

NOAA Technical Memorandum NOS ORCA 100



## Contaminants in Aquatic Habitats at Hazardous Waste Sites: Mercury

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Seattle, Washington

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National Ocean Service

**Office of Ocean Resources Conservation and Assessment  
National Ocean Service  
National Oceanic and Atmospheric Administration  
U.S. Department of Commerce**

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**Contaminants in Aquatic Habitats at Hazardous Waste Sites: Mercury**

**Nancy Beckvar** <sup>1</sup>  
**Jay Field** <sup>1</sup>  
**Sandra Salazar** <sup>2</sup>  
**Rebecca Hoff** <sup>1</sup>

<sup>1</sup>NOAA/HAZMAT  
<sup>2</sup>EVS Consultants  
Seattle, Washington



Seattle, Washington

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United States  
Department of Commerce  
Mickey Kantor  
Secretary

National Oceanic and  
Atmospheric Administration  
D. James Baker  
Under Secretary for Oceans  
and Atmosphere

National Ocean Service  
W. Stanley Wilson  
Assistant Administrator  
for Ocean Services and  
Coastal Zone Management

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**Hazardous Materials Response and Assessment Division  
Office of Ocean Resources Conservation and Assessment  
National Ocean Service  
National Oceanic and Atmospheric Administration  
U.S. Department of Commerce  
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## EXECUTIVE SUMMARY

This document reviews published literature on mercury chemistry, bioaccumulation and toxicity, and is intended to serve as guidance for NOAA Coastal Resource Coordinators in their work with EPA on hazardous waste sites. The purpose of this document is to highlight factors to consider in designing and evaluating ecological risk assessments; and, in the sampling, monitoring and analyses of environmental media in aquatic habitats affected by mercury. Though many questions about mercury remain, the science is evolving rapidly. This paper should be reviewed with the knowledge that information can change as new studies are published.

### Environmental Chemistry

The fate of mercury in the environment depends on the chemical form of mercury released and the environmental conditions. Elemental mercury, inorganic mercury, and methylmercury are the three most important forms of mercury in natural aquatic environments. Most mercury is released into the environment as inorganic mercury, which is primarily bound to particulates and organic substances and may not be available for direct uptake by aquatic organisms. The process of methylation of inorganic mercury to methylmercury, which is highly bioavailable, is thus an important key to the fate of mercury in the environment.

Elemental mercury has a high vapor pressure, a low solubility, does not combine with inorganic or organic ligands, and is not available for methylation. The mercurous ion (Hg[I]) combines with inorganic compounds only and cannot be methylated. The mercuric ion (Hg[II]) combines with both inorganic and organic ligands, and can be methylated. Methylation in aquatic habitats is primarily a biological process. Mono- and dimethylmercury are formed by microorganisms in both sediment and water through the methylation of inorganic mercuric ions (Hg[II]). Dimethylmercury, which is highly volatile, is generally not persistent in aquatic environments.

Methylation is influenced by environmental variables that affect both the availability of mercuric ions for methylation and the growth of the methylating microbial populations. Methylation rates are higher under anoxic conditions, in

freshwater compared to saltwater, and in low pH environments. The presence of organic matter can stimulate growth of microbial populations (and reduce oxygen levels), thereby enhancing the formation of methylmercury. Sulfide can bind mercury and limit methylation. Methylmercury production can vary due to seasonal changes in nutrients, oxygen, temperature, and hydrodynamics. In most studies, methylation increased during the summer months when biological productivity was high, and decreased during the winter months.

Measurements of total mercury concentrations in the sediment do not provide information on the form of mercury present, methylation potential, or availability to organisms locally and downstream. If environmental conditions are conducive for methylation, methylmercury concentrations may be high in proportion to the supply and distribution of total mercury.

### **Bioaccumulation**

Mercury is accumulated by fish, invertebrates, mammals, and aquatic plants and the concentration tends to increase with increasing trophic level (mercury biomagnifies). Although inorganic mercury is the dominant form of mercury in the environment and is easily taken up, it is also depurated relatively quickly.

Methylmercury accumulates quickly, depurates very slowly, and therefore biomagnifies in higher trophic species. The percentage of methylmercury, as compared to total mercury, also increases with age in both fish and invertebrates.

Uptake and depuration rates vary between tissues within j T3n, aee8tmercj T vai wimi6uration rates v



Invertebrates generally have a lower percentage of methylmercury, as compared to total mercury, in their tissues than do fish and marine mammals. The percentage of methylmercury in invertebrates varies greatly and can range from one percent in deposit-feeding polychaetes, to close to 100% in crab.

Bioconcentration factors (BCFs) reflect uptake from water in laboratory experiments. BCFs for mercury are variable, with the highest factors determined for methylmercury. BCFs for methylmercury in brook trout range from 69,000 to 630,000, depending on the tissue analyzed. BCFs for inorganic mercury (mercuric chloride) in saltwater species range from 129 for adult lobster (*Homarus americanus*) to 10,000 for oysters (*Crassostrea virginica*).

While sediment is usually the primary source of mercury in most aquatic systems, the food web is the main pathway for accumulation. High trophic level species tend to accumulate the highest concentrations of mercury, with concentrations highest in fish-eating predators. Mercury concentrations in higher trophic species often do not correlate with concentrations in environmental media. Correlations have been made between sediment and lower trophic species that typically have a high percentage of inorganic mercury, and between mercury concentrations in higher trophic species and their prey items. The best measure of bioavailability of mercury in any system can be obtained by analyzing mercury concentrations in the biota at the specific site.

### **Toxicity**

Toxicity is influenced by the form of mercury, the environmental media, environmental conditions, the sensitivity or tolerance of the organism, and the life history stage. Inorganic mercury is less acutely toxic to aquatic organisms than

Reproductive endpoints are generally more sensitive than growth or survival, with embryos and the early developmental stages the most sensitive. Mercury can be transferred from tissues of the adult female to developing eggs. Exposure to low concentrations of mercury may not result in mortality directly, but may retard growth thereby increasing the risk of predation.

Data available on the effects of mercury-contaminated sediment on aquatic organisms reviewed by Long and MacDonald (1992) resulted in effects range-low (ERL) and effects range-median (ERM) concentrations of 0.15 mg/kg and 0.71 mg/kg, respectively. However, these numbers were less accurate than other metals in predicting adverse effects, highlighting the need for site-specific effects data to determine concentrations of mercury in sediment that pose a threat to aquatic biota.

Few studies report both tissue residues and effects in long-term exposure to low concentrations of mercury. However, results from studies on different freshwater species indicate that reproductive effects could be expected to occur in sensitive fish species at tissue concentrations close to the FDA action level of 1 mg/kg (ppm). The interaction of mercury and other trace elements (e.g., cadmium, copper, selenium, and zinc) can be both antagonistic and synergistic, primarily depending on exposure concentrations and form of mercury. Effects were generally less than additive (antagonistic) at lower exposure levels and greater than additive (synergistic) at higher levels. Zinc and cadmium were reported to reduce the teratogenic effects of methylmercury to killifish while selenium reduced mercury's toxic effects on development in medaka embryos.

### **Applications**

Ecological assessments of waste sites with elevated concentrations of mercury in the aquatic environment are particularly challenging due to the complexity of the factors that affect the availability of mercury to aquatic organisms. Depending on the magnitude of the problem (local versus system-wide), the level of effort necessary to evaluate mercury contamination may range from simple monitoring of chemical concentrations to more complex programs including monitoring of numerous physical, chemical and biological parameters. The distribution of total mercury in sediment, which in most cases is predominantly inorganic mercury, may not by itself provide useful information about the bioavailability of mercury to



## Summary

NOAA recommends a site-specific approach that focuses on determining the availability of mercury and the potential for toxic effects. The accumulation of mercury in aquatic biota is often the primary concern at mercury sites and is useful for assessing availability. Bioaccumulation studies should measure tissue concentrations in more than one resident and/or transplanted caged species, preferably with species representing different trophic levels or different food web pathways. It may not be possible to correlate sediment mercury concentrations with concentrations in biota. However, correlations between mercury concentrations in predator and prey species may be useful in determining pathways of mercury transfer.

Toxicity tests such as the standard amphipod tests should also be conducted to assess mercury toxicity to benthic organisms. At major mercury sites, chronic toxicity endpoints should be included in the assessment—in particular, fish early life stage or reproductive endpoint tests. Because of the persistence of mercury in aquatic systems, source control alone may not be sufficient to permit recovery. Additional remedial actions may be required to reduce the total mercury burden in the system. Long-term monitoring of tissue concentrations of mercury in aquatic biota is needed to assess remedial effectiveness.

## ACRONYMS AND ABBREVIATIONS

AVS	acid-volatile sulfides
AWQC	Ambient Water Quality Criteria
BAFs	Bioaccumulation factors
BCFs	Bioconcentration factors
Cd	cadmium
CLP	Contract Lab Program
Cu	copper
DOC	dissolved organic carbon
Eh	oxidation-reduction potential
ERL	effects range-low
ERM	effects range-median
FDA	U.S. Food and Drug Administration
Fe	iron
Hg	mercury
Mn	manganese
MT	metallothioneins
$\mu\text{eq/l}$	micro equivalent per liter
$\mu\text{g/l}$	micrograms per liter
$\mu\text{m}$	micrometer
$\text{mg/kg}$	milligrams per kilogram
$\text{mg/l}$	milligrams per liter
ppm	parts per million
Se	selenium
SRB	sulfate-reducing bacteria
TOC	total organic carbon
Zn	zinc

## **GLOSSARY**

### **acid labile mercury**

Determined by  $\text{SnCl}_2$  reduction on acidified samples, includes inorganic complexes, labile organic associations, elemental mercury, and labile particulate mercury. Doesn't measure organic forms (C-Hg bound) of mercury such as methylmercury. Same as reactive mercury.

### **acid soluble mercury**

Mercury that passes through a  $0.45 \mu\text{m}$  membrane filter after the sample is acidified to pH 1-2.0 with nitric acid (EPA 1984). Strongly sorbed Hg is not measured, but all toxic forms as well as some non-toxic forms are measured.

### **alkylmercury**

Includes phenyl-, monomethyl-, and dimethylmercury

### **bioaccumulation**

Net uptake of a contaminant into tissue from all pathways

### **bioaccumulation factors (BAF)**

Ratio of tissue concentration to concentration in medium, with exposure from the food web and the medium

### **bioconcentration factors (BCF)**

Ratio of tissue concentration to concentration in medium, with exposure only through the medium

### **biomagnification**

Tissue concentration increases as trophic level increases

### **DOC (dissolved organic carbon)**

Includes all sources of carbon, including humic and fulvic matter as well as carbohydrates, proteins, etc.

### **demethylation**

Conversion of methylmercury back to an inorganic form.

### **depuration**

Elimination of a contaminant from the body of an organism

### **dimethylmercury**

Organic mercury, an organomercurial compound

available screened sediment toxicity data for predominantly marine and estuarine toxicity studies. This number represents the low end of the range of concentrations at which effects were observed in the studies compiled (Long and MacDonald 1992).

**Effects range-median**

Concentration equivalent to that reported at the 50th percentile of the available screened sediment toxicity data for predominantly marine and estuarine toxicity studies (Long and MacDonald 1992).

**elemental mercury**

Not in ionic form, cannot be methylated

**halide**

Binary compound of a halogen (fluorine, chlorine, bromide, iodine and astatine)

**inorganic mercury**

Includes elemental mercury and mercury bound to other inorganic molecules and compounds, including inorganic ligands and sulfides.

**labile mercury**

Includes  $\text{Hg}(\text{OH})_2$ ,  $\text{HOHgCl}$ ,  $\text{HgCl}_2$ , and weakly bound organo-complex forms

**ligand**

Any group, ion, or molecule that binds to another, called a receptor

**methylmercury**

Includes both mono- and dimethylmercury

**mercuric-Hg[II]**

Forms both inorganic and organic complexes, this is the only ionic form that can be methylated

**mercurous-Hg[I]**

Forms inorganic complexes, cannot be methylated

**methylation**

Addition of a methyl ( $\text{CH}_3$ ) group

**monomethylmercury**

Organic form of mercury with one methyl group attached to a mercury atom ( $\text{CH}_3\text{Hg}$ ) - highly toxic and readily accumulated by living organisms

**organic mercury**

Includes mercury complexes with organic ligands (e.g. humic/fulvic acids,

amino acids, but without a Hg-carbon bond) and organic mercury bound via a carbon atom ( $\text{CH}_3\text{-HgOH}$ ,  $\text{CH}_3\text{HgCl}$ ,  $\text{CH}_3\text{HgCH}_3$ )

**organo-mercury**

Mercury compounds with a Hg-carbon bond

**pinniped**

Mammals of the family Pinnipedia, includes all seals and walruses

**piscivorous**

Feeds on fishes

**reactive mercury**

“Easily reducible,” determined by  $\text{SnCl}_2$  reduction on acidified samples, includes inorganic complexes, labile organic associations, elemental mercury, and labile particulate mercury, doesn't include C-Hg bound mercury such as methylmercury and dimethylmercury. Same as acid labile mercury.

**total mercury**

Includes all forms of mercury



## **INTRODUCTION**

As a trustee for marine, estuarine, and anadromous resources, NOAA is responsible for ensuring the well-being of those trust resources potentially affected by releases from hazardous waste sites. Metals, in particular, pose a threat because of their persistence and toxicity in aquatic environments. The importance of mercury in many aquatic environments is underscored by the fact that 35 states have fish and wildlife consumption advisories in place for mercury (EPA 1996).

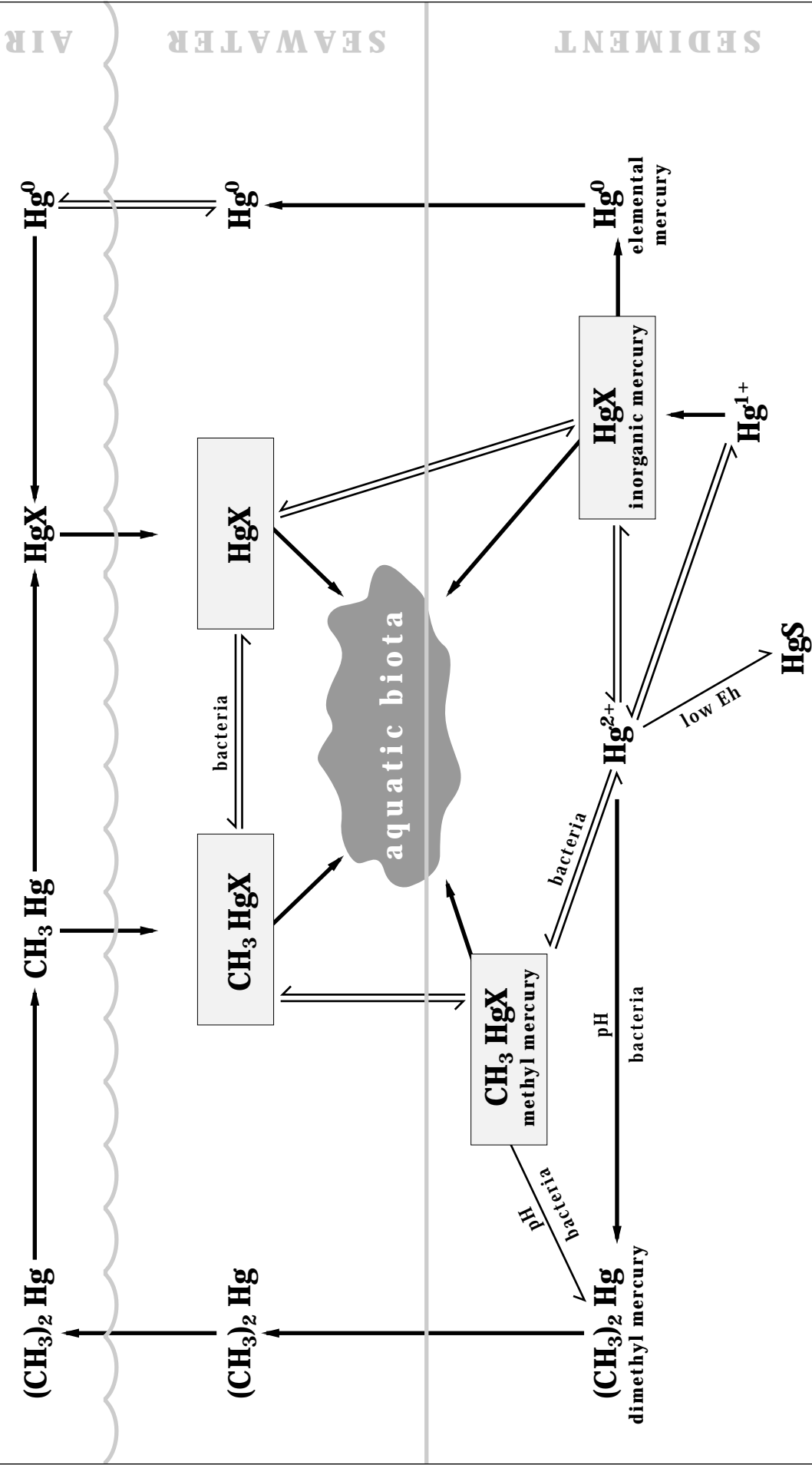
Although the hazards of mercury to humans are well-known, less information is available on the risks to aquatic organisms. In order to define and address the potential effects and extent of mercury contamination at hazardous waste sites, a number of questions are often asked: Is the mercury present in a bioavailable form? What concentrations in water, sediment, and tissues are potentially harmful to aquatic resources? What types of sampling and analysis are necessary to define potential risks to aquatic organisms? Is there a relationship between sediment concentrations and tissue concentrations in aquatic organisms? What level should be used for cleanup? What are important factors to consider when selecting a remedy and designing monitoring plans at a site?

## **ENVIRONMENTAL CHEMISTRY**

Mercury is among the most toxic of the heavy metals, has complex behavior in the environment, and may persist for decades following abatement of the source. Mercury's environmental persistence is due in part to its high affinity for particulates and organic matter. Even if mercury concentrations in sediment and water decrease over time, concentrations in organisms may not decrease due to the slow rate of elimination of the highly bioavailable methylmercury form. The physical properties, bioavailability, and toxicity of mercury are governed by speciation into both organic and inorganic forms.

Elemental mercury, bivalent inorganic mercury, and monomethylmercury are the three most important forms of mercury occurring in natural aquatic environments (Battelle 1987). Elemental mercury in aquatic environments has a high vapor pressure, a low solubility in water, and an octanol-water partition coefficient ( $K_{OW}$ )=4.15 (Shoichi and Sokichi 1985 as cited in Major et al. 1991). Elemental and

dimethylmercury can occur as dissolved gaseous mercury. Mercury can also occur as particulate and dissolved ionic and monomethylmercury species. In natural water, ionic mercury is consumed by methylation, reduction, and particulate scavenging (Mason et al. 1995a). Bivalent inorganic mercury binds to inorganic and



$X = Cl_n, (OH)_n, (SH^-), \text{humic/fulvic acids, amino acids}$

Figure 1. Important pathways of mercury speciation in the aquatic environment.

(e.g., high-chloride lake water), the proportion of  $\text{HgCl}_2$  increases and the other two species constitute only a few percent of the total inorganic mercury. As pH increases, more Cl is needed than at lower pHs to increase the percent of  $\text{HgCl}_2$ . At even higher chloride concentrations,  $\text{HgCl}_4^{2-}$  becomes the dominant species. This speciation chemistry affects the accumulation and toxicity as described later in this report.

The term organic mercury can include different types of organically bound mercury. Hg [II] combines with organic compounds (humic/fulvic acids, amino acids) via an organic ligand bond to form organomercury salts. The Hg [II]-organic ligand bond is relatively weak compared to a C-Hg bond. The organomercury salts resemble their corresponding inorganic mercuric salts in their properties and reactions. The organomercury compounds methylmercury, dimethylmercury, and phenylmercury have a C-Hg bond; methyl ( $\text{CH}_3$ ) and phenyl groups ( $\text{C}_6\text{H}_5$ ) link to a mercury atom via a carbon atom. Some authors group the organically bound Hg [II] complexes (without a C-Hg bond) with inorganic mercury compounds, while others group all organically bound mercury together as organic mercury.

Mercury compounds may be grouped according to their form based on chemical speciation discussed above, or based on the analytical technique used to measure the mercury. The analytical technique determines which forms of mercury are detected. Mercury terms based on analytical procedures include names such as acid-soluble, reactive or acid labile, and calcium chloride-extractable.

Measurements of reactive mercury include Hg [II] bound to inorganic substances and weakly bound to organic matter (however, methylmercury is not included due to the strong C-Hg bond). To estimate methylmercury concentrations, some authors measure total mercury and reactive mercury, then subtract the reactive from the total measurement. Total mercury measurements include all the various inorganic and organic forms of mercury, including dissolved, colloidal, and/or particulate states. Analytical groupings are defined in the glossary. Unless the

concentration, organic matter content, and microbial activity. Similarly, biological and chemical processes control the conversion of inorganic mercury to methylmercury. The factors that enhance and inhibit methylation, and affect the distribution of inorganic and methylmercury are discussed in this section of the paper.

### Methylation of Mercury

In both freshwater and saltwater environments, mercury is converted from inorganic bivalent mercury (Hg[II]) to methylmercury primarily by microorganisms (Berman and Bartha 1986), although chemical methylation also occurs (Craig and Moreton 1985; Weber 1993). Two forms of monomethylmercury, methylmercuric hydroxide ( $\text{CH}_3\text{HgOH}$ ) and methylmercuric chloride ( $\text{CH}_3\text{HgCl}$ ) occur in both fresh and saltwater, with the former dominant at low chloride concentrations (low chloride freshwater) and the latter dominant at high chloride concentrations (high chloride lakes, seawater). As with inorganic mercury, the organic chloride species ( $K_{\text{OW}} = 1.7$ ) is more hydrophobic than the hydroxide species ( $K_{\text{OW}} = 0.07$ ; Major et al. 1991; Faust 1992; Mason et al. 1996). Dimethylmercury ( $K_{\text{OW}} = 182$ ) readily volatilizes from surface water and is generally not persistent in aquatic environments at concentrations of concern; therefore, discussions of methylmercury in this review refer to the monomethylmercury species, unless otherwise stated.

Methylmercury production depends on both the availability of Hg[II] for methylation and microbial activity. Methylation is usually greatest at the sediment-water interface, but also occurs in the water column. Net methylmercury production is a function of both the rate of methylation and the rate of demethylation (Korthals and Winfrey 1987). Methylmercury is not readily decomposed so the methylation rate is usually higher than the demethylation rate. Degradation of methylmercury is also primarily a microbial process.

Methylation is influenced by the availability of Hg[II], oxygen concentration, pH, redox potential (Eh), presence of sulfate and sulfide, type and concentrations of complexing inorganic and organic agents (Parks et al. 1989), salinity (Blum and Bartha 1980), and organic carbon (Jackson 1989; Winfrey and Rudd 1990). Strongly bound Hg[II] is not available for methylation. For example, insoluble mercuric

sulfide (HgS) will be methylated in aerobic sediments at rates 100 to 1,000 times slower than for the less strongly bound HgCl<sub>2</sub> (Olson and Cooper 1976).

Anaerobic, sulfate-reducing bacteria (SRB) are the primary methylators of mercury in both lacustrine and estuarine sediments (Compeau and Bartha 1985; Gilmour and Henry 1991). The primary methylators of mercury in the water column have not been identified. SRB are common in sulfate-rich estuarine sediments (Hines et al. 1989) but are more limited in freshwater sediment with lower sulfate concentrations. A sulfate concentration of 200-500 µM in the water column is optimal for mercury methylation by SRB in sediment (Gilmour and Henry 1991). The activity of the methylating microbes is affected by environmental conditions (Jackson 1986) with nutrient availability and seasonality particularly important. The concentration of inorganic mercury in environmental media may not be a good indication of the concentration of methylmercury present due to the influence of environmental variables and biological activities. The importance of environmental factors in the production of methylmercury is as follows:

**pH:** Neutral or low pH conditions favor the production of monomethylmercury over dimethylmercury (Beijer and Jernelov 1979). An alkaline (high) pH favors the formation of dimethylmercury, which tends to escape into the atmosphere. Elevated tissue concentrations of methylmercury have been noted in numerous pristine lakes of the northern United States and Canada that receive acid rain and no point sources of mercury (Xun et al. 1987; Bloom et al. 1991). The mechanism(s) causing increased bioaccumulation in low pH lakes are not understood (Ramlal et al. 1985; Winfrey and Rudd 1990; Richardson and Currie 1996). The factors primarily responsible for net methylmercury production in lakes are, in decreasing order of importance, pH, dissolved organic carbon (DOC) concentration, and microbial respiration (Miskimmin et al. 1992). The importance of pH and sediment properties (Fe and Mn content) on methylation rates in saltwater environments has not been well studied.

**Sulfide, Sulfate, and Other Ions:** In the presence of sulfides, the mercuric ion (Hg[II]) becomes tightly bound to sulfide as insoluble mercuric sulfide and is not available for methylation. Sulfide activity may be the main factor influencing the availability of Hg[II] (Bjornberg et al. 1988) and the concentration of methylmercury in sediment (Craig and Moreton 1983). If pH is high or Eh is low, sulfide activity

will be high and mercury will be precipitated as insoluble mercuric sulfide. If the





The percentage of total mercury that is methylmercury is higher in freshwater sediments (up to 37%) and water (up to 25% in aerobic water and 58% in anoxic bottom water) than in estuarine and marine water (<5%) and associated sediments (<5%) (Gilmour and Henry 1991). Dissolved reactive mercury (inorganic species) forms the majority of the total mercury in open oceans (Bloom and Crecelius 1983; Gill and Fitzgerald 1987).

**Season:** Biological productivity of methylating microbes is affected by seasonal changes in temperature, nutrient supply, oxygen supply, and hydrodynamics (changes in suspended sediment concentrations and flow rates). Methylmercury concentrations varied seasonally by an order of magnitude at most sites studied (Parks et al. 1989). Methylation may tend to increase during the summer months when biological productivity and temperature are high and decrease during winter months when biological productivity and temperature are low (Callister and Winfrey 1986; Jackson 1986; Weis et al. 1986; Korthals and Winfrey 1987; Parks et al. 1989; Kelly et al. 1995; Leermakers et al. 1995). Although the potential methylmercury production is greatest during the summer, actual production may not peak during this time (Kelly et al. 1995). In Onondaga Lake, New York, the mercury species in the water column varied temporally (Battelle 1987; Bloom and Effler 1990). Total mercury concentrations may also vary seasonally due to physical factors such as winter storms resuspending mercury-contaminated sediments (Gill and Bruland 1990).

### **Distribution in the Environment**

The distribution and abundance of inorganic mercury and methylmercury in the environment may vary independently as they are controlled by different physicochemical processes. The concentration of total mercury (which is mainly inorganic) in the environment is generally not a good predictor of methylmercury concentration (Gilmour and Henry 1991; Kelly et al. 1995). Inorganic mercury has a high affinity for sediments; a significant portion of the total mercury in fresh water is in particulate form (Gill and Bruland 1990). Most of the mercury in estuaries was associated with particulate matter (Cossa and Noel 1987). The environmental distribution of inorganic mercury appears to be controlled by processes such as transport, sorting, and sedimentation as related to the hydrologic regime. Resuspension and resettling of sediments caused persistently high concentrations of mercury in the surface sediments of Lavaca Bay (Reigel 1990).

Total mercury concentrations in surface water may decrease as mercury bound to particulate matter settles or is transported downstream (Bonzongo et al. 1996). The distribution of biotically produced methylmercury initially depends on the microbial populations that methylate the mercury. Although more abundant in the sediment where it is formed, methylmercury forms a greater percentage of the total

decreased after the runoff stopped. In contrast, lower mercury concentrations were found in plankton in a freshwater lake after input of high concentrations of clean, fine-grained sediment. Sediments washed into the lake during rainfall bound the mercury, inhibiting uptake by plankton (Jackson 1988).

Sediment composition can also affect the way that mercury is distributed in the environment. Mercury concentrations in freshwater benthic organisms appeared to be determined by the sediment composition, such as the concentration of hydrated Fe and Mn oxides and carbon-rich humic matter in bottom sediment. The mercury appeared to be less available when it was bound by iron hydroxide (FeOOH), manganese hydroxide (MnOOH), and possibly by higher-molecular-weight humic substances (Jackson 1988).

In a freshwater river-lake system in Canada (Parks et al. 1989) methylmercury concentrations in surface water were highest 80 kilometers downstream from the most contaminated sediments (contaminated with inorganic mercury). Fish were contaminated as far as 270 km downstream from the inorganic mercury source, with the most contaminated fish found more than 100 km downstream of this source. Methylmercury concentrations in the water increased as inorganic mercury concentrations in the sediment decreased. The most highly contaminated sediments were located near a sewage outfall. The researchers surmised that the mercury in these sediments was bound to sulfide and thus not available for methylation. Further downstream the mercury became available for methylation probably due to a decrease in sediment sulfide levels. Even though concentrations of inorganic mercury in the sediment here were much lower than upstream concentrations, methylmercury production was much higher and biota were more contaminated.

There may be a similar situation in low-salinity water of Berrys Creek, New Jersey, where high inorganic sediment mercury concentrations were also found next to a sewage outfall (Weis et al. 1986). However, concentrations of mercury in fish inhabiting the area were not as high as expected. This was attributed to the presence of sulfide, which binds mercury and limits methylation. No downstream studies have been conducted to determine whether the mercury is more bioavailable further from the source of high sulfide concentrations.

An eight-ton cargo of elemental mercury located within the hold of the sunken *Empire Knight* in offshore marine waters did not contaminate invertebrates living outside the hold of the ship (Hoff et al. 1994). Only a small percentage of invertebrates sampled from within the hold had elevated concentrations of total mercury. However, it is not known whether the mercury was incorporated into the tissue of the organisms. The large source of elemental mercury in this environment was not bioavailable to organisms located away from the source.

## BIOACCUMULATION OF MERCURY

Mercury bioaccumulates in aquatic plants, invertebrates, fish, and mammals. Concentrations increase (biomagnify) in higher-trophic-level organisms. Even though the different types of mercury have relatively low  $K_{OW}$  values (compared to organic compounds such as PCBs), they are readily accumulated. Inorganic mercury (excluding elemental) and methylmercury's strong reactivity with intracellular ligands is thought to be responsible for their high degree of accumulation. Uptake and accumulation of mercury are affected by the type of mercury present, with neutral mercury species (e.g.,  $HgCl_2^0$  and  $CH_3HgCl^0$ ) absorbed more efficiently than charged mercury species (e.g.,  $HgCl^-$  and  $CH_3Hg^+$ ; Mason et al. 1996).

Despite the fact that the neutral inorganic and organic complexes have similar lipid solubilities, methylmercury is selectively accumulated (due to a higher transfer efficiency and lower rate of elimination), resulting in biomagnification in higher trophic levels (Mason et al. 1995b). Inorganic mercury species are not biomagnified (Surma-Aho and Paasivirta 1986; Riisgård and Hansen 1990; Hill et al. 1996).

Environmental factors that enhance mercury methylation result in greater bioavailability and accumulation of methylmercury. Environmental variables also influence the bioavailability and accumulation of inorganic mercury. Although concentrations of mercury in the environment may correlate with concentrations in resident plants and biota, correlation is often difficult. Correlating total mercury in sediment with total mercury in upper-trophic-level organisms is complicated by high methylmercury concentrations in high-trophic-level organisms relative to low methylmercury concentrations in the environment.

Tissue concentrations of mercury are often positively correlated with organism length, weight, and/or age. Diet has a significant role in the overall body burden of mercury, both between and within species. Differences in total mercury concentrations between species reflect diet differences due to trophic position; within-species differences are related to dietary requirements of various developmental stages.

### **The Effect of the Form of Mercury on Bioaccumulation**

Both inorganic and methylmercury are taken up directly from water and food (or ingested sediment). However, methylmercury is more efficiently accumulated than inorganic mercury for most aquatic organisms (Fowler et al. 1978; Julshamn et al. 1982; Riisgård and Hansen 1990; Mason et al. 1995b). The uptake and depuration of mercury depends on the form of mercury, source of mercury (water or food), and the type of receptor tissue, resulting in different patterns of accumulation. Methylmercury is readily transferred across biological membranes. Within the organism, methylmercury is strongly bound to sulfhydryl groups in proteins of tissues such as muscle, and is much slower to depurate than inorganic mercury. Thus, methylmercury has a much greater potential for bioaccumulation and a longer half-life in organisms than inorganic mercury.

#### *Fish*

The accumulation of mercury from water occurs via the gill membranes. Gills take up aqueous methylmercury more readily than inorganic mercury (Huckabee et al. 1979; Boudou et al. 1991). Methylmercury is eventually transferred from the gills to muscle and other tissues where it is retained for long periods of time (Julshamn et al. 1982; Riisgård and Hansen 1990).

Inorganic mercury taken up with food initially accumulates in the tissues of the posterior intestine of fish (Boudou et al. 1991). Inorganic mercury is not easily transferred through this organ to other parts of the body. After 15 days, 80% had depurated from the fish intestine. Liver and kidney in fish tend to have higher percentages of inorganic mercury than muscle tissue, although percentages vary by organ and species (Windom and Kendall 1979; Riisgård and Hansen 1990).

Methylmercury ingested in food is efficiently transferred from the intestine to other organs (Boudou et al. 1991). Methylmercury has been reported to constitute from 70 to 95% of the total mercury in skeletal muscle in fish (Huckabee et al. 1979; EPA 1985; Riisgård and Famme 1988; Greib et al. 1990; Spry and Wiener 1991).

Methylmercury accounted for almost all ( 99%) of the mercury in muscle tissue in a wide variety of both freshwater and saltwater fish found in waters not highly contaminated by other organomercurial species (Bloom 1992).

The ratio of liver to muscle total mercury concentration usually fluctuates around one and can reflect the exposure history of the organisms. For example, the liver:muscle ratio may be less than one in chronically exposed fish, while a recent exposure to mercury may result in a ratio greater than one (Riisgård and Hansen 1990).

McKim et al. (1976) reported that mercury could be transferred from adult to offspring in brook trout. Exposure of the parent population to aqueous methylmercury concentrations of 0.03 to 2.93 µg/l in the laboratory resulted in mercury concentrations as high as 2 mg/kg in their embryos. Total mercury concentrations in eggs of several species of adult fish from Swedish lakes were much lower than concentrations in other tissues; therefore, spawning did not lower their total mercury body burden (Lindqvist 1991).

The main depuration pathway is through the kidney and liver in fish. Half-lives for methylmercury in fish range from one to three or more years (McKim et al. 1976; Pentreath 1976a, b; Riisgård and Famme 1986; Riisgård and Hansen 1990), while estimates of half-lives for inorganic mercury are much lower, ranging from approximately five days to five months (Pentreath 1976a, b; Huckabee et al. 1979).

### **Invertebrates**

Invertebrates accumulate and partition inorganic and methylmercury in tissues similar to the trends exhibited by fish ( Fowler 1978; Riisgård and Famme 1986; Saouter et al. 1991; Saouter et al. 1993). However, invertebrates generally contain a lower percentage of methylmercury than fish or mammals (Lasorsa and Allen-Gil 1995), with highly variable concentrations. This wide variation of mercury content in invertebrates is most likely a function of different feeding strategies (and trophic

levels) and different environmental exposures. Reported percentages of methylmercury compared to total mercury concentrations are less than 1% for the polychaete *Nereis succinea* (Luoma 1977); 10% in copepods, mussels and shrimp (Horvat 1991); 10-100% in the cockle (Møhlenberg and Riisgård 1988); 16% in urchin gonads (Eganhouse and Young 1978); 30-90% in lake zooplankton (Lindqvist 1991); 87% in crab muscle (Eganhouse and Young 1978); and 100% in red rock crab, Dungeness crab, and spot shrimp (Bloom 1992). Becker and Bigham (1995) found an increasing percentage of methylmercury compared to total mercury in higher trophic levels in the Onondaga lake food web. Lake water contained 5% of total mercury as methylmercury; phytoplankton 24%; benthic macroinvertebrates 26%; zooplankton 40%; and fish fillets 96%.

Viscera in mussels contained the highest tissue concentration of total mercury (Fowler et al. 1978). The total mercury concentration was highest in the midgut and muscle tissue in crab (Bjerregaard and Christensen 1993) and in the viscera in shrimp (Fowler et al. 1978). The shrimp molts had the lowest mercury content; therefore, molting is not considered an important depuration pathway in crustaceans (Fowler et al. 1978).

Half-lives for total mercury in salt-water mussels ranged from two months to one year (Riisgård et al. 1985). Inorganic mercury was eliminated more rapidly than methylmercury in mussels and shrimp (Fowler et al. 1978).

#### *Marine mammals*

Marine mammals have some of the highest tissue mercury concentrations of all marine organisms investigated (Andre et al. 1991a); however, concentrations are highly variable both within and among species. These variations have been attributed to collection locations (Wren 1986), concentrations in prey items (Szefer

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In contrast to fish, adult marine mammals have a much higher percentage of total mercury as inorganic mercury, although the concentration of methylmercury may also be elevated. Less than 10% of the total mercury content is methylmercury (Eisler 1987). Juveniles tend to have higher percentages of methylmercury.

The liver generally exhibits the highest total and methylmercury concentration (Holden 1978; Wagemann et al. 1983; Julshamn et al. 1987; Thompson 1990; Andre et al. 1991a), followed by kidney and muscle tissues (Szefer et al. 1993). Julshamn et al. (1987) measured the highest concentrations of methyl- and total mercury (13 and 150 mg/kg) in pilot whale livers (*Globicephalus meleanus*) compared to total and methylmercury concentrations in muscle (2.8 mg/kg total mercury; 1.7 mg/kg methylmercury) and kidney (15.3 mg/kg total mercury; 5.1 mg/kg methylmercury). Andersen et al. (1987) also measured the highest methylmercury concentrations in pilot whale liver (20 mg/kg; 14% of total mercury). The fraction that is methylated, however, is usually lower in the liver compared to muscle and kidney. The methylated fraction of total mercury ranged from 1% to 36% in seal liver (Holden 1978); 30% in older specimens to 100% in young specimens in the muscle of harbor porpoise (Joiris et al. 1991); and 24% to 86% in the muscle of pilot whales (*Globicephalus meleanus*; Julshamn et al. 1987). The liver:muscle ratio for methylmercury concentration in harbor porpoises was approximately one, while the ratio for liver:muscle for total mercury concentration was two. In some of the harbor porpoises and some other species (sperm whale, common dolphin, and adult bottle-nose dolphin) the liver:muscle ratio for total mercury ranged up to 20 (Joiris et al. 1991) while the liver:muscle ratio for methylmercury was still one. Schintu et al. (1992) observed an age-related change in the percentage of methylmercury compared to total mercury in pilot whale livers. The liver of three- to seven-year old pilot whales (with a relatively low total mercury body burden) contained 30% to 60% organic mercury, compared to 3% to 17% organic mercury in livers of 30- to 40-year old pilot whales (with a relatively high total mercury load). Porpoises exhibited a similar trend. Juveniles had a higher percentage of methylmercury in liver (100%), while the percentage of methylmercury in adult specimens decreased to 2 to 3% of the total mercury (Joiris et al. 1991).

Although mercury in the diet of many marine mammal species is predominantly methylmercury, it has been proposed that the mammals are able to mineralize methylmercury into the more harmless inorganic form, which then accumulates in the liver of adult specimens (Holden 1978; Joiris et al. 1991). The estimated half-life



of total mercury in pinnipeds and dolphins is about 1.4 and 2.7 years, respectively (Eisler 1987; Andre et al. 1991b).

### *Plants*

Vascular plants accumulate both inorganic and methylmercury from sediment and water in root, stem, and leaf sections (Alberts et al. 1990; Boudou et al. 1991). The rooted macrophyte *Elodea densa* accumulated different concentrations of methylmercury versus inorganic mercury from sediment (uptake was 40 times higher for methylmercury). Tissue concentrations were similar throughout the plant when the mercury source was water (ratio of 1.5 methylmercury to inorganic; Boudou et al. 1991).

Chloride concentration and pH influenced uptake of inorganic mercury by a marine diatom. Rates were low in seawater and low-chloride freshwater with neutral pH (Mason et al. 1996). Methylmercury uptake rates were high in high-chloride waters and were not influenced by pH. The uptake rate of methylmercury only became limited when very low chloride concentrations decreased the concentration of  $\text{CH}_3\text{HgCl}$ . Elemental and dimethylmercury were not significantly accumulated.

### **Exposure Pathways**

Aquatic organisms can accumulate mercury from water (including pore water) and food sources (including sediment). Quantity accumulated is a function of the exposure pathway and the physical and environmental factors such as temperature, pH, salinity, total organic carbon, and sulfides. If conditions are favorable for methylation, organisms can accumulate high concentrations of mercury even with low concentrations in the water and sediment.

### *Water*

Phytoplankton, invertebrates, fish (including eggs and larvae), and mammals take up inorganic and organic mercury from the water column (McKim et al. 1976; Pentreath 1976a; 1976b). In phytoplankton, algae, and microorganisms, mercury uptake is primarily a passive process that occurs by adsorption to the cell surface either through interaction with functional groups in the cell wall or through sorptive properties associated with the extracellular matrices (Darnell et al. 1986; Gadd 1988). Passive diffusion of lipid-soluble species (uncharged chloride

complexes) is responsible for mercury uptake in a marine diatom (Mason et al. 1996). Uptake in phytoplankton and aquatic plants has been correlated with the concentration of mercury in the water (Windom and Kendall 1979; Lenka et al. 1990). Water is an important exposure pathway for mercury uptake by lower organisms and thus into the food web (Francesconi and Lenanton 1992). Dissolved mercury concentrations in water are typically very low; the major increase in mercury concentrations occurs between water and phytoplankton of about a factor of  $10^5$  to  $10^6$  (Mason et al. 1995b). In contrast to microorganisms, uptake is primarily an active process for fish and invertebrates, and is related to respiration rate and metabolic rate (Rodgers and Beamish 1981). Uptake of methylmercuric chloride in water by different tissues of brook trout was found to be directly related to the water concentration of the mercury (McKim et al. 1976).

BCFs are the concentration of mercury in tissue divided by the concentration in the exposure water. They have been calculated from laboratory experiments for many species of aquatic organisms to estimate uptake from water. However, BCFs have limited use for several reasons. First, BCFs re Uptalodo Wive pTorasuremoastlikelny

Bioconcentration factors for inorganic mercury (mercuric chloride) in saltwater species were 129 for adult lobster (*Homarus americanus*), 1,000 for mussels, and 10,000 for oysters (*Crassostrea virginica*; Kopfler 1974; Roesijadi et al. 1981).

in surface sediments, the physical factors that affect the rate of methylation (and demethylation) also affect the availability of mercury for uptake by organisms. Sediment total-mercury concentrations alone may not provide information on the exposure potential of resident organisms.

#### *Food web*

Though sediment may be the ultimate source of mercury for many higher trophic species, the food web is the primary pathway to most organisms (Lindqvist 1991; Bryan and Langston 1992). Most of the differentiation between inorganic and

The relative importance of dietary versus aqueous mercury uptake pathways is unclear. Probably less than 10% of the mercury in fish tissue residues is obtained by direct (gill) uptake from water (Francesconi and Lenanton 1992; Spry and Wiener 1991). Methylmercury concentrations used in laboratory studies of aqueous uptake are 1,000 to 10,000 times the ambient concentration of methylmercury in natural water (Spry and Wiener 1991), thereby overestimating the significance of direct aqueous uptake. The proportion of mercury taken up from dietary sources versus water in invertebrates has not been estimated. Suspension-feeding bivalves may principally accumulate mercury by consuming algal cells (Riisgård and Hansen 1990).

Although mercury correlations are complicated by the importance of the food-chain exposure pathway, mercury concentrations in predators and prey have been correlated (e.g., Allard and Stokes 1989; Lindqvist 1991; Spry and Wiener 1991). For example, mercury concentrations in smallmouth bass from Ontario lakes were directly correlated with mercury in crayfish, which comprised 60% of their diet.

Detritus can be a very important source of mercury, particularly in estuarine habitats. Organic detritus from *Spartina alterniflora* may contain 30 times more mercury than plankton. Organisms in detritus-based food webs are thus exposed to higher mercury concentrations than are animals feeding on plankton (Lindberg and Harriss 1974). Mercury associated with humic matter in lakes is fed upon by bacteria and zooplankton, which incorporate mercury into the detrital food web (Lindqvist 1991).

Mercury in the fecal matter of marine mammals can also be a significant source to other aquatic organisms near breeding colonies or haul-out areas (Eisler 1987).

### **Biological Factors Affecting Accumulation of Mercury**

The primary biological factors governing the accumulation of mercury include age, weight, and diet. Differences in accumulation between the sexes have been attributed to differences in diet.

## *Fish*

Numerous field studies have shown that the concentration of total mercury in fish positively correlates with length, age, and weight (Hall et al. 1976a, b; Huckabee et al. 1979; Rada et al. 1986; Møhlenberg and Riisgård 1988; Greib et al. 1990; Leah et al. 1992). However, total mercury concentrations may not always correlate with size due to differences associated with diet, residence time in a contaminated habitat, and type of mercury (Francesconi and Lenanton 1992). The percentage of methylmercury increases with age in both fish and invertebrates (Møhlenberg and Riisgård 1988; Riisgård and Hansen 1990).

In some species of fish and invertebrates, sex differences in mercury tissue concentrations have been reported. For example, total mercury concentrations in the muscle tissue of freshwater sunfish were greater in females than males at ages 2 to 3 (Nicoletto and Hendricks 1987). This may be due to increased food demands for females related to reproduction. In contrast, there was little relationship between sex and bioaccumulation of mercury in three species of fish (roach, perch, and pike) collected from Swedish lakes (Lindqvist 1991).

Bloom (1992) did not find a relationship between lipid content and methylmercury concentrations in a variety of fresh- and saltwater fish.

## *Invertebrates*

Cockles (*Cardium edule*) from a polluted estuary were found to have a positive linear correlation between their age and the percentage of organic mercury in their tissues (Møhlenberg and Riisgård 1988). Organic mercury comprised 30% of the total mercury in two-year old cockles; 60% in three-year olds; and 90% in four-year olds. This relationship was attributed to the rapid loss of inorganic mercury and continued uptake of organic mercury over time. However, the correlation was not as strong when weight was used instead of age due to variations in growth rate at different locations. Total mercury concentrations in mussels were found to be higher in 27 mm than 31-mm sized individuals (Riisgård and Hansen 1990). This difference was perhaps due to a decrease in both weight-specific filtration rate and surface area-to-volume ratio in larger mussels (Fowler et al. 1978; Riisgård et al. 1985).

Total mercury concentrations may (Allard and Stokes 1989) or may not (Rada et al. 1986) correlate with weight or age in crustaceans.

Concentrations of mercury in male and female emergent mayflies (*Hexagenia bilineata*) in the upper Mississippi River differed. The authors recommend sampling male and female mayflies separately (Dukerschein et al. 1992).

### *Marine Mammals*

Mercury concentrations (both organic and inorganic) are positively correlated with body length in marine mammals (Arima and Nagakura 1979; Wagemann et al. 1983; Joiris et al. 1991). Hansen et al. (1990) found a highly significant correlation between age and tissue content of mercury in whales from West Greenland. This correlation has been used to separate immature specimens from adults. Joiris et al. (1991) found that the concentration of methylmercury in muscle and liver tissue in harbor porpoises did not increase with increasing length as strongly as did total mercury.

Leonzio et al. (1992) suggest that the elevated concentrations of inorganic mercury measured in mammals, as compared to fish, may be related to differences in respiratory systems. In contrast to fish, where the gills allow contaminants to be lost to the environment because blood flow has contact with the water, the mammalian respiratory system does not have a similar exchange. Mammals have developed different defense mechanisms. For example, selenium combines with mercury to form the non-toxic compound tiemannite that is stored within cells. The processes of intracellular storage tend to increase concentrations of the metal in certain organs while reducing the toxicity. In marine mammals, intracellular storage of mercury occurs as complexes of both selenium and metallothioneins (MTs).

### **Other Factors Affecting Accumulation**

Temperature and season influence the availability and accumulation of mercury in addition to the factors already discussed. Changes in temperature can affect mercury concentrations in organisms either directly by affecting metabolic rate and thereby exposure, or indirectly by influencing the methylation of mercury and therefore enhancing availability. Rates of methyl- or inorganic mercury uptake

increase with increasing aqueous concentrations and/or increasing temperature in the water for some species (e.g., phytoplankton, gastropods, fish; Windom and Kendall 1979; Rodgers and Beamish 1981; Tessier et al. 1994). A rise in temperature (and a corresponding rise in respiratory volume) can increase the rate of uptake via the gills (EPA 1985).

Total concentrations of mercury in killifish from an estuarine wetland were five times higher in spring and summer than in other seasons (Weis et al. 1986), presumably due to higher methylation rates in summer. Zooplankton mercury concentrations peaked in June in Swedish lakes and fish tissue levels varied by a factor of two, reaching a maximum in spring (Lindqvist 1991). Mercury content of mussels from the Gulf of St. Lawrence estuary varied seasonally by a factor of two (Cossa and Rondeau 1985).

The relationship of pH, conductivity, and salinity to mercury accumulation is not well understood. Elevated mercury concentrations have frequently been found in piscivorous fish in poorly buffered (alkalinity < 55  $\mu\text{eq/l}$  and calcium < 2 mg/l), low-pH lakes (pH 6.0-6.5) in areas removed from industrial inputs of mercury (Rada et al. 1989a; Winfrey and Rudd 1990; Spry and Wiener 1991). Total mercury concentrations in yellow perch were inversely correlated with pH in ten Wisconsin lakes (Cope et al. 1990). Mercury concentrations in zooplankton in Swedish lakes were correlated with pH but the relative importance of this correlation changed over time (Lindqvist 1991).

In freshwater lakes removed from direct sources of mercury, conductivity explained 54% of the variability in mercury concentrations in crayfish (Allard and Stokes 1989). Conductivity was also highly correlated with calcium, magnesium, alkalinity, pH, and sodium. This correlation suggests that the buffering capacity of the lake was an important influence on crayfish accumulation of mercury. Low calcium ion concentrations enhanced the efficiency of methylmercury uptake across the gills of rainbow trout (Rogers and Beamish 1983).



## TOXICITY OF MERCURY

The toxicity of mercury to aquatic organisms is affected by both abiotic and biotic factors including the form of mercury (inorganic versus organic), environmental conditions (e.g., temperature, salinity, and pH), the sensitivity of individual species and life history stages, and the tolerance of individual organisms. Toxicological effects include neurological damage, reproductive impairment, growth inhibition, developmental abnormalities, and altered behavioral responses. Wiener and Spry (1996) concluded that neurotoxicity seems to be the most probable chronic response of wild adult fishes to methylmercury exposure, based on observed effects such as uncoordination, inability to feed, diminished responsiveness, abnormal movements, lethargy, and brain lesions. In laboratory studies, reproductive endpoints are generally more sensitive than growth or survival, with embryos and the early developmental stages being the most sensitive (Hansen 1989). Impaired reproduction in sensitive aquatic organisms has been shown to occur at aqueous concentrations of mercury between 0.03 and 1.6  $\mu\text{g/l}$  (Eisler 1987). Long-term mercury exposure to adult fish also has been shown to result in retarded growth of offspring (Snarski and Olson 1982) and teratogenic effects (Weis et al. 1981). Chronic exposure to low concentrations of mercury may result in populations that become tolerant to the toxic effects of mercury contamination (Weis and Weis 1989).

The toxic concentration of mercury compounds can vary by an order of magnitude or more depending on the exposure condition. For example, toxicity is greater at elevated temperatures (Armstrong 1979), at lower oxygen content (Sloof et al. 1991), and at reduced salinities in marine environments (McKenney and Costlow 1981). Site-specific factors (such as TOC) affect the bioavailability and toxicity of mercury-contaminated sediment (Langston 1990). Even though correlations exist between toxicological observations and sediment pollution gradients, Langston (1990) recommends collecting site-specific data because biological responses can not always be satisfactorily predicted from chemical data or modeling results.

The sensitivity of aquatic organisms to either inorganic or methylmercury varies considerably between species – more than the difference in sensitivity of a particular species to various mercury compounds (EPA 1985). Methylmercury is more acutely toxic to aquatic organisms than inorganic mercury, but the range

among different species in sensitivity to either compound is quite large. For example, the concentration of inorganic mercury inducing acute toxicity was observed to range over almost three orders of magnitude from 0.1  $\mu\text{g/l}$  to more than 200  $\mu\text{g/l}$  when results from tests with different species were compared (Eisler 1987). Tests on the same freshwater species with both inorganic and methylmercury showed that methylmercury was more than 30 times more acutely toxic than inorganic mercury (EPA 1985).

The general mechanism of action for toxic effects for inorganic mercury which has the form  $\text{Hg (II)}$ , the divalent mercury cation, is believed to be the high affinity for thiol or sulfhydryl groups of proteins (Clarkson 1972; Hughes 1957, Passow et al. 1961) resulting in altered protein production or synthesis (Syversen 1977).

## Toxicity of Mercury in Water

Nearly all of the studies evaluating the toxicity of mercury compounds where the route of exposure is through water have been conducted under laboratory conditions. Due to the nature of laboratory studies and differences in experimental design and technique, a wide range of toxic concentrations have been reported for a given species (Table 1). For example, toxicity tests using flow-through systems generally show higher toxicity at lower concentrations than static-renewal systems using the same (nominal) concentrations and the same species. This difference is probably due to loss of mercury from the test container in the static-renewal tests (Birge et al. 1979; Biesinger et al. 1982; WHO 1989).

### *Fish*

Fish tend to be more sensitive to sublethal effects from chronic exposure to both inorganic and organic mercury than invertebrates, but fish are less sensitive to acute effects (EPA 1985; Hansen 1989). The early life stages of fish are generally the most sensitive to mercury. Birge et al. (1979) conducted several tests designed to evaluate embryo survival, hatching success, teratogenic effects, and the effects of mercury on six species of freshwater fish. The sensitivity of the embryo-larval stage for various species was correlated with the length of time for eggs to develop and hatch and the duration of exposure. Trout eggs treated in a flow-through system experienced approximately 40% mortality after a five-day exposure and 100% mortality after an eight-day exposure to an average mercury concentration of 0.12 µg/l.

Birge et al. (1979) also evaluated the long-term effects of mercury exposure on fish reproduction by conducting chronic bioassays with rainbow trout. Their results suggest that exposure of adult fish to mercury can have significant adverse effects on their offspring, with the effects enhanced if the embryos are also reared in a mercury-contaminated environment. Their data show a dose-dependent response in both bioaccumulation of mercury in gonadal tissues and toxic effects on embryos. Short-term exposures of embryos to high concentrations of mercury can also elicit significant adverse effects (Sharp and Neff 1980) and such exposures should be taken into account in the evaluation of potential long-term impacts to

**Table 1. Toxicity resulting from exposure to mercury in water.**

Fish Species	Hg ( $\mu\text{g/l}$ )	Hg Form	Exposure	Effect(s)	Reference
Brachydanio rerio Zebrafish (adults & fertilized eggs)	0.1, 5, 10, & 20	phenylmercuric acetate	25 days	83% spawning inhibition at 5 $\mu\text{g/l}$ ; 99% inhibition at 20 $\mu\text{g/l}$ ; significant decrease in hatching frequency at 0.2 and 1 $\mu\text{g/l}$ .	Kihlstrom et al. 1971
Brachydanio rerio Zebrafish (fertilized eggs)	10, 20 & 50	phenylmercuric acetate	~ 6 days	increased hatching success at 10 $\mu\text{g/l}$ ; increased time to hatch and reduced hatching success at 20 $\mu\text{g/l}$ ; no hatch at 50 $\mu\text{g/l}$	Kihlstrom and Hulth 1972
Poecilia reticulata Medaka guppies	1.8	methylmercury	3 months	impaired spermatogenesis	Wester 1991
Oryzias latipes Medaka (fertilized eggs)	15	mercuric chloride	16 days	80% egg mortality; cardio-vascular abnormalities in eggs (hemorrhaging, blood vessel deterioration, loss of circulating blood cells and blood vessels), teratogenic effects in fry (i.e., non- functioning caudal fins, skeletal defects, spinal curvature)	Heisinger and Green 1975
Fundulus heteroclitus Killifish (fertilized eggs)	20 & 30 0, 4, 10, 20, 30, 40, 60, 80 & 100	mercuric chloride	32 days	100 % egg mortality decreased hatching at $[\text{Hg}] > 10 \mu\text{g/l}$ ; lateral curvature of the spine in larvae at $[\text{Hg}] 30 \mu\text{g/l}$ .	Sharp and Neff 1980
Fundulus heteroclitus Killifish (fertilized eggs)	30 & 40	methylmercuric chloride	up to 48 days	reduced axis formation, development of cycloopia, defective cardiovascular system, skeletal malformations	Weis and Weis 1977
Pimephales promelas Fathead Minnow	0.26 1.02 2.01	mercuric chloride	41 days	decreased growth in females and reduction in number of spawning pairs cessation of spawning severe stunting and scoliosis	Snarski and Olson 1982
Oncorhynchus mykiss Rainbow trout (fertilized eggs)	0.12	mercuric chloride	5 & 8 days	40% mortality in fertilized eggs; 100% mortality after 8 days	Birge et al. 1979

**Table 1. continued**

Molluscs/Bivalves Species	Hg ( $\mu\text{g/l}$ )	Hg Form	Exposure	Effect(s)	Reference
Crepidula fornicata Limpet	>0.25  0.42	mercuric chloride	16 weeks	growth impairment, diminished condition  suppressed fecundity, reductions in larval settlement	Thain 1984
Mercenaria mercenaria Clams	1.0 15	mercuric chloride	8 & 10 days	significant growth reductions reduced growth	Calabrese et al. 1977
Crassostrea virginica Oysters	12			reduced growth	
Mytilus edulis Mussels	0.3 >1.6	mercuric chloride	10-22 days >3 days	reduced growth cessation of growth	Stromgren 1982
Echinoderm Species					
Anthocardaris crassispina Sea urchin	10	mercuric chloride	Not available	fertilization and development interference	Kobayashi 1984
Crustacean Species					
Callinectes sapidus Blue crab (megalopae through 2nd crab stage)	10 to 20	mercuric chloride	22 days	reduced survival in megalopae	McKenney and Costlow 1981
Mysidopsis bahia Mysids	1.6  2.5	mercuric chloride	full life cycle	delayed sexual maturation, delayed brood release, decreased brood production  increased brood development time; aborted developing juveniles	Gentile et al. 1983

could result in inhibition of hatching, teratogenic development, and possible population effects.

Low concentrations of mercury in freshwater reportedly result in olfactory and chemoreceptor impairment in salmonids and other fish, which may interfere with normal migratory behavior (Hara et al. 1976; Rehnberg and Schreck 1986). For example, Hara et al. (1976) reported that rainbow trout exposed to inorganic mercury concentrations as low as 0.1 mg/l for two hours showed reduced olfactory responses. Further physiological and behavioral studies by Rehnberg and Schreck (1986) showed that mercury exposure reduced the ability of coho salmon to detect natural odors and disrupted simple upstream movement in laboratory experiments.

Weis and Weis (1989) suggest that prior exposure to mercury may produce populations that are more tolerant to the toxic effects of mercury contamination. Differences in tolerance to the effects of methylmercury were observed between organisms from mercury-contaminated and clean environments. Eggs collected from killifish in a contaminated area were mostly resistant to the teratogenic effects of methylmercury, while eggs of fish from the clean area showed a range of sensitivity. The susceptible eggs from the clean area also accumulated higher levels of mercury than did the eggs from the contaminated area (Weis et al. 1981; 1982). Offspring from fish previously exposed to mercury contamination were more tolerant to environmental mercury concentrations than offspring from clean environments (Weis and Weis 1984).

The situation is complicated by the fact that some fish that build up a tolerance to low concentrations of mercury can also detoxify the free metal within cells via the production of metallothioneins (MTs) and other metal-binding proteins. Brown et al. (1983) proposed that toxic effects occur as the binding capacity of MT becomes saturated, due to the interaction of excess free metal in the cell with the enzyme pool.

#### *Invertebrates*

Calabrese et al. (1977) suggest that marine bivalves embryos are more sensitive than the larvae in their susceptibility to mercury. They further indicated that growth of fully-developed larvae may be retarded at concentrations too low to elicit

significant mortality, thus prolonging the pelagic stages and increasing the risk of predation, disease, and dispersion. Several endpoints have been used to measure the effect of mercury exposure on bivalves, including biomarkers. The prophyrin precursor  $\delta$ -aminolevulinic acid (ALA) may be useful as a biomarker of mercury exposure in bivalves (Brock 1993).

The effects of salinity on the toxicity of mercury have been demonstrated in a study conducted with the megalopae of the blue crab, *Callinectes sapidus* (McKenney and Costlow 1981). Their results indicated that as salinity was reduced below 20 parts-per-thousand, less mercury was required to produce equivalent toxicity among megalopae. This is significant for blue crab and other estuarine species which inhabit, migrate through, and use areas of lower salinity for foraging, spawning, and nursery grounds. Their data imply that the impact to a given population of fish or invertebrates is highly dependent on the life stage and surrounding environmental conditions.

The significance of experimental design and exposure period on evaluating the toxicity of mercury was demonstrated in a series of studies conducted by Biesinger et al. (1982). In acute flow-through toxicity tests with *Daphnia magna*, methylmercuric chloride was about 10 times more toxic than inorganic mercury, but only about 4 times as toxic under static-renewal conditions. In the static-renewal tests with methylmercury, it was discovered that about 90 percent of the mercury had been converted to inorganic mercury during the testing period. In chronic flow-through toxicity tests with *Daphnia magna*, methylmercuric chloride was about 30 times more toxic than inorganic mercury.

### *Plants*

Chronic toxicity (as demonstrated by reduced population growth) in a marine diatom (*Thalassiosira weissflogii*), exposed to inorganic mercury, methylmercury, dimethylmercury, and elemental mercury, was related to the aqueous concentration of a single mercury species, (the chloride species  $\text{HgCl}_2$  or  $\text{CH}_3\text{HgCl}$ ), not to the total mercury or free mercury ion concentration (Mason et al. 1996). Approximately the same concentration of  $\text{CH}_3\text{HgCl}$  and  $\text{HgCl}_2$  reduced growth in the diatom by 50 percent. Mason et al. (1996) explain the apparently higher toxicity of methylmercury compared to inorganic mercury (expressed as a total

concentration of all inorganic forms) observed by numerous authors as a result of the low percentage of the chloride form ( $\text{HgCl}_2$ ) in the inorganic mercury fraction of seawater (3.3 %) compared to the high percentage of the methyl mercuric chloride species ( $\text{CH}_3\text{HgCl}$ ), which forms 100% of the methylmercury in seawater. Elemental and dimethylmercury, even though more hydrophobic than  $\text{HgCl}_2$  and  $\text{CH}_3\text{HgCl}$  respectively, were neither accumulated nor toxic to the diatom. The hypothesis by Fisher et al. (1984), that the metals that are most bioavailable





maternal transfer) are critical factors in producing toxic symptoms in aquatic receptors.

According to Wiener and Spry (1996), mercury transferred from the female to the eggs during oogenesis may pose a greater risk to embryos than exposure to mercury in the water column. For rainbow trout, mercury residues in ovaries of 0.5 mg/kg were associated with a significant reduction in larval survival and abnormal



with adverse effects. The "thresholds" presented in these papers are based on effects in adult fish and probably do not represent a truly protective level for all species and life stages, including maternal transfer. We begin to become concerned about reproductive or early life stage effects when total Hg in whole bodies of fish are between 0.5 and 1.0 ppm.

### **Interactions with Other Metals**

The effects on aquatic organisms due to interactions of mercury with cadmium, copper, selenium, and zinc were found to be dependent on exposure concentrations (Birge et al. 1979). In general, effects were less than additive at lower exposure concentrations and greater than additive (synergistic) at higher concentrations. Zinc and cadmium were reported to reduce the teratogenic effects of methylmercury to killifish (Weis et al. 1981). Cadmium added to methylmercury reduced the retardation effect on fin regeneration in mullet (Weis and Weis 1978).

The percentage of embryos affected and degree of malformation observed due to exposure of killifish eggs to 20-50 µg/l methylmercury was reduced when cadmium or zinc was added. Selenium was reported to reduce the developmental effects of inorganic mercury to embryos of the medaka (Japanese ricefish), but only after the formation of the embryonic liver (Bowers et al. 1980). Interactions between inorganic mercury and zinc, PCBs, and a PAH (fluoranthene) were observed to be generally additive in sediment exposure to a marine amphipod (Swartz et al. 1988). A mixture of an inorganic form of mercury (mercuric chloride) and the chlorides of zinc and lead had a synergistic toxic effect on the water exposure of a marine ciliate *Uronema marinum* (Parker 1979).

## **CRITERIA AND GUIDELINES**

This section briefly discusses EPA's AWQC for mercury in freshwater and marine systems and various guidelines that have been proposed for evaluating the potential toxicity of mercury in sediments.

### **Ambient Water Quality Criteria (AWQC)**

The AWQC, promulgated by the U.S. EPA, are intended neither as rules nor regulations, but present data and guidance on the effects of pollutants that can be

used to derive regulations based on considerations of water quality impacts (EPA 1993). The AWQC consist of two concentrations: the Criterion Maximum Concentration (usually referred to as the acute AWQC) and the Criterion Continuous Concentration (usually referred to as the chronic AWQC). The acute AWQC are derived from short-term toxicity tests using statistical methods that estimate the LC<sub>50</sub> concentrations for the lowest 5 percent of the most sensitive species tested. Acute AWQC for mercury are 2.4 and 2.1 µg/l for freshwater and marine organisms, respectively. They are based on inorganic mercury because it is the predominant form of mercury released into the environment (EPA 1985).

The chronic AWQC are defined by EPA as the lowest (most protective) concentrations from three categories of tests: the final chronic value, derived from chronic toxicity tests with animals; the final plant value, derived from toxicity tests using aquatic plants; and the final residue value (FRV), derived from maximum permissible tissue concentrations (for protection of human health) and bioconcentration factors (BCF). For mercury, the chronic AWQC of 0.012 µg/L for freshwater species and 0.025 µg/l for marine species represent FRVs, which are based on the Food and Drug Administration's (FDA) action level of 1 mg/kg and BCFs for methylmercury.

The use of the FDA action level to derive the chronic AWQC assumes that aquatic organisms would not be adversely affected by methylmercury tissue concentrations greater than or equal to 1 mg/kg. This is based on a study in which long-term exposure of brook trout to methylmercury resulted in tissue residue concentrations

the chronic AWQC would be expected to have tissue concentrations above 1 mg/kg (EPA 1985).

### **Sediment Guidelines**

No sediment criteria are currently available for either methylmercury or total mercury. Several approaches have been proposed for developing guidelines for screening contaminated sediments, but two of the more frequently used approaches are the National Status and Trends Effects Range approach (Long and MacDonald 1992) and the AET (PTI 1988) approach developed for screening sediments in Puget Sound, Washington. The State of Washington used the AET approach as the basis

considerations to assist in sampling, risk assessment, monitoring, and remedial decisions.

## **Sampling and Monitoring Considerations**

### *Target Species and Analysis*

Mercury concentrations in resident aquatic organisms may provide the best measure of the availability of mercury in a particular area, both because of potential human health concerns and because it is the best indicator of availability of mercury under the specific conditions present at a site. In selecting target species, the trophic level, size, age, sex, life habit, metabolism, and life span of organisms are all important factors to consider. Higher trophic-level fish species are useful for determining whether a problem exists since mercury biomagnifies, and for long-term monitoring, since mercury concentrations are slower to decrease. However, even fish occupying the same trophic level, with similar diets and feeding habits, may exhibit different temporal patterns of mercury accumulation due to differences in habitat preferences, behavior, and metabolic rate causing different exposures (Jackson 1991). Mercury concentrations in biota may not correlate with sediment mercury concentrations. Correlations between mercury concentrations in predator and prey species may be useful in determining the food web pathways that connect the mercury in the sediment to the biota.

Whole body analyses of fish are typically done to determine food chain exposure, while fish fillets are typically analyzed to assess human health exposure. Whole-body mercury concentrations may be less than the concentration in the fillet; however the difference may not be statistically significant. For example, although methylmercury concentrations were higher in fillet than in whole body samples measured in four fish species (white perch, small mouth bass, bluegill, and gizzard

In developing assessment endpoints and sampling objectives, the potential for direct toxicity to aquatic organisms should not be overlooked. Laboratory and in-situ toxicity testing are useful approaches for assessing the direct biological effects of elevated mercury concentrations to aquatic organisms in sediment and water. Toxicity testing at mercury sites should include standard toxicity tests. In addition, early life-stage tests (exposure of test species from post-fertilization through embryonic, larval, and early juvenile development) or partial life-cycle tests (early juvenile through post-hatch of next generation with measurements of survival, growth, and reproductive endpoints) are sensitive tests for mercury toxicity. Monitoring changes in abundance and diversity in macrobenthic community composition may also provide useful information in assessing the toxicity of mercury in aquatic habitats.

#### *Environmental Sampling*

Investigations should be designed to include both spatial and temporal sampling. Seasonal and spatial variations in mercury concentrations, including its forms and partitioning, within a single waterbody can be significant (e.g., Gill and Bruland



Accurately modeling the fate of mercury in aquatic environments and the availability of mercury to aquatic organisms requires the collection of detailed information on the forms of mercury and their relative concentrations in different environmental compartments (e.g., the amounts of inorganic, methyl-, and elemental mercury in dissolved and particulate forms in the water column, sediment [particulate and pore water], and biota). The scope of a project like this is enormous and the effectiveness of this comprehensive approach has yet to be demonstrated. The transfer of mercury through the food web was modeled using a descriptive approach to explain the high levels of mercury in Lavaca Bay fish and shellfish (Evans and Engel 1994). Tissue burdens for multiple food web components are required. This approach was useful in identifying critical factors responsible for localized elevations in mercury concentrations, but also demonstrated the limitations and large effort required for modeling.

### **Approaches to Remediation**

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techniques that are selective and sensitive enough to measure ambient concentrations of the different mercury species.

A primary goal of many remedial investigations is to establish cleanup concentrations for mercury in various environmental media that will be protective of both human health and the environment. Establishing target cleanup concentrations for mercury is extremely difficult due to the many environmental factors that influence the transformation of inorganic mercury to methylmercury. Target cleanup concentrations should be determined on a site-by-site basis due to the variability in the bioavailability of mercury and conditions between sites. Determining a cleanup concentration requires knowing the effect threshold and translating that to a sediment concentration that is protective. Cleanup concentrations should be chosen that both reduce the source of total mercury to the system and its bioavailability to organisms. Confirmation of the effectiveness of the target cleanup concentration requires long-term monitoring of both sediment and biota.

Removing hot spots (by dredging or capping) may eliminate important sources of inorganic mercury but may not provide substantial improvement in environmental conditions if methylation rates are much higher in less contaminated areas, such as freshwater wetlands (St. Louis et al. 1994). Other factors affecting the site also need to be considered. Methylation of mercury left in sediments could be increased by dredging, increased organic loading (without sulfides), and increased thermal loading (Rada et al. 1986).

Where source control has not been feasible due to the volume and extensive mobility of mercury and conditions that are difficult to control, the use of

taking two or more years (Lindqvist 1991; Meili 1995). The long-term effectiveness of these remedies and the potential adverse effects on the environment have not been well-studied.

## **Analytical Considerations**

### *Detection Limits in Water, Sediment, and Biota*

Detection limits should be chosen based on the objective of the study. Analysis of mercury in water samples is particularly difficult due to the very low concentrations (parts per trillion) that need to be measured. Achieving low detection limits is further complicated by the possibility of external contamination of samples which can be a significant problem (Fitzgerald 1990).

The chronic AWQC for methylmercury are 0.012 and 0.025  $\mu\text{g/l}$  for freshwater and saltwater, respectively. Using the AWQC as a detection limit may be difficult as few labs have analytical procedures that can reach these low concentrations. The detection limit for the EPA standard contract lab program (CLP) method for analysis of total mercury in water is 0.2  $\mu\text{g/l}$ . To achieve ecologically relevant detection limits it may be necessary to employ analytical methodologies other than those specified under the CLP, or to modify the CLP methods. For example, mercury detection limits to determine the mass balance of mercury in the Onondaga Lake Superfund site were established as follows: 0.00001  $\mu\text{g/l}$  for methylmercury in water; 0.0001  $\mu\text{g/l}$  for total mercury in water; and 0.01 mg/kg wet weight in fish (PTI 1991).

These detection limits were achievable by modifying standard procedures. Unfiltered water samples are analyzed for comparison to criteria concentrations. In the EPA criteria document, the measurement of acid-soluble mercury (the mercury that passes through a 45- $\mu\text{m}$  filter following acidification to a pH of 1.5 to 2.0) is recommended, although no EPA-approved protocol has been established (EPA 1985). Some recent analytical approaches for the analysis of methylmercury are described by the following authors: Bloom and Crecelius (1983), Gill and Fitzgerald (1987), Bloom (1989), Gill and Bruland (1990).

Choosing appropriate detection limits for sampling of sediment is particularly important for mercury sites because even low concentrations can cause significant

accumulations in biota. Detection limits for sediments should be below the ERL value of 0.15 mg/kg developed by Long and MacDonald (1992).

Quality control is an important aspect of any testing program but is particularly important for the analysis of mercury in environmental samples. It is highly recommended that analyses of mercury in water, sediment, and tissue also include analyses of certified standards for the appropriate matrix as part of the quality control plan to verify the extraction and analytical processes.

Difficulties in the extraction and analysis of mercury residues in tissues are apparently not uncommon. For example, in three recent Superfund projects in three different regions, methylmercury concentrations in fish tissue were reported to be higher than total mercury concentrations. In another study of contaminant concentrations in tissues of aquatic organisms, spike-recovery values for mercury in tissue samples were in the range of 50 percent (Tetra Tech 1988).

The National Research Council of Canada has certified standards for methylmercury and total mercury in animal tissue samples (e.g., dogfish liver and

toxicity endpoints should be included in the assessment—in particular, fish early life stage or reproductive endpoint tests. Because of the persistence of mercury in aquatic systems, source control alone may not be sufficient to permit recovery. Additional remedial actions may be required to reduce the total mercury burden in the system. Long-term monitoring of tissue concentrations of mercury in aquatic biota is needed to assess remedial effectiveness.

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