Assessment

Under CERCLA, EPA has established a comprehensive program for identifying, investigating and remediating sites contaminated with hazardous substances. The Hazard Ranking System (HRS) is a scoring system used to assess the relative threat associated with actual or potential releases of hazardous substances at sites. The HRS is the primary way of determining whether a site is to be included on the National Priorities List (NPL), EPA's list of sites that are priorities for long-term evaluation and remedial response. The HRS score is the result of an evaluation of four pathways: (1) ground water migration, (2) surface water migration, (3) soil exposure, and (4) air migration. Bioaccumulation is evaluated for two threats in the surface water migration pathway, the human food chain and the environmental food chain. The bioaccumulation potential of each hazardous substance is determined using a tiered system employing (1) BCF data, (2) the logarithm of the n-octanol-water partition coefficient (log K_{ow}) data, and (3) water solubility data (55 FR 51532).

Risk assessments for Superfund sites involve a longer and more costly process than an HRS evaluation. Under CERCLA, EPA carries out a detailed analysis of risks posed by contaminants at the site to human health and the environment, and the feasibility of various response action alternatives to reduce risk. The *Risk Assessment Guidance for Superfund* (RAGS) (USEPA, 1989, 1991b, 1991c,1997c) provides a framework for the assessment of human health and environmental impacts. Various EPA publications, including guidance in RAGS, Ecological Updates, and fact sheets, are used to develop assessments that are presented as a part of the Remedial Investigation/Feasibility Study (RI/FS) of a CERCLA site. The process is not designed specifically for sediments, but rather for the purpose of assessing all exposure routes from contamination at CERCLA sites. Nine criteria are used in the FS to evaluate options for remedial actions at CERCLA sites: (1) overall protectiveness of human health and the environment; (2) compliance with ARARs, i.e., national and state standards and criteria; (3) long-term effectiveness and permanence; (4) reduction of toxicity, mobility, or volume through treatment; (5) short-term effectiveness; (6) implementability; (7) cost; (8) state acceptance; and (9) community acceptance.

There is a widely recognized need for Agency-wide guidance for determining which chemicals have the potential to bioaccumulate. There is regional variation in the log K_{ow} cutoff for determining chemicals that have the potential to bioaccumulate, with some using log K_{ow} greater than 5 and others using log K_{ow} greater than 4. There is also no consensus on the degree of bioaccumulation of heavy metals and

lipophilic organic halogens. Other issues concerning bioaccumulation data and their interpretation in the Superfund Program are summarized below.

Estimates and Measurements of Bioaccumulation

Regions prefer to use site-specific information on bioaccumulation whenever possible, using models and literature values for preliminary or screening assessments. Site-specific data are usually collected for more complex sites or sites requiring further investigation. Types of empirical data used to evaluate bioaccumulation include

- Fish and mammal tissue sampling and analysis
- Toxicity testing
- Field and *in situ* (caging) bioaccumulation studies
- Surface water and sediment chemical analyses
- Sediment leachability tests

In one region, the U.S. Fish and Wildlife Service is using an "artificial" fish with a lipid-filled membrane bag to conduct bioaccumulation studies. Bioaccumulation models being used by the regions include a K_{ow} model and a fish-gill exchange transfer model (USEPA, 1991a). Literature values used by the regions include chemical-specific bioaccumulation factors (BAFs).

Effects Concentrations for Chemicals

To identify effects concentrations, the regions are using values from peer-reviewed journal articles, AQUIRE, USFWS Hazard Reviews, information from other sites, and the Oak Ridge National Laboratory database. A number of regions mentioned using toxicity tests to measure effects concentrations. Most Regions estimated effects concentrations using NOEL and LOEL values, the hazard quotient method, and food web models. Partitioning coefficients (K_{ow} and K_{oc}) are obtained from USEPA and USFWS documents, the Superfund Chemical Data Matrix, and the ASTER database (part of AQUIRE). Approaches to identify effects concentrations and partitioning coefficients vary among the regions.

Use of Background Data to Assess Bioaccumulation

Most regions use background data as a reference for comparison to site conditions. One region uses background data to evaluate non-site-related stressors such as widespread pesticide use, agricultural input, and other nonpoint sources of pollution. Some regions screen out potential chemicals of concern (COCs) based on their presence in background or reference samples, whereas others take background information into account during the risk management, rather than the risk assessment phase. Background data may be particularly relevant during remediation, when cleanup levels are determined. The regions agree that background data should be collected and presented with site-specific data, but none suggest that empirical data collected to assess the effects of bioaccumulation should be used on both background and site-impacted samples.

Remediation

Cleanup and Endpoints Based on Bioaccumulation

Several regions reported that cleanups at sites within their jurisdiction had been driven by risks associated with bioaccumulation of chemicals. Generally, numerical cleanup for COCs was back-calculated, using either site-specific BAFs or published values for representative species. In two cases, sites were remediated to a predetermined numerical standard, and tissue sampling and analysis of the local habitat followed cleanup. Overall, the examples mentioned by the regions involved cleanups of soil, not sediment. The Regions agreed that endpoints for bioaccumulation effects should protect and preserve local habitats, species, or populations. Target species for protection were generally fish-eating mammals and birds such as minks, shrews, wrens, raptors (hawks, eagles), and raccoons. Reproduction endpoints in these species were a major concern, followed by mortality and growth. One region suggested specific endpoints for DDT (avian reproduction) and mercury (fish-eating mammals and birds).

Assessment

Bioassay procedures can be valuable tools that provide efficiency and realism in assessing contamination. This was demonstrated in Puget Sound, Washington, where caged mussels were used to assess the bioavailability of sediment contaminants at the Harbor Island Superfund site and at a Carr Inlet reference site (Salazar et al., 1995). The caged mussels were held one meter from the bottom for an exposure period of 82 days. Accumulation of contaminants in adult mussel tissues was used to identify the extent and magnitude of contamination in overlying water, while reduced growth in juveniles was used to indicate adverse bioeffects. The analysis revealed a statistically significant inverse relationship between growth rate, toxicity-normalized tissue accumulation, and toxicity-normalized sediment contamination. Based on these results, the researchers recommended an integrated approach for evaluating contaminated sediments that includes conducting *in situ* bioassays, estimating bioaccumulation in addition to bioeffects, and evaluating water overlying sediments.

5.1.4.2 Office of Solid Waste (OSW)

OSW manages a complex regulatory program addressing solid waste disposal and hazardous waste management under RCRA. RCRA regulates the identification, transportation, treatment, storage, and disposal of solid and hazardous wastes. The act regulates such matters as hazardous waste generators and transporters; land disposal restrictions (LDR); federal procurement of products that contain recycled materials; municipal solid waste landfill criteria; solid and hazardous waste recycling; treatment, storage, and disposal facilities; and waste minimization and hazardous waste combustion.

Assessment/Prevention

Currently, OSW is conducting several multimedia risk analyses to support regulatory development efforts under the Resource Conservation and Recovery Act (RCRA). Examples of these include determining chemical-specific waste stream concentrations that represent a threshold below which Subtitle C disposal will not be required and thus the waste stream may exit the hazardous waste system; determining whether specific industrial wastes should be listed as hazardous under Subtitle C; and evaluating the risks of special types of wastes to determine the appropriate level of waste management required. As part of these efforts, OSW is developing a risk assessment modeling tool in coordination

with the Office of Research and Development. The tool will address multimedia exposures through several pathways for multiple receptors, including various types of human and ecological receptors.

Major components of the risk assessment methodology are various food chain modules in both the terrestrial and aquatic environments; within each environment several different types of habitats are being investigated. The key function of the aquatic food chain module is to determine suitable BAFs for chemical constituents and use these values to predict concentrations in the tissues of aquatic biota. Mechanistic models, regression equations, EPA analyses, and empirical data are used in a weight-of-evidence approach to determine the appropriate BAFs and, where possible, distributions of these factors. The approach is organized around five types of constituents—hydrophobic organics, hydrophilic organics, ionizable organics, PAHs, and metals (including mercury). The module involves a weight-of-evidence approach that considers the appropriateness of simulation modeling and regression equations to derive suitable BAFs, as well as measured BAFs from field studies. Although the Gobas model (and other similar models) adapted for use in the tool have been validated (e.g., for Lake Ontario), they have not been validated across all of the aquatic systems included in this analysis, particularly small streams (i.e., stream order 2 and 3). In addition, estimates of fish tissue concentrations are limited by the quality and quantity of data on bioaccumulation.

For farm food chain exposures, waste constituent concentrations are estimated in major plant and animal categories. For most organic constituents, regression equations relate simulated air and soil concentrations to plant tissue concentrations and, in turn, soil and plant concentrations to beef/milk concentrations (as described in the IEM [1997]). Steady-state and equilibrium are assumed between soil and roots, between soil and aerial parts, and between air and aerial parts. No flow between compartments is considered. A simple partition coefficient between the plant and an environmental medium (air or soil) is used to estimate the concentrations in vegetables and forage grasses. Each of the mechanisms considered for plant uptake is represented by a biotransfer factor and includes the following:

- Root uptake and translocation
- Air-to-plant transfer of vapor-phase contaminants
- Deposition of particle-bound contaminants on plant surfaces

Similarly, biotransfer factors are developed for each of the mechanisms considered for uptake into beef and dairy cattle, including

- Uptake from ingestion of contaminated forage, silage, and grain
- Uptake from incidental ingestion of contaminated soil
- Uptake from ingestion of contaminated surface water (e.g., local pond)

For all organic constituents except dioxins (and congeners), selected PAHs, and several hydrophobic constituents that are well studied, biotransfer factors are predicted using the empirical relationships represented by the regression equations. For these organic constituents, values are selected that are specific to both the chemical and, in some cases, the category of plant or cattle (i.e., beef or dairy). For metals, including mercury, plant uptake factors are derived from field data, including but not limited to values reported in EPA's sludge risk assessment work.

Biotransfer factors are used to represent major categories of plants (and animal tissues) without regard to site-based conditions such as soil type, plant species, application matrix, or environmental conditions (e.g., temperature). As a result, predicted concentrations in plants and beef/dairy products may be

associated with substantial uncertainty. For example, the biotransfer factors for metals may vary over several orders of magnitude depending on the study conditions.

In the terrestrial environment, uptake and accumulation in food items (flora and fauna) are used to estimate concentrations in higher trophic levels found in the terrestrial habitat. Four major categories are evaluated: (1) plants, (2) earthworms, (3) soil invertebrates, and (4) vertebrates. Each major category is divided into several subcategories that reflect significant differences in the dietary habits of receptors; for example, forage grasses and forbs would not be treated the same as nuts and berries. Generally speaking, mechanistic models and regression equations are lacking for terrestrial systems, particularly models that address variability in the environmental setting (e.g., differences in soil characteristics).

The same limitations noted above for the aquatic and farm food chain estimates also apply to the terrestrial environment with respect to predicting plant concentrations (e.g., an empirically based approach). In addition, the lack of data on uptake and accumulation of constituents in other terrestrial food items introduces significant uncertainty. In many cases, only a single point estimate may be available to determine the bioaccumulation potential in a given category.

Remediation

Subtitle C of RCRA provides EPA with the authority to assess whether releases from a hazardous waste treatment, storage, or disposal facility have contaminated sediments and to require corrective action, including possible remediation, if contamination is discovered. RCRA corrective action authorities apply to, among other things, all releases of hazardous waste or constituents from any solid waste management unit at a treatment, storage, and disposal facility seeking a RCRA permit, regardless of when the waste was placed in the unit. EPA assesses hazardous waste facilities that have RCRA permits. These assessments are called RCRA Facility Assessments (RFAs). If an RFA suggests that a release has occurred, hazardous waste permit writers can require facility operators or owners to conduct extensive RCRA Facility Investigations (RFIs) to determine the extent of any contamination. In the corrective action program, EPA sets priorities using the National Corrective Action Prioritization System (NCAPS). NCAPS priorities are generally based on information gathered during the RFA. EPA's policy is to focus its corrective action resources first on facilities and areas at facilities that present the greatest relative risk to human health and the environment. Accordingly, NCAPS considers the environmental setting of a facility and potential receptors, actual and potential releases of hazardous wastes or constituents from the facility, and the toxicity of constituents of concern to group facilities into high, medium, and low priority groups. NCAPS rankings are based on risk, but NCAPS does not involve a traditional site-specific risk assessment. NCAPS is a resource management tool that EPA and authorized states use to set relative priorities among corrective action sites to focus limited agency resources (61 FR 19432).

Prevention/Research

In November 1994, EPA released the Waste Minimization National Plan (WMNP). The WMNP focuses on reducing the generation and subsequent release to the environment of the most persistent, bioaccumulative, and toxic chemicals in hazardous wastes. It establishes three goals:

- To reduce, as a nation, the presence of these chemicals in hazardous wastes by 25 percent by the year 2000 and by 50 percent by the year 2005.
- To avoid transferring these chemicals across environmental media.

- To ensure that these chemicals are reduced at their source whenever possible, or, when not possible, that they are recycled in an environmentally sound manner.

The first goal has also been included as a Government Performance and Results Act (GPRA) objective for the RCRA program.

Stakeholders involved in the development of the WMNP emphasized the need to prioritize source reduction and recycling activities based on risk and requested a flexible screening tool that would assist them in identifying priorities. EPA subsequently committed in the WMNP to develop a tool that would prioritize chemicals based on persistence, bioaccumulation potential, toxicity, and quantity. EPA's Office of Solid Waste (OSW) and Office of Pollution Prevention and Toxics (OPPT) developed this tool, the Waste Minimization Prioritization Tool (WMPT), and released a Windows-based beta-test version for public review in June 1997 (EPA530-C-97-003). Based on the public comments received, a number of improvements were made to the WMPT, and a modified spreadsheet version was released in November 1998 in support of OSW's draft RCRA PBT List (described below).

Bioaccumulation scoring in the revised WMPT is based on measured bioaccumulation factors, measured bioconcentration factors, predicted bioaccumulation factors, and predicted bioconcentration factors, in order of preference. Chemicals with bioaccumulation or bioconcentration factors greater than or equal to 1,000 are classified as high concerns for bioaccumulation, chemicals with values below 250 are classified as low concerns, and the rest are classified as medium concerns. Additional information on the revised WMPT and its bioaccumulation scoring approach is provided in the *Waste Minimization Prioritization Tool Spreadsheet Document for the RCRA Waste Minimization PBT Chemical List Docket* located in RCRA docket F-98-MMLP-FFFFF and on EPA's homepage at www.epa.gov/wastemin.

The revised WMPT was used as the starting point for selecting chemicals for the RCRA PBT List, a list of chemicals that will serve as the focus of national hazardous waste minimization program activities. Four equally weighted criteria were used to score and rank candidate chemicals for the draft list, including the higher of human health and ecological concern scores from the revised WMPT, the quantity and prevalence of chemicals in RCRA hazardous waste, the presence of chemicals in the environment, and RCRA programmatic concerns associated with the chemicals. Additional information on the list is provided in RCRA docket F-98-MMLP-FFFFF and on EPA's homepage at www.epa.gov/wastemin.

5.1.5 Office of Water (OW)

OW is responsible for EPA's water quality activities, which represent a coordinated effort to restore the nation's waters. The functions of this program include developing national programs, technical policies, and regulations relating to drinking water, water and sediment (including dredged material) quality, and ground water; establishing environmental and pollution source standards; and providing for the protection of wetlands. In addition, the Office furnishes technical direction, support, and evaluation of regional water activities; enforces standards; and develops programs for technical assistance and technology transfer. The Office oversees the provision of training in the fields of water quality, economic and long-term environmental analysis, and marine and estuarine protection.

5.1.5.1 Office of Science and Technology (OST)

OST is responsible for developing sound, scientifically defensible standards, criteria, and advisories and effluent guidelines, effluent limitations, and standards guidelines under the Clean Water Act and the Safe

Drinking Water Act. OST is also responsible for developing risk assessment methodologies and for providing risk assessment support for the Office of Water.

Research

In August 1998, OST proposed revisions to its human health methodology for deriving ambient water quality criteria (see 63 FR 43755, EPA-822-Z-98-001 for Federal Register notice; see EPA-822-B-98-005 for Technical Support Document). The existing methodology uses BCFs to predict exposure from the consumption of contaminated aquatic species. The revisions to the methodology propose to use BAFs instead of BCFs. BAFs are preferred over BCFs because BAFs are a better predictor of the concentration of a chemical within aquatic organisms since they include consideration of the uptake of contaminants from all routes of exposure, not just uptake from water. EPA's human health methodology includes a methodology for establishing BAFs. The BAF methodology consists of four different approaches. Each approach is ranked (i.e., tiered) in order of preference. Using the proposed methodology, OST is developing National Default BAFs for 28 chemicals to assist states and tribes in updating their ambient water quality criteria. OST is also developing guidance on how to plan and collect field data for deriving BAFs.

OST has developed a simulation tool called AQUATOX, for evaluating bioaccumulation risks. AQUATOX is an ecosystem model that has the ability to model the combined environmental fate and ecological effects of pollutants in aquatic ecosystems. It can simulate the fate of pollutants, including bioaccumulative organic compounds, beginning with their input into the water body, partitioning to the water, sediments, and biotic components, and transfer throughout the food web, and culminating in the tissues of fish that might be consumed by humans or wildlife. Significant ecological processes are simulated, including primary and secondary productivity, trophic structure and dynamics, predator/prey interactions, toxicity, and nutrient dynamics. The model has undergone several validation studies (including one on bioaccumulation of PCBs in Lake Ontario), and is expected to be released in early 2000.

Another EPA model, WASTOX (Water Quality Analysis Simulation for Toxics), is composed of sequential models for calculating the fate and bioaccumulation of toxic chemicals in surface water systems (rivers, lakes, estuaries). The fate model computes time-variable or steady-state concentrations of toxic chemicals in the water column and sediments based on mass balance equations for advective-dispersive transport, phase transfers, and chemical transformations within a multidimensional, segmented water-sediment domain. The bioaccumulation model uses water column and sediment exposure concentrations from the fate model to compute time-variable or steady-state transfers of toxic chemicals through pelagic and/or benthic food webs. In this calculation, toxic chemical accumulations in various compartments of the food web are determined from information on the bioenergetic structure of the food web, gill transfer rates, chemical uptake through ingestion of contaminated prey, chemical egestion/excretion rates, chemical metabolism, and fish migration behavior.

WASTOX was originally developed under cooperative agreements with EPA's ORD laboratory in Gulf Breeze, Florida, and the Large Lakes Research Station of EPA's ORD laboratory in Duluth, Minnesota. The model has been applied to toxic contamination problems at various sites including kepone in the James River (through striped bass), PCBs in Lake Michigan and Green Bay (through lake trout), and PCBs in the Hudson River (through striped bass). A Windows version of the WASTOX model is being developed under a cooperative agreement with EPA's Office of Water, Washington, DC.

EPA is developing a series of analytical tools to screen environmental samples (i.e., sediment, tissue, effluent, ambient water) for chemicals that have the potential to bioaccumulate and move through the food web. The screening methods and background information were first released as draft guidance in 1993. These methods isolate acid-stable, nonpolar organics that have log partition coefficients (log P) values greater than 3.5. Detection levels associated with the different environmental media are 100 ng/L for aqueous samples (e.g., effluent or ambient water) and 50 Fg/kg for sediment and tissue samples.

The screening methods have undergone field validation at two discharge sites. The results of the field validation have been published in scientific journals and as an addendum to the draft guidance. In addition, the analytical procedures have also been the focus of a round robin study to evaluate inter- and intra-laboratory variability. Participants in the round robin study were from 16 national, industrial, and academic laboratories. EPA is currently analyzing the data from the round robin study. As EPA completes the data analysis for each medium, EPA will publish the results in scientific journals and revise the screening methods to address any deficiencies identified in the round robin exercise.

These screening methods will provide an alternative to the "target list" approach for evaluating environmental samples. Instead of looking for specific chemicals, the screening methods generate a list of any compound present in the sample that has a potential to bioaccumulate and its approximate concentration. This approach allows environmental managers to quickly identify chemicals of potential concern and focus on them. EPA recommends that the screening protocol be followed up by chemical-specific analysis to confirm the identification of a chemical and to more precisely determine its concentration.

Assessment

National Study of Chemical Residues in Lake Fish Tissue

The Office of Water is conducting a National Survey of Chemical Residues in Lake Fish Tissue. This study will meet objectives presented in the President's Clean Water Action Plan (CWAP, February 1998) and provide information about persistent, bioaccumulative, and toxic chemicals for the Agency's PBT Initiative.

- CWAP Key Action — EPA and NOAA will conduct a national survey of mercury and other contaminant levels in fish and shellfish throughout the country and will coordinate the effort with states and tribes to maximize geographic coverage. The shellfish survey will be based on the data obtained by NOAA's ongoing Mussel Watch Project.

- The PBT Initiative, begun by EPA's Office of Prevention, Pesticides, and Toxic Substances, seeks to identify areas of concern for human or ecological health. The lake fish tissue study may reveal where PBTs not previously considered a problem are present at levels of concern.

A workshop was held on October 27 and 28, 1998, in Crystal City, Virginia, to review the survey design. More than 40 workshop attendees representing states, other federal agencies, and EPA headquarters, regional offices, and labs reviewed, commented on, and added to the survey design components, including the statistical design, target analytes, field sampling procedures, and data management. This study expands the scope of the 1987 study (USEPA, 1992b) which focused on chemical residues in fish tissue near point source discharges. This new study will

- Provide information on the national distribution of selected persistent, bioaccumulative, and toxic chemical residues (PBTs) in game fish and bottom-dwelling fish in lakes and reservoirs of the continental United States (excluding the Great Lakes).

- Include lakes and reservoirs selected according to a probability design.

- Involve the collection of fish from those randomly selected lakes and reservoirs over a 3-year survey period.

- Include the analysis of fish tissue for PBT chemicals selected from the Agency's multimedia candidate PBT list of 451 chemicals and a list of 130 chemicals from several contemporary fish and bioaccumulation studies.

The study will not be used to set fish consumption advisories. However, states and Native American tribes may choose to initiate a detailed fish study in a particular lake based on the screening contaminant concentrations provided by the national study.

Contaminants monitored in fish tissue will include mercury, PCBs, dioxin, and pesticides as well as other PBT chemicals. The workshop participants form the initial study workgroup consisting of EPA program offices, state and tribal agencies, and federal agencies. EPA will work closely with the state/tribal/federal partners to carry out the study.

National Sediment Quality Survey

The National Sediment Quality Survey (USEPA, 1997d) was prepared in response to the requirement in the Water Resources Development Act of 1992 that EPA conduct a comprehensive national survey of data regarding sediment quality in the United States and report to Congress biennially on the assessment results. For calculations related to bioaccumulation, the survey makes use of fish tissue residue data and models bioaccumulation from sediment using the theoretical bioaccumulation potential approach. Data were compiled from 11 regional and nationwide databases to identify locations throughout the United States where accumulated persistent organic chemicals could pose a threat to aquatic and terrestrial biota and humans. OST used screening-level assessment to identify watersheds for further assessment and management actions to protect sediment quality. As part of the peer-reviewed evaluation methodology, OST compiled benthic and pelagic BSAFs from information provided by NHEERL-Narragansett and NHEERL-Duluth, worked with NERL-Athens to review chemical-specific K_{ow}s, compiled final chronic values (FCVs) from various sources, and developed sediment quality advisory levels (SQALs) for nonionic organics using an equilibrium partitioning methodology. By substituting a protective tissue reside value (TRV) for human or wildlife consumers for a theoretical bioaccumulation potential (TBP; see Section 4.3.2.5), sediment guidelines can be derived for more than 100 chemicals by using the TBP model:

$$\text{TBP-based sediment guideline } (\mu g/g_{oc}) = TRV(\mu g/g_{tissue}) / [f_{lipid}(g_{lipid}/g_{tissue}) * BSAF(g_{oc}/g_{lipid})]$$

Field-measured BSAFs vary depending on food chain biomagnification, metabolism, and many site-specific environmental variables. In most cases, USEPA (1997d) used median values from frequency distributions of field-measured BSAFs by chemical class reported by Tracey and Hansen (1996). Risk-based TRVs for protection of human consumers are available in USEPA (1997a). Information needed to calculate TBP-based sediment guidelines is available in the National Sediment Quality Survey appendices online at www.epa.gov/ost/cs/report.html.

Assessment of Mercury and PCB Contamination

To address a current public health concern, OST is collecting fish tissue data from state and federal agencies to develop a more detailed national picture of the nature and extent of mercury contamination. The project is ongoing, with the initial phase (data collection and compilation) completed in late FY 1997. A data summary report will be published in early 1999. Future directions of this project involve statistical analysis of the spatial patterns of fish tissue residue levels and related factors such as atmospheric deposition, local mercury sources, watershed size, pH, dissolved organic carbon, and acid-neutralizing capacity using GIS. OST also sponsored a technical assistance conference that addressed concerns about mercury in fish (September 1994) and another on PCBs in fish (May 1993).

Assessment/Prevention

OST's Standards and Applied Science Division uses bioaccumulation data and modeling in support of effluent guidelines for industries that discharge persistent organic pollutants in significant amounts, such as the promulgation of effluent limitations guidelines for the pulp, paper, and paperboard industry. In-stream pollutant concentrations are estimated for various treatment technologies based on estimated pollutant loadings. Potential fish tissue concentrations are calculated by multiplying the pollutant-specific BCF by the estimated in-stream concentrations of all pollutants evaluated, except dioxins and furans. Fish tissue levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF are estimated using EPA/ORD's draft Dioxin Reassessment Evaluation (DRE) model (USEPA, 1994f), which estimates fish tissue levels by including the amount of dioxin adsorbed to the organic carbon fraction of sediments suspended in the water column. Carcinogenic risks and noncancer hazards to recreational, subsistence, and Native American anglers are estimated based on different rates of consumption of these potentially contaminated fish.

Dredged Material Management (with Office of Wetlands, Oceans, and Watersheds)

See "Dredged Material Management" under Office of Wetlands, Oceans, and Watersheds (Section 5.1.5.2).

Outreach/Technical Guidance

Guidance for Conducting Fish and Wildlife Consumption Surveys (USEPA, 1998b) provides explicit instructions for selecting a survey approach and designing a survey to obtain consumption rate information. A statistician should also be consulted to provide advice on the specific sampling and statistical analysis considerations for each fish consumption rate assessment project. The survey methods presented in this document may be used by regional, state, tribal, or local agencies to obtain information on the consumption of noncommercially obtained fish and wildlife. This information can then be used to estimate risks to persons who could consume organisms that might contain bioaccumulative and potentially dangerous levels of toxicants, and to develop consumption advisories and point-source discharge loads to protect human health. Such surveys can also provide demographic information about a population for which advisories are issued, which might assist in the communication of risks and advisory recommendations.

OST developed a four-volume series of documents titled *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume I: Fish Sampling and Analysis (*second edition) (USEPA, 1995d) provides information on sampling strategies for a contaminant monitoring program. In addition, information is provided on selection of target species, selection of chemicals as target analytes, development of human health screening values, sample collection and analysis procedures, and data

reporting and analysis. *Volume II: Risk Assessment and Fish Consumption Limits* (second edition) (USEPA, 1997a) provides guidance on the development of risk-based meal consumption limits for the high-priority chemical fish contaminants (target analytes). It also contains a discussion of risk assessment methods used to derive the consumption limits, as well as a discussion of methods to modify the limits to reflect local conditions. *Volume III: Risk Management* (USEPA, 1996b) provides guidance on risk management procedures regarding the selection and implementation of various options for reducing health risks associated with the consumption of chemically contaminated fish and shellfish. A tiered approach to developing fish advisories is discussed. Templates are included to enable risk managers to organize their information to evaluate needs and to identify the optimal group of options and consumption limits. *Volume IV: Risk Communication* (USEPA, 1995e) provides guidance on risk communication as a process for sharing information with the public on the health risks of consuming chemically contaminated fish and shellfish.

Outreach/Database Management

The *Listing of Fish and Wildlife Consumption Advisories* (USEPA, 1997b) is a database of all fish and wildlife consumption advisories issued by various state, federal, and local agencies. Included in the database is information regarding types of advisories; species and chemical included in the advisory; contaminant levels; segments of the population affected; percentage of water bodies under advisory by state, region, or nationally; georeferenced locations of advisories; dates of issue; and agency contacts with phone numbers. The database can also generate maps that illustrate any combination of these parameters. The database is updated annually and is available on the Internet at www.epa.gov/ost/fish.

5.1.5.2 Office of Wetlands, Oceans, and Watersheds (OWOW)

OWOW was created to integrate the protection and management of our nation's watersheds, coastal and marine waters, and wetlands. OWOW is made up of three Divisions—the Oceans and Coastal Protection division, the Wetlands Division, and the Assessment and Watershed Protection Division—all three of which manage national programs that use bioaccumulation testing.

OWOW plays a significant role at regional, national, and international levels in efforts to manage dredged material. The Oceans and Coastal Protection Division (OCPD) manages the disposal of dredged material in the ocean under the Marine Protection, Research and Sanctuaries Act (MPRSA). Under MPRSA, OCPD develops regulations that set forth the criteria for ocean dumping, which include criteria for designating ocean dumping sites, issuing ocean dumping permits, and testing material proposed for ocean dumping. The Wetlands Division (WD) manages the discharge of dredged material in waters of the United States under section 404 of the Clean Water Act. WD develops regulations that set forth the criteria for such discharge, which include criteria for choosing disposal sites, issuing permits, and testing material proposed for disposal in inland waters.

OWOW's responsibilities include development of the environmental criteria used by the U.S. Army Corps of Engineers (USACE, the permitting authority for dredged material) in evaluating dredged material for proposed disposal. In addition, OWOW develops national guidance to the regions (jointly with the USACE) regarding dredged material management, and it provides technical assistance to the regions on site selection or designation, testing, and permitting issues.

The Assessment and Watershed Protection Division (AWPD) serves as the national program manager for EPA's nonpoint source control efforts. AWPD assists states in implementing programs that target watersheds for Total Maximum Daily Loads (TMDLs), thus helping to control potential sources of

sediment contamination, including bioaccumulative material; develops nonpoint source management practices; and assesses the conditions of our nation's watersheds.

Dredged Material Management

OWOW manages the national dredged material management program for EPA. OCPD and WD regulate and manage dredged material disposed of in ocean and inland waters, respectively. OCPD manages dredged material disposal in ocean waters under MPRSA and the Ocean Dumping Regulations. The regulations describe the criteria that must be met for materials disposed of in the ocean (dredged material or other materials). The national testing manual (the "Green Book"), developed jointly with the USACE, describes the tests and procedures recommended for use in determining whether dredged materials meet the regulatory requirements (USEPA and USACE, 1991). Bioaccumulation of contaminants is one of the factors described in the regulatory criteria and is one of the factors for which test procedures and evaluation guidance are contained in the Green Book. As provided in the Green Book, each EPA region or USACE district involved in ocean dumping is to use the national guidance in developing local testing and evaluation procedures based on the contaminants of concern and species existing in a given area, and the levels of contaminants in the sediments already existing in the area of the disposal site (the reference). Based on the regulatory requirements and the 1991 Green Book guidance, the regions follow a tiered approach to testing that includes conducting 28-day bioaccumulation tests on the dredged material with at least two species, and comparison of the resultant data with FDA action limits, bioaccumulation levels observed in the same species exposed to reference sediments in 28-day bioassays, and other factors listed in the Green Book such as magnitude of bioaccumulation above reference and toxicological importance of the resultant bioaccumulation. Toxicological importance of the 28-day bioaccumulation results is evaluated by comparison to regionally appropriate values of specific contaminants in tissue that have been shown to indicate tissue concentrations associated with significant undesirable effects.

WD regulates dredged material disposed in inland waters under section 404 of the Clean Water Act (CWA). These 404(b)(1) guidelines, regulations promulgated by EPA under the CWA, describe the criteria that must be met for materials disposed of in inland waters. WD is also responsible for implementing the testing procedures in the Inland Testing Manual (USEPA/USACE, 1998), jointly developed by EPA and the USACE.

Assessment/Prevention

Section 301(h) of the 1977 Clean Water Act allows EPA, with concurrence from states, to issue NPDES permits to Publicly Owned Treatment Works (POTWs) for the discharge of less-than-secondary-treated effluent. The marine discharge waiver program under section 301(h) provides an opportunity for waiver of the secondary treatment requirements for sewage discharged by cities and towns to marine waters and unstressed estuaries. Applicants must demonstrate that the discharge will not degrade water quality from levels that ensure the protection of public water supplies, the protection and propagation of balanced, indigenous populations of shellfish, fish and wildlife, and the protection of recreational activities on or in the water. OCPD develops the criteria used to evaluate such waiver requests. The deadline for 301(h) applications closed in 1982, and 45 applicants/permittees remain in the program.

OCPD also developed a revised technical support document for modifications of secondary treatment requirements for POTWs under the National Pollutant Discharge Elimination System (NPDES) permitting program (USEPA, 1994a). The support document provides technical guidance for implementing the 301(a) requirements and the accompanying regulations (40 CFR Part 125, Subpart G).

Among other things, the support document explains the toxic control requirements of section 301(h), which include consideration of bioaccumulation of sediment contaminants. POTWs are required to provide a schedule for development and implementation of nonindustrial toxic control programs if their discharges contain these contaminants. The law also requires POTWs to describe their public education programs for minimizing entrance of nonindustrial toxic pollutants and pesticides into their treatment systems and to describe industrial pretreatment requirements, if applicable.

Section 403(c) requires that discharges from point sources into ocean waters cause "no unreasonable degradation" to the marine environment. OCPD develops the environmental criteria used under section 403 in evaluating requests for NPDES permits for discharges to ocean waters. Both the 403(c) and 301(h) programs evaluate the ecological impacts of direct discharges to the marine environment and provide the Agency with a geographically targeted approach toward managing risk and protecting sensitive habitats that need the greatest protection.

Under both the 301(h) and 403 programs, the Agency considers the quantities of and potential for bioaccumulation of discharged pollutants, the potential for pollutant transport, potential harm to biological communities, and direct and indirect effects on humans. The 301(h) program developed a series of technical guidance documents to provide state-of-the-art methods of marine environmental monitoring and assessment to 301(h) applicants/permittees to aid in preparing 301(h) waiver applications, making waiver decisions, and designing and evaluating marine environmental monitoring programs.

OCPD has prepared a bibliography of documents that address methods for monitoring toxic substances and investigating bioaccumulation of toxic substances by marine and estuarine organisms (USEPA, 1994c). Bioaccumulation monitoring guidance documents address the qualities of target species and methods for assessing bioaccumulation; monitoring program design, including sampling of caged or indigenous indicator species; the type of tissue to be analyzed in invertebrates and fishes; and techniques for extracting and analyzing chemical contaminants. For example, the technical documents provide guidance on selecting target species for bioaccumulation studies in coastal areas (USEPA, 1987a). Tissue chemistry data for the target species recommended in the first volume were compiled in the second volume (USEPA, 1987b).

The 301(h) technical guidance has generally been well received and adapted as a basis of marine monitoring in other EPA marine-related programs, including programs related to section 403 ocean discharges and other marine discharges and marine disposal activities. OCPD developed *CWA Section 403: Procedural and Monitoring Guidance* (USEPA, 1994d) and similar guidance for the National Estuary Program, including the design and conduct of bioaccumulation monitoring studies to link exposure and effects and to examine risks to target species and humans (USEPA, 1992a). States have also adapted the 301(h) technical guidance for use in marine/ocean discharge programs.
OCPD also supports studies of environmental conditions at point sources and ocean dumping sites to manage impacts and protect the marine environment. Field surveys are conducted to support the designation of ocean disposal sites and to assess impacts of past and ongoing ocean disposal operations and discharges.

Remediation

The MPRSA and CWA regulate all discharge of material dredged from navigable waters and set forth the environmental criteria to be used in making such permit decisions. For example, when existing contaminated sediment in navigable waters requires *in situ* remediation using dredged material, the

proposed remediation material is evaluated based on applicable environmental criteria set forth in the MPRSA and CWA regulations. The criteria include bioaccumulation assessment when appropriate.

Research

There are ongoing research efforts in dredged material management and testing. For example, EPA, jointly with the USACE, is continuing to develop the Environmental Residue Effects Database (ERED), which contains bioaccumulation data from published research linked with concentration and its effects (USACE, 1997). ERED has been developed to reduce the level of uncertainty associated with interpreting bioaccumulation data for the purpose of making regulatory decisions regarding dredged material.

Outreach

OWOW and the EPA regions are involved in many forms of outreach regarding dredging-related issues. OCPD's outreach efforts include educating the general public about the ocean and coastal programs and making program information readily available to the public. Dredged material management-related testing and evaluation manuals, which include *Evaluating Environmental Effects on Dredged Material Management Alternatives - a Technical Framework*, *Overview of Dredged Material Testing Framework*, *Ocean Dumping Testing Requirements*, and the Green Book are available on the OCPD homepage (http://www.epa.gov/owow/oceans/).

The National Dredging Team (NDT) is an interagency group cochaired by EPA and the USACE. It includes the U.S. Fish and Wildlife Service (USFWS), the Maritime Administration, the National Oceanic and Atmospheric Administration's Office of Ocean and Coastal Resource Management, and NOAA's National Marine Fisheries Service. It was established in 1995 to promote national and regional consistency on dredged material management issues and to provide a forum for conflict resolution and information exchange. NDT's homepage is located at http://www.epa.gov/owow/oceans/ndt/.

OWOW and the USACE developed a guidance document, *Identifying, Planning and Financing Beneficial Use Projects Using Dredged Material.* Beneficial use of dredged material is considered an environmentally and economically sound way of disposing of dredged material. This document provides information to the general public on how to seek opportunities for beneficial uses of dredged material.

Information (fact sheets) regarding other marine and coastal programs (e.g. "Clean Water Act Section 403 - a Framework for Ecological Risk Assessment") are available on the OCPD homepage.

5.1.5.3 Office of Wastewater Management (OWM)

OWM oversees a range of programs contributing to the well-being of our nation's waters and watersheds. Through its programs and initiatives, OWM promotes compliance with the requirements of the Federal Water Pollution Control Act (Clean Water Act).

Prevention

Section 402 of the CWA authorizes the National Pollutant Discharge Elimination System (NPDES) permitting program, administered by the Office of Wastewater Management (OWM) within OW, to regulate the discharge of pollutants from point sources into navigable waters. Bioaccumulation screening methods can be used to identify chemicals of potential concern in the sediments, followed by chemical-

specific analysis for confirmatory purposes. Until the states adopt numeric criteria into their standards for sediment contaminants based on bioaccumulation, the NPDES program will not require permitting authorities to include, in their NPDES permits, sediment bioaccumulation-based numeric limits. However, states have the discretion to include such limits in permits based on an interpretation of their narrative standards for toxic substances. To establish such permit limits, it will be necessary for permitting authorities to develop Waste Load Allocations (WLAs) for the relevant sediment contaminants. After reviewing available fate, transport, and effect models, EPA's Office of Science and Technology (OST) has identified models that will allow development of WLAs. EPA's Office of Water will supply technical support for users of these models. Current resources for addressing the challenges of sediment bioaccumulative contaminants are the Technical Support Document (TSD), the Great Lakes Initiative (GLI), the draft User's Guide for Multi-program Implementation of Sediment Quality Criteria in Aquatic Ecosystems (under development by EPA OST), and the watershed permitting approach.

5.2 EPA Regions

Regional Administrators develop, propose, and implement regional programs for comprehensive and integrated environmental protection activities. The regional offices support the Agency's overall mission by translating technical program direction and evaluation for various Assistant Administrators and heads of headquarters staff offices into effective operating programs at the regional level. In addition, regional offices ensure that such programs are executed efficiently, that approval authority for proposed state standards and implementation plans is exercised appropriately, and that overall and specific evaluations of regional programs are provided. All EPA regions implement the dredging programs under the CWA and MPSRA as described in Section 5.1.5.2 of OWOW programs.

5.2.1 Region 1

The Region 1 office oversees environmental protection issues in the states of Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont.

Remediation

In EPA New England (Region 1) various data have been collected to assess the potential for bioaccumulation during the evaluation of ecological risks at several stages within the CERCLA process, which include the Remedial Investigation, Feasibility Study, and long-term monitoring as part of the Record of Decision (ROD) requirements.

During screening-level ecological risk assessments, predictive food chain models have been calculated using literature-derived BAFs. If the results of the literature-derived food chain models demonstrate an unacceptable risk to the ecological receptors, a risk management decision is usually made to revise risk analysis and decrease the uncertainties carried through risk characterization since contaminant-specific BAFs are quite variable. At this point within the ecological risk assessment process, revisions to risk analysis may include the collection of site-specific biota such as fish and invertebrates in order to develop a site-specific BAF to integrate into an avian or mammalian food chain model to provide a more realistic and confident assessment of exposure.

Over the last several years, through the efforts of the regional Biological Technical Advisory Group (BTAG) and the assistance of USFWS, the majority of bioaccumulation studies have focused on the collection and chemical analysis of various fish species as part of the baseline ecological risk assessment within the Remedial Investigation phase. In general, fish species are collected with electrofishing methods

to represent the three major feeding guilds—bottom feeders (i.e., brown bullheads), forage feeders (i.e., pumpkinseeds or bluegills), and predators (i.e., largemouth bass)—so as to be able to evaluate both piscivorous avian (i.e., great blue heron) and mammalian (i.e., river otter) receptors of concern. Once the fish species are collected, fish may be analyzed as whole bodies or separately as fillet and offal (remainder of fish minus the fillet) portions and then fillet and offal information added together so that both the human health and ecological risk assessments can benefit from this information. The greatest confidence with these types of bioaccumulation field efforts is associated with the integration of site-specific tissue residue concentration into the ecological risk assessment. In contrast, the greatest amount of uncertainty is associated with the inability to evaluate the potential adverse effects on the fish population itself from the exposure data. Therefore, tissue residue contaminant concentrations are predominately used to indirectly evaluate the effects on secondary consumers. Unfortunately, there is a paucity of effects data that can be correlated with exposure data to be able to determine the likelihood of ecological risk, especially for contaminant concentrations for terrestrial vegetation, submerged aquatic vegetation, and nonvascular plants such as seaweeds.

Following the collection and analysis of these data, along with other measures of exposure and effects (which could include the laboratory results of a toxicity test or the analysis of the benthic community), the weight of this evidence is discussed in the final phase of the ecological risk assessment, risk characterization. As part of the Feasibility Study process in which the remedial alternatives are evaluated, the results of the ecological risk assessment, which may be supported through the collection and interpretation of bioaccumulation data, are used to select a potential remedial action.

For sites in which the major contaminants of concern have been compounds known to bioaccumulate, such as DDT and its breakdown products DDD and DDE along with methylmercury, site-specific food chain models have been generated. These models have been used to establish the preliminary remedial goal (i.e., cleanup number) for contaminated sediments if both the sediment and biota were collected and analyzed so as to be able to develop the site-specific BSAF.

The collection and use of bioaccumulation has also been used as a component of the long-term monitoring at sites where actions have occurred at source areas and measures such as fish tissue residue data are needed to ensure the effectiveness of the remedial action. In contrast, these activities may be undertaken to monitor the consequences of a no-further-action risk management decision.

5.2.2 Region 2

EPA’s Region 2 includes the states of New Jersey and New York, as well as Puerto Rico and the U.S. Virgin Islands.

Remediation

In Region 2, bioaccumulation testing is being used during the evaluation of ecological risks at the Remedial Investigation stage of the CERCLA process. Such testing is also a condition of the Record of Decision (ROD) to ensure that long-term monitoring is conducted when contaminants of concern are left in place following the completion of a remedial action. Tissue data are used to determine whether there is a risk to ecological receptors; they have not been used to calculate sediment clean-up numbers. Further, tissue numbers in themselves are not used as clean-up numbers or preliminary remedial goals.

Bioaccumulation Studies and the Remedial Investigation

During Step 4 of the ecological risk assessment process (*Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments*, EPA 540-R-97-006), it is recommended that tissue be collected to gain a better understanding of the bioavailability of contaminants. These site-specific data are also employed in models to reduce the uncertainty associated with calculating the dose to higher-trophic-level receptors. In situations where a water body might be affected by site contaminants, the BTAG often recommends the collection of whole body fish. In some instances, to take advantage of the human health data being collected, it is requested that fish fillets collected for human health purposes be recombined (e.g., the carcass and the fillet are analyzed and mathematically combined) to enable data to be used for ecological purposes. Fish recommended for collection include bottom dwellers, those with a limited home range, and those most likely to be consumed by piscivorous receptors of concern (such as blue heron or mink). In some studies EPA recommends that caged bivalves (placed in contact with the sediment) be used to gain a better location-specific understanding of the system. The study is designed so that sediment chemistry, benthic community assessments, toxicity studies, and caged bivalves are collected from one location.

Although not frequently requested, benthic tissue data collection may also be used to gain a better understanding of site-specific characteristics. These data also help to reduce uncertainty by allowing the risk assessor to use a real bioaccumulation factor (between sediment and organism) in models.

Tissue studies of other organisms include small mammals such as shrews, voles, and mice. The data are then used to calculate a dose to upper-trophic-level receptors such as fox, mink, weasel, woodcock, owl, and hawk. The calculated dose is then compared to literature values and hazard quotients are computed to determine whether there is a potential for risk. These types of studies have been conducted at a number of Superfund sites.

Bioaccumulation Studies at the ROD Stage and Beyond

To determine the effectiveness of the remedy proposed at some CERCLA sites, long-term monitoring, which may include tissue collection, is being recommended more frequently. This approach is particularly useful at those sites where contaminants left in place have the potential to adversely affect the environment. In some cases it has been determined that the value of the habitat outweighs the risk of leaving contaminants in place. At two Superfund sites, PCBs are being left in place because of the value of the wetland habitat. Baseline fish tissue will be collected, and fish tissue will be collected following remedial action at one site and after a couple of years at the other. In the event that fish body burden levels do not drop after a period of time, further remedial action (i.e., sediment excavation) might be warranted.

At one site, postremedial monitoring includes tissue residue analyses for PCBs in field-collected fiddler crab and mummichog, as well as in clams exposed to site sediments in the laboratory. The goal is to demonstrate a negative trend in biotic PCB concentrations by the 5-year ROD review.

At one site EPA is proposing that amphibians (frogs) be used to determine whether soil and sediment removal for lead has successfully removed the contaminant from the ecosystem. In this situation, the availability of an adequate database to which tissue values could be compared is not critical. The study will examine lead body burdens and will look for a reduction over a period of time. At another site, the need to remediate the Westerly Wetlands will depend on the detection of significant reduction in growth or survival, or significant impact on higher-trophic-level receptors based on tissue residues (which are

then compared to literature values). Some organisms that might be included for studies are shrews and voles, which have been previously collected.

5.2.3 Region 3

Region 3 is composed of Delaware, the District of Columbia, Maryland, Pennsylvania, Virginia, and West Virginia.

Assessment/Outreach

On December 10, 1992, the Chesapeake Bay Program's (CBP) Toxics Subcommittee sponsored a "Chesapeake Bay Contaminated Sediment Critical Issue Forum" as part of the ongoing reevaluation of the Chesapeake Bay Basinwide Toxics Reduction Strategy. In 1993, the Chesapeake Executive Council designated three areas as toxic "hot spots" or "Regions of Concern," due in large part to sediment contamination: Baltimore Harbor, Anacostia River, and Elizabeth River.

The CBP's Toxics Subcommittee's Regional Focus Workgroup is currently conducting a toxics characterization outside these three Regions of Concern to identify any additional chemical contamination problems in the tidal tributaries of the bay. This characterization is based on an analysis and integration of water/sediment/fish tissue contaminant concentration data, water/sediment toxicity data, benthic community structure data, and any other biological effects data available. Based on a weight-of-evidence approach, the CBP will place segments of the bay's tidal tributaries into one of four categories, depending on the level of contamination: Regions of Concern (hot spots); Areas of Emphasis (warm spots); Areas with Low Probability for Adverse Effects (no problem spots); and Areas with Insufficient Data. The CBP has developed a set of "decision rules" for how to interpret the data. Sediment contaminant concentration data are compared to a variety of sediment thresholds (e.g., equilibrium-partitioning sediment guidelines [ESGs], NOAA effects range-low [ER-L] and effects range-median [ER-M] values; Environment Canada threshold effects level [TEL] and probable effects level [PEL] values). Fish tissue contaminant concentrations are compared to FDA action levels, FDA levels of concern, and EPA screening levels. Based on these comparisons and any associated water chemistry data and effects data, the Regional Focus Workgroup uses best professional judgement to characterize an area into one of the four categories. The workgroup is composed of scientists, regulators, industries, and managers. This characterization will be used as an outreach tool to put information in the hands of the public, scientists, and managers to target the appropriate areas for additional monitoring and management activities. This characterization will be updated every 3 years.

Prevention

The Toxics Subcommittee has also developed a risk-based chemical ranking system to evaluate chemical contaminant data in order to identify a short list of chemicals causing or having the potential to cause an adverse impact on the Bay's living resources. This chemical ranking system was used to revise the Chesapeake Bay Toxics of Concern chemical list. This revised list is still under review. The list was developed considering the source (loadings), fate (bioconcentration and environmental persistence), and exposure/effects (water column, sediment, and fish tissue) of chemical contaminants measured in the Chesapeake Bay.

Research/Remediation

The NOAA Chesapeake Bay Office (NOAA CBO) has a committee called the Chesapeake Bay Environmental Effects Committee, which sponsors research on environmental effects of toxicants, some of which includes bioaccumulation and food web work. In 1996 the program funded sediment transport research to provide managers with critical information to aid them in decisions regarding how to effectively deal with contaminated sediment in the Regions of Concern. This work may help managers make wise decisions regarding remediation, dredging, and capping projects. The CBP is working in concert with the NOAA CBO to develop a 5-year plan for the research program that will be finalized in late 1998.

5.2.4 Region 5

Region 5 consists of Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin.

Assessment/Remediation

Water Division and Superfund/RCRA-driven sediment remediations tend to use site-specific risk assessment information in deriving sediment clean-up goals. For bioaccumulative contaminants such as PCBs, the main exposure and risk pathways are ingestion of contaminated fish and incidental ingestion of contaminated sediment. To assess the fish ingestion pathway, a model/algorithm (BSAF) is used to derive acceptable levels in sediment that will allow for safe fish consumption, based on site-specific exposure assumptions. In addition, best professional judgment and negotiations will shape data issues (and resulting clean-up goals) such as defining area, averaging methods, conservatism of assumptions, and use of background contaminant data. The most recent regional thinking on how to approach these clean-up decisions is the subject of the draft S2F document (see Research below) and has been applied at some sites. In some cases the incidental ingestion pathway-driven clean-up goal (vs. fish ingestion) can result in lower clean-up goals. In another example, fish consumption, coupled with RCRA-benzene determinations and nonbioaccumulative NOELs/LOELs, is being used to leverage more removal.

Situations without PCBs can also be problematic. Dioxin sediment contamination can also result in fish contaminant concerns and thus lead to examination of sediment levels and effluent discharges. Control of existing effluents has usually been determined to be the most appropriate remedy, with sediment remediation not deemed necessary.

Research

The Region 5 Sediments to Fish (S2F) Workgroup, a joint project of the Region 5 In Place Pollutant Task Force and Health Effects Forum, reviewed relevant material and deliberated on risk and sediment issues. Because fish consumption might be a significant exposure pathway for humans and fish-eating mammals and birds, the workgroup agreed that a sound methodological approach for sediment-to-biota modeling was needed to provide support for both human health and ecological risk assessments. Results of the workgroup's study are compiled in a report entitled *Predicting Bioaccumulation of Sediment Contaminants to Fish* (USEPA, 1994h).

Research/Outreach

The *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors* (USEPA, 1995c) provides technical information and a rationale in

support of the methods to determine BAFs. BAFs, together with the quantity of aquatic organisms eaten and the percent lipid, determine the extent to which wildlife and humans are exposed to chemicals through the consumption of aquatic organisms. The more bioaccumulative a pollutant is, the more important the consumption of aquatic organisms becomes as a potential source of contaminants to humans and wildlife. BAFs are needed to determine both human health and wildlife Tier I water quality criteria and human health Tier II values, as well as to define bioaccumulative chemicals of concern, which were identified for the GLI to focus pollution prevention and remediation efforts.

Great Lakes National Program Office (GLNPO)

Assessment/Remediation

Thirty-one problem harbors and tributaries in the Great Lakes have been identified and labeled as Areas of Concern (AOCs). Contaminated bottom sediments have been identified as a significant problem that must be addressed to attain beneficial uses at all of these AOCs. The Assessment and Remediation of Contaminated Sediments (ARCS) Program was a 5-year demonstration project to help address the contaminated sediment problem at these locations. The goals of the ARCS Program were to develop an integrated, comprehensive approach to assess the extent and severity of sediment contamination; to assess the risks associated with that contamination; and to select appropriate remedial responses. This information was developed to help support implementation of Remedial Action Plans at the AOCs. Major findings of the ARCS Program are presented in a summary report (USEPA, 1994b).

As part of the ARCS Program, baseline human health risk assessments were conducted for five AOCs, and baseline aquatic and wildlife risk assessments were performed for the Buffalo River, New York. Comparative human health risks associated with direct and indirect exposures to contaminated sediments in the lower Buffalo River under selected remedial alternatives were estimated for carcinogenic and noncarcinogenic effects (Crane, 1995). Additionally, noncarcinogenic risks of ingestion of PCB-contaminated carp were estimated for mink, as an indication of ecological risks to piscivores. It was shown that risks could be reduced under the different remedial alternatives compared to no action, particularly if dredging was the selected option.

Currently, as a follow-up to the ARCS Program, GLNPO is conducting sediment assessments in many of the Great Lakes AOCs. As part of the assessment package, sediment bioaccumulation work is conducted on a case-by-case basis using the *Lumbriculus* bioaccumulation test. To date, this test has been conducted in Waukegan Harbor, Illinois; White Lake, Michigan; and Duluth Harbor, Minnesota.

In a number of locations around the Great Lakes, high contaminant concentrations in fish tissue have been key factors in moving forward with remedial activities. In the Ottawa River in Toledo, Ohio, PCB concentrations up to 510 ppm were found in carp. Fish consumption advisories are in effect for the entire river. Due in large part to these extremely high fish contaminant concentrations, a sediment remediation project was conducted in the spring of 1998. A total of 10,000 cubic yards of PCB-contaminated sediment (including 56,000 pounds of PCBs) was removed from a tributary to the Ottawa River. Fish will continue to be monitored to determine the success of the remedial project. High PCB concentrations in fish are also driving a second sediment remedial project on the Hayton Mill Pond of the Manitowoc River in Wisconsin. Fish tissue concentrations in the vicinity of the Hayton Mill Pond average 16 ppm PCB and range up to 77 ppm. Fish advisories have been in effect on the river since 1991. These bioaccumulation findings are helping move the site forward toward remediation, which is currently scheduled for the spring of 1999.

5.2.5 Region 6

EPA's Region 6 consists of the states Arkansas, Louisiana, New Mexico, Oklahoma, and Texas.

Assessment

EPA Region 6 performs very few bioaccumulation tests other than those required for the ocean dumping program. Typically, the region and states conduct chemical analysis of sediment and fish tissue to assess the degree of bioaccumulation and whether the sediment could be a source. A number of years ago, Region 6 required 28-day bioaccumulation tests performed with effluent, as well as collection of ambient water and sediment data, to evaluate whether effluent limits for several facilities discharging PCBs were appropriate and adequately protective. The EPA freshwater methodology (USEPA, 1994g) will aid in future sediment bioaccumulation work. The most easily implemented approach to assess bioaccumulation would be the development of chemical-specific guidelines for sediments that address bioaccumulative effects.

5.2.6 Region 7

Region 7 consists of the midwestern states Iowa, Kansas, Missouri, and Nebraska.

Assessment

Fish tissue analysis is the only bioaccumulation analysis being conducted in the Environmental Services Division. Two programs are involved in the collection and analysis of fish tissue—the Regional Ambient Fish Tissue Monitoring Program (RAFT) and the Regional Environmental Monitoring and Assessment Program (R-EMAP).

5.2.7 Region 9

Region 9 consists of Arizona, California, Hawaii, Nevada, American Samoa, and Guam.

Monitoring

Bioaccumulation testing and data are important components in numerous state and federal programs taking place within the region, such as the following: the San Francisco Bay Regional Monitoring Program, the Southern California Bight Regional Monitoring Program, and the routine monitoring of ocean disposal sites. In addition, several dischargers collect bioaccumulation data as part of their regular permit monitoring under the NPDES program.

Assessment/Remediation

The Region 9 Superfund program and Federal Facilities Cleanup Office (FFCO) routinely collect and use sediment bioaccumulation data. These programs use whole sediment, and occasionally chemical-specific, bioaccumulation data in their project-specific risk assessments. For example, Superfund's United Heckathorn remediation and Palos Verdes Shelf EE/CA involve comprehensively evaluating both human health and ecological risk endpoints, primarily for DDT compounds. The FFCO's numerous base closure-related projects typically evaluate a variety of contaminant mixtures in whole sediments.

5.2.8 Region 10

Alaska, Idaho, Oregon, and Washington are included in Region 10.

Assessment

The Columbia River Inter-Tribal Fish Commission (CRITFC) Exposure Study is a multiphase study sponsored by EPA to assess the exposure of the Nez Perce, Warm Springs, Umatilla, and Yakama Tribes to contaminants through fish consumption (USEPA, 1995b). The first phase of the study determined fish consumption patterns of the tribes. A study design for the second phase has been developed and includes collection and contaminant analysis of fish tissue at a number of sites. Tissue will be collected from resident and anadromous fish species consumed by tribal members and caught from tribal fisheries in the Columbia River Basin.

Remediation/Assessment

For bioaccumulative contaminants, sediment remediations tend to use site-specific field measurements as well as laboratory test data as the basis for risk assessment/management evaluations in deriving sediment clean-up goals. The main exposure and risk pathways are ingestion of contaminated fish or shellfish and incidental ingestion of contaminated sediment, although dermal contact and respiratory contact have been issues at some sites. PCBs, tributlytin (TBT), and mercury are the most frequent bioaccumulative chemicals of concern encountered. The Superfund program and the state of Washington's Toxic Cleanup Program coordinate routinely with the technical staff of the interagency Cooperative Sediment Management Program (CSMP) and frequently include them as part of the remediation study team as well as on special studies.

Region 10 Superfund published a final report on TBT, *Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, Washington* (USEPA, 1996c). An extensive literature search was conducted to develop screening values, including review of published research, regulatory standards and criteria, calculations of apparent effects threshold (AET) values and effects ranges, and examination of sediment-tissue and sediment-water partitioning. Bioaccumulation testing is recommended, in conjunction with bioassays and use of a sublethal effects endpoint, to confirm the ecological significance of interstitial water TBT concentrations. The approach will be used to identify TBT-contaminated sediments that should be addressed in remedial actions.

Assessment/Research

Human Health Sediment Quality Criteria

Taking the lead for the CSMP, the Washington State Department of Ecology ("Ecology") is developing human health-based criteria for sediments in Puget Sound. Technical development efforts have resulted in a number of technical reports, which are available from Ecology. (Many of the reports are available through the Internet at http://www.wa.gov/ecology.) The most significant issues facing the agency are determination of a fish consumption rate, development of chemical-specific BSAFs, and implementation within the structure of the State Sediment Management Standards. See the discussion in Section 3.5 for more information about Ecology's approach.

Quantifying Mercury Bioaccumulation

Mercury bioaccumulation presents a potential risk to human health at several sites in Puget Sound. Since mercury is of human health concern, there is a need to quantify the relationship between tissue mercury concentrations and sediment concentrations so that health-protective clean-up and source control decisions can be made. However, surprisingly few data are available in the literature that describe this relationship. As a result, Ecology has been evaluating a number of statistical approaches for determining an acceptable mercury sediment concentration given available data sets in Puget Sound. The Puget Sound Ambient Monitoring Program (PSAMP) has provided the most robust data set currently available.

5.3 International Efforts

The United States is engaged in a number of international efforts to reduce human and environmental exposure to persistent toxic compounds. Current efforts include a wide variety of activities, but the greatest focus is on efforts aimed at the reduction of persistent organic pollutants such as PCBs and selected heavy metals, most notably mercury and lead. Longstanding measures taken by the United States, Canada, and other western nations to reduce the domestic use and emissions of many of the most harmful of these substances have recently been recognized as insufficient to fully control the risks posed by these substances. This is largely due to the proclivity of such substances to travel long distances through environmental media and thereby pose risks of a transboundary or even global nature. In response, the United States and other countries have promoted a growing number of international efforts to assess and manage the transboundary risks.

Years of work in Scandinavia, Canada, and the United States has focused international attention on a group of chemicals known as “persistent organic pollutants,” or POPs. The precise definition of these pollutants is a matter of scientific and even political debate, but there is general agreement on four basic characteristics—persistence, toxicity, bioaccumulation potential, and ability to be transported long distances through the atmosphere or water. A more detailed discussion of the relevant characteristics is presented under Section 4.4.1. International fora at both the regional and global level are faced with four essential tasks: selecting an initial list of POPs for joint action; agreeing on needed control measures, which could be of either a legally binding or voluntary nature; establishing a process for selecting additional POPs for control; and determining the efficacy of joint action. The United Nations Environment Programme’s (UNEP) list of 12 POPs is generally accepted as the principal focus of international action in the near term. The list of 12 includes aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, and dioxins and furans. Separate, but related international efforts are also under way to address lead, mercury, and cadmium.

Each of the persistent organic pollutants identified above, as well as lead, mercury, and cadmium, is a potential bioaccumulative chemical of concern in contaminated sediments. Consequently, actions taken in the international context to reduce or eliminate emissions of these substances are critical to reducing sediment loadings over the long term.

In light of the continued use and release of persistent toxic substances in many countries and the effect on U.S. ecosystems and human health (including sediment bioaccumulation), the United States is pursuing international action in many international fora. The principal fora are described in the subsections that follow:

5.3.1 U.S.-Canada Great Lakes Water Quality Agreement (GLWQA)

[EPA leads: Great Lakes National Program Office, OW] In keeping with the objective of the Revised Great Lakes Water Quality Agreement of 1978, as amended by the Protocol signed November 18, 1987 (1987 GLWQA) to restore and protect the Great Lakes, Canada and the United States signed "The Great Lakes Binational Toxics Strategy" on March 27, 1997. The Strategy sets forth a collaborative process by which Environment Canada and the United States Environmental Protection Agency, in consultation with other federal departments and agencies, Great Lakes states, the Province of Ontario, tribes, and first nations, will work in cooperation with their public and private partners toward the goal of virtual elimination of persistent toxic substances resulting from human activity, particularly those which bioaccumulate, from the Great Lakes Basin, so as to protect and ensure the health and integrity of the Great Lakes ecosystem. In cases where the strategy addresses a naturally occurring substance, it is the anthropogenic sources of pollution that, when warranted, will be targeted for reduction through a life-cycle management approach so as to achieve naturally occurring levels. An underlying tenet of this strategy is that the governments cannot by their actions alone achieve the goal of virtual elimination. The strategy challenges all sectors of society to participate and cooperate to ensure success. The Binational Toxics Strategy will protect human health and ecosystem health, as well as further the environmental justice objectives of the Agency, through the targeting of PCBs and mercury, the contaminants primarily responsible for fish consumption advisories. Successful implementation of the Binational Toxics Strategy will assist in eliminating fish advisories in the Great Lakes. Recognizing the long-term nature of virtual elimination, the strategy provides the framework for actions to achieve quantifiable goals in the timeframe 1997 to 2006 for specific persistent, bioaccumulative toxic pollutants. Flexibility is provided in the strategy to allow for the revision of targets, time frames, and the list of substances.

5.3.2 North American Commission for Environmental Cooperation (NACEC)

[EPA leads: OPPTS, ORD, OIA] The NACEC Council Resolution on the "Sound Management of Chemicals," adopted in October 1995, establishes a general framework for United States-Canada-Mexico cooperation on chemicals, including a high-level working group to direct this cooperation. Under the resolution, priority for work is to be given to persistent toxic substances. Substantive work began with the development of regional action plans (NARAPs) for PCBs, DDT, chlordane, and mercury, as well as the development of and agreement on a process for selecting additional substances for joint action. At present, work is focused on implementation of the DDT and chlordane NARAPs and screening of other persistent toxics for eventual submission to the formal substance selection process.

5.3.3 United Nations Economic Commission for Europe/Convention on Long-Range Transboundary Air Pollution (LRTAP)

[EPA lead: OAR] Based on 5 years of technical substantiation work by the United States, Canada, western Europe, and most of the former Soviet bloc states, the LRTAP Executive Body agreed in November 1995 that its Working Group on Strategies should begin work on legally binding protocols on POPs and heavy metals in early 1996. Both protocols were concluded in spring 1998 and signed by most LRTAP parties in June 1998. The POPs protocol (Economic Commission for Europe, 1994) addresses 16 substances (the UNEP short list, plus chlordecone, hexabromobiphenyl, HCH, and PAHs), which have in large measure already been addressed by the United States, Canada, and Western Europe. The protocol allows flexibility in dealing with specific POPs; for example, certain pesticides such as DDT would be subjected to use restrictions and gradually phased out while others would be banned outright and at a much earlier date. For stationary sources (e.g., sources of dioxin and furan emissions), best available technology or best environmental practice requirements would be applied.

Among other things, the protocol also provides differentiated control action timelines for western countries and former Soviet bloc countries, establishes a variety of reporting and monitoring efforts, and sets forth a mechanism for selecting other POPs for joint action. To promote widespread compliance with this protocol, the United States has initiated, and won significant political and financial support from the other arctic countries for, a PCB identification and phase-out project in the Russian Federation. The heavy metals protocol focuses on lead, mercury, and cadmium and establishes a substance selection mechanism, monitoring and reporting requirements, and a variety of legally binding and voluntary provisions for reducing the release of and exposure to these heavy metals.

5.3.4 United Nations Environment Program (UNEP), and Intergovernmental Forum on Chemical Safety (IFCS)

[EPA leads: OPPTS, OIA] The May 1995 UNEP Governing Council Decision on POPs (GC.18/32) invited the Inter-Organizational Program for Sound Chemical Management working with the International Program on Chemical Safety and the IFCS, to initiate a process to assess the chemistry, toxicology, transport, and socioeconomic factors associated with the UNEP short list of POPs (PCBs, dioxins and furans, aldrin, dieldrin, DDT, endrin, chlordane, hexachlorobenzene, mirex, toxaphene, and heptachlor). Based on the results of this assessment, the decision invited the IFCS to develop recommendations for international actions on POPs, including an appropriate international legal mechanism. This assessment report was the basis for the decision of the 19th session of the UNEP Governing Council to mandate the development of a legally binding global instrument aimed at the reduction and/or elimination of emission and discharges and, where appropriate, the manufacture and use of these pollutants. The first negotiating session was held in June-July 1998, the second session was held in late January 1999, and the negotiations are to be concluded before the end of calendar year 2000. As with the LRTAP POPs protocol, the UNEP convention will establish a process by which additional substances can be selected for joint action. Compared to the LRTAP protocol, the UNEP convention will greatly emphasize the capacity building needs of developing countries.

5.3.5 Arctic Council

[EPA lead: OIA] The Arctic Council is a ministerial-level body that brings together the eight countries with arctic territory (United States, Canada, Denmark, Norway, Sweden, Finland, Russian Federation) to cooperate voluntarily to protect human health and the environment in the Arctic. Although it was established only in 1997-98, the Council subsumes and continues all of the work initiated in 1991 by these same countries under the auspices of the Arctic Environmental Protection Strategy. Of particular interest is the priority work of the Arctic Monitoring and Assessment Program (AMAP) on POPs and heavy metals, which is not surprising given the proclivity for these substances to migrate to and settle into the Arctic. The AMAP work offers the United States an additional opportunity to develop and exchange information on the transport and fate of persistent toxics, especially with respect to sensitive human subpopulations and ecological areas. The voluntary nature of the Council's work dictates that risk management measures on POPs and heavy metals must be undertaken voluntarily by the arctic countries or prompted by legally binding international agreements to which the eight countries, and others farther to the south, are already a party (e.g., the LRTAP POPs and heavy metals protocols).

At the North Sea Conferences, ministers representing countries bordering the North Sea agreed to the reduction and elimination of hazardous chemical contaminants, as stated in the Esbjerg Declaration, June 1995. The Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM) is developing activities pertaining to concerns about DDT, PCBs, PCTs, mercury, cadmium, organotin compounds, and pesticides. A ministerial meeting was held in 1998 to decide on the

program of action. The Paris Commission-OSPAR (Oslo-Paris Convention for the Prevention of Marine Pollution from Land-based Sources to the North-East Atlantic) (PARCOM 1974 and 1992) is working to adopt the targets of the Esbjerg Declaration in 1997 and examining PAHs, chlorinated paraffins, nonylphenols and related substances, suspected endocrine disruptors, and mercury, cadmium, and lead. The European Union has issued several directives on the use, marketing, discharge, and management of persistent organic pollutants, in particular, nonylphenol/ethoxylate, phthalates, organotin compounds, polybrominated diphenylethers/biphenyls, and short-chain chlorinated paraffins. The United States and the European Union will be working together to examine a number of complex scientific and political issues related to their own and other international efforts to better assess and manage the known and suspected risks associated with persistent toxic substances.

5.4 Summary of Regional and Headquarters Activities

This review has identified a variety of activities under way in EPA that are important for interpreting bioaccumulation data in relation to sediment quality. Most of the programs represent individual and different approaches that address specific statutory mandates as well as the goals of EPA's Contaminated Sediment Management Strategy. Following are the highlights of the bioaccumulation-related activities that are ongoing in the EPA.

Research on bioaccumulation and the use of bioaccumulation to assess sediment contamination are ongoing activities in OPPT, NHEERL, NERL, OERR, OSW, OST, OWOW, the Chesapeake Bay Program, and all EPA regions. OPPT, OSW, OST, and OERR have been working on identifying, based on various chemical properties, chemical structure, and structure-activity relationships, which chemicals might bioaccumulate and cause adverse environmental effects. Intra-Agency agreement on which chemicals should be considered to be bioaccumulative and how risks to humans and ecosystems should be assessed is still developing, and consensus is building through various workgroups and activities. NHEERL has conducted numerous studies of bioaccumulation in freshwater and marine biota, examining conditions and factors affecting bioaccumulation, determination of BAFs and BSAFs in numerous species, trophic transfer, and metabolism of bioaccumulative chemical contaminants, and developing and validating toxicity and bioaccumulation test procedures and sediment-based ecological risk assessment methods. NERL has used data obtained from the field and laboratory studies to model bioaccumulation processes to examine risks to higher tropic levels. Bioaccumulation of sediment contaminants in fish that might be consumed by humans is a major concern in the development of water quality criteria for the protection of human health, and research is under way on the most appropriate methods for predicting bioaccumulation in fish (Region 5) and developing chemical-specific BSAFs for setting tissue residue-linked sediment chemical levels for the protection of human health, particularly for mercury (Region 10). The Chesapeake Bay Program, in concert with NOAA, is developing a 5-year plan for a toxics research program that will include work on bioaccumulation and food webs.

Assessment procedures are of concern to or used by OERR, OPP, OPPT, OAR, ORD, OST, OSW, OWOW, GLNPO, the Chesapeake Bay Program, and all EPA regions. OERR is working on issues such as improving consistency in methods used to determine potential bioaccumulative chemicals at Superfund sites, effects concentrations for these chemicals, and use of background data to assess bioaccumulation. OPP uses bioconcentration and bioaccumulation tests to evaluate whether and under what conditions pesticides and other chemical products pose risks to aquatic and terrestrial biota, and OPPT can require manufacturers to conduct such tests on compounds that might pose risks based on chemical characteristics, suspected toxicities, and loadings information. OAR incorporates information on bioaccumulation of air toxics in certain analyses (e.g., ranking chemicals for the draft Urban Air Toxics Strategy). OST is developing methods for quickly screening effluent discharges for

bioaccumulative contaminants. OST has used bioaccumulation modeling procedures to assess potential risks to human health in support of industrial effluent discharge limitation guidelines and to help identify sites around the nation having potentially bioaccumulative contaminants in sediments that might present risks to aquatic and terrestrial biota and humans. The Office of Water is conducting a National Survey of Chemical Residues in Lake Fish Tissue. This study will meet objectives presented in the President's Clean Water Action Plan and provide information about persistent, bioaccumulative, toxic chemicals (PBTs) for EPA's PBT Strategy. OPP uses a 28-day test of channel catfish or bluegill to assess bioaccumulation, whereas ORD assesses sediment bioacccumulation with invertebrates (such as *Hyalella*, *Chironomus*, and *Lumbriculus*) and freshwater and marine fish species. OSW is developing a rule establishing chemical-specific waste stream concentrations that represent a threshold below which Subtitle C disposal will not be required and thus the waste stream may exit the hazardous waste system. Under development (with ORD) is a risk-based methodology that will be used as the basis for the waste stream concentrations. OWOW developed guidance for conducting bioaccumulation tests required under section 403 of the CWA. GLNPO and the regions are using bioaccumulation tests and fish tissue concentrations of bioaccumulative contaminants to assess the extent and magnitude of sediment contamination and evaluate ecological and human health risks. In addition, they are evaluating BAF and BSAF models, the incorporation of site-specific data, and new techniques such as semipermeable membrane devices. The Chesapeake Bay Program is conducting a toxics characterization to identify chemical contamination problems in the tidal tributaries of the Chesapeake Bay. This characterization is based, in part, on an analysis and integration of water, sediment, and fish tissue contaminant concentration data. A variety of assessment procedures are thus being developed, applied at various sites, and used under various statutes to reduce or eliminate exposures to bioaccumulative contaminants.

OERR, OSW, GLNPO, and a number of international organizations are focusing on the use of bioaccumulation information to identify and evaluate sediments for remediation efforts. Clean-up levels at several Superfund sites have been derived based on the presence of bioaccumulative contaminants. Subtitle C of RCRA provides EPA (OSW) with the authority to assess whether releases from a hazardous waste treatment, storage, or disposal facility have contaminated sediments and to require corrective action, including possible remediation, if contamination is discovered. The regions are using different approaches to target remediation of contaminated sediments; many are evaluating the fish ingestion pathway and various factors influencing clean-up decisions. Region 2 employs bioaccumulation tests with fishes and other organisms (small mammals, clams, amphibians) during the evaluation of ecological risk. GLNPO operated the ARCS Program to identify AOCs and to help select appropriate remedial actions in harbors and tributaries of the Great Lakes. Western Europe, Canada, and the North Sea countries have begun talks and developed agreements that pertain to the remediation of sediment-associated bioaccumulative contaminants.

Preventing the release of bioaccumulative contaminants is of concern to OPPTS, OSW, OST, OWM, OWOW, the Chesapeake Bay Program, and numerous countries around the world. OPPT is using its screening and prioritizing procedures to determine those chemicals that might accumulate in sediments and pose risks so that dangerous levels of loadings can be targeted. Under the Waste Minimization National Plan, OSW and OPPT are developing a tool that would prioritize chemicals in hazardous waste based on persistence, biaoaccumulation potential, toxicity, and quantity. OWOW and OST use bioaccumulation data in the control of discharges of bioaccumulative chemicals under the CWA Several international conferences have been held to examine methods for reducing or eliminating persistent organic and metal pollutants, and some have resulted in agreements.

The dissemination of information pertaining to the bioaccumulation of chemicals has been important for OPPT, OST, OWOW, the Chesapeake Bay Program, NHEERL, and all EPA regions. OPPT recently

released a draft multimedia strategy to reduce risks from exposures to priority persistent, bioaccumulative, and toxic pollutants through increased coordination among EPA national and regional programs. This approach also requires the significant involvement of stakeholders, including international, state, local, and tribal organizations, the regulated community, environmental groups, and private citizens. OST has published a series of documents on the analysis of fish tissue concentrations of contaminants and the use of such data to determine risks to humans from consumption of fish, as well as providing a database listing all fish and wildlife consumption advisories currently operating in the states. OWOW's outreach efforts include educating the public about the ocean and coastal programs and making program information readily available to the public. The toxics characterization of tidal tributaries of the Chesapeake Bay being performed by the Chesapeake Bay Program will be used as an outreach tool to put information in the hands of the public, scientists, and managers to target appropriate areas for additional monitoring and management activities. NHEERL has prepared guidance documents pertaining to bioaccumulation methods and has developed several databases to assist in the interpretation of bioaccumulation data. Region 5 developed guidance for determining BAFs that are used in the evaluation of risks to wildlife and humans from bioaccumulative chemicals under the Great Lakes Water Quality Initiative.

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6. ISSUES AND RESEARCH NEEDS FOR INTERPRETING BIOACCUMULATION DATA FOR THE PURPOSE OF SEDIMENT QUALITY ASSESSMENT

This chapter contains issues touched on previously, as well as research needs, for interpreting bioaccumulation data for the purpose of assessing sediment quality. The interpretation of bioaccumulation data will require an understanding of the relationship between environmental media concentrations, tissue concentrations, and effects on specific organisms or consumers of those organisms. The role of physical, chemical, and biological variables in mediating toxic effects should also be considered. "Research needs" were taken from the proceedings of EPA's National Sediment Bioaccumulation Conference, held September 11-13, 1996 (USEPA, 1998), and input from EPA's Bioaccumulation Analysis Workgroup.

It is anticipated that the research needs presented below will be used as a starting point to identify future work. Cost and feasibility considerations were not factored into the development of these research needs. Due to differences in mandates among EPA offices, the issues and needs presented here might not be applicable to all EPA programs.

Results of multivoting on the research needs indicate that 11 are of high priority (denoted by **H**), 12 are of intermediate priority (denoted by **I**), and 7 are of low priority (denoted by **L**).

Methods

Issue: Laboratory and field methods for assessing bioaccumulation (Sections 3.1, 3.2)

Needs:

H 1. Conduct round-robin tests to determine the precision and variability of new and existing methods and how well laboratories are conducting bioaccumulation tests

H 2. Identify additional species for sediment bioaccumulation test methods, and develop the methods

H 3. Conduct research to provide better understanding of how reference sites can be selected.

I 4. Standardize the use of microlipid analytical methods

I 5. Continue to field-validate laboratory bioaccumulation methods, particularly for PAHs and metals

L 6. Conduct further research on the development and use of formulated sediments and sediment spiking techniques

L 7. Standardize the sampling and handling procedures for assessing bioaccumulation (field-collected samples)

L 8. Determine most appropriate means of storing sediment samples

Chemical Identification

Issue: Identification of bioaccumulative chemicals (Chapter 4)

Needs:

H 9. Determine additional BAF and BSAF values for known persistent bioaccumulators or identify potential persistent bioaccumulators

H 10. Reach a better understanding of bioavailability processes of chemicals occurring in sediments

I 11. Develop a forensic chemical approach to assist in identification of bioaccumulative compounds

Species Considerations

Issue: Species selection for bioaccumulation testing (Sections 3.2.1.1, 3.2.2.2, 4.4)

Needs:

H 12. Determine tissue residue values for terrestrial and avian wildlife

I 13. Provide guidance on further identification or development of contaminant-specific receptors of choice, where relevant, so that appropriate target species can be selected

Toxicology

Issue: Dose-response relationships for bioaccumulative contaminants (Section 4.4, Chapter 3)

Needs:

H 14. Determine the relationship of tissue residue concentrations and adverse effects

H 15. Determine the applicability of the critical body residue (CBR) approach to multiple classes of chemical mixtures

I 16. Determine the additivity of chemicals for specific modes of action

I 17. Determine differential partitioning of bioaccumulative contaminants among tissues

I 18. Develop the appropriate guidance for selecting species/effects endpoints that should be used

I 19. Confirm exposure route independence (e.g. dietary, sediment)

L 20. Provide procedures to evaluate experimental data that are suitable for use in generating CBRs

Further research is needed on how to resolve or compensate for uncertainties related to the assessment of bioaccumulation of sediment-associated contaminants. Specific areas of research required to address uncertainty in bioacccumulation testing include the following:

I 21. Environmental factors that affect toxic responses

I 22. Rates at which contaminants are metabolized or eliminated

L 23. The modes and time course of toxic action

L 24. The toxicities of intermediate metabolites relative to parent compounds

L 25. Dose-related induction of enzymatic systems

Models

Issue: Development, selection, application, and interpretation of models (Sections 2.4.2, 3.2.1.3, 3.3, 4.4)

Needs:

H 26. Continue work on developing food chain multipliers and trophic models. Further refine the relationship of BAFs to BCFs (Predicted BAF may be derived by multiplying the laboratory BCF by a food chain multiplier)

H 27. Develop extrapolation models that will take us from single-species endpoints to more ecologically relevant endpoints that involve community and population-level impacts

H 28. Determine how the toxicity risks of complex mixtures of PBTs, bioaccumulated by organisms with no direct exposure to sediments, can be related to sediment contamination levels

I 29. Develop a better understanding of physiologically based models or kinetic models. When are time-dependent exposure models preferable to steady-state BSAFs?

I 30. Determine whether the BAF methodology applied to the Great Lakes region can be applied to Toxic Release Inventory (TRI) PBT chemicals that may be manufactured and released at sites in several states, in one or more regions, or even throughout the United States.

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