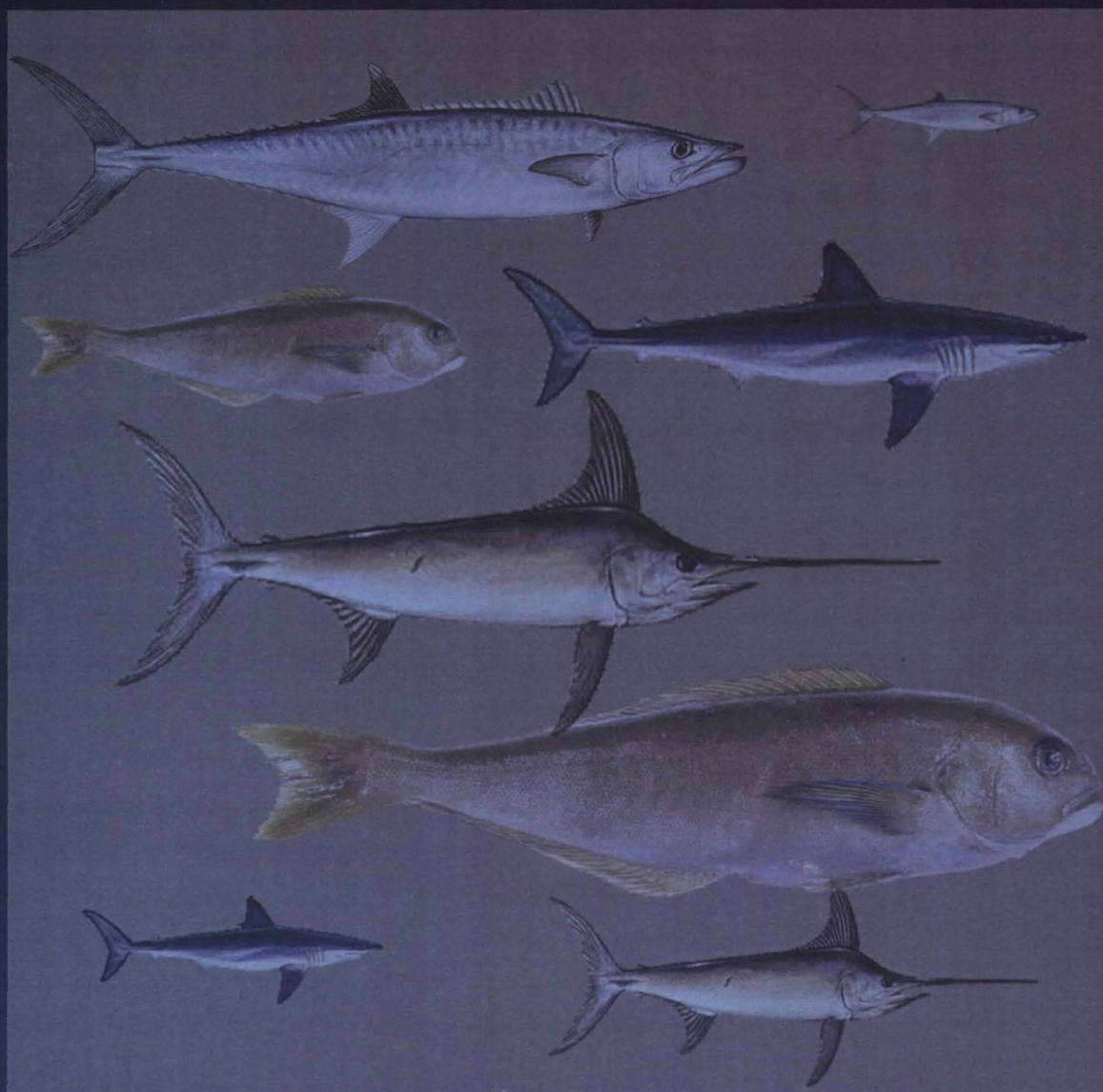


Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion



United States Environmental Protection Agency
Office of Science and Technology (4305T)
1200 Pennsylvania Ave., NW
Washington, D.C. 20460
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August 2006

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DISCLAIMER

This guidance provides advice on how to implement the water quality criterion recommendation for methylmercury that the U.S. Environmental Protection Agency (EPA) published in January 2001. This guidance does not impose legally binding requirements on EPA, states, tribes, other regulatory authorities, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA, state, tribal, and other decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from those in the guidance where appropriate. EPA may update this guidance in the future as better information becomes available.

The Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency has approved this guidance for publication. Mention of trade names, products, or services does not convey and should not be interpreted as conveying official EPA approval, endorsement, or recommendation for use

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FOREWORD

On January 8, 2001, the Environmental Protection Agency (EPA) announced the availability of its recommended Clean Water Act (CWA) section 304(a) water quality criterion for methylmercury. This water quality criterion, 0.3 mg methylmercury/kg fish tissue wet weight, describes the concentration of methylmercury in freshwater and estuarine fish and shellfish tissue that should not be exceeded to protect consumers of fish and shellfish among the general population. EPA recommends the criterion to be used as guidance by states, territories, and authorized tribes in establishing or updating water quality standards for waters of the United States and in issuing fish and shellfish consumption advisories.

This is the first time EPA has issued a water quality criterion expressed as a fish and shellfish tissue value rather than as a water column value. EPA recognizes that this approach differs from traditional water column criteria and may pose implementation challenges. In the January 8, 2001 notice, EPA stated that it planned to develop more detailed guidance to help states, territories, and authorized tribes with implementation of the methylmercury criterion in water quality standards and related programs. This document provides that detailed guidance.

EPA wrote the *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* to provide the technical guidance to states, territories, and authorized tribes exercising responsibility under CWA section 303(c) on how to use the new fish tissue-based criterion recommendation in developing their own water quality standards for methylmercury and in implementing these standards in Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) permits. EPA also wrote the guidance to discuss approaches for managing the development of TMDLs for waterbodies impaired by mercury and to recommend an approach for directly incorporating the methylmercury tissue criterion in NPDES permits.

For more information on the methylmercury criterion, see the criteria page on EPA's Web site at <http://www.epa.gov/waterscience/criteria/methylmercury/criteria.html>. For more information on EPA's water quality standards program, see the standards page on EPA's Web site at <http://www.epa.gov/waterscience/standards>. For more information about this guidance document, contact U.S. Environmental Protection Agency, Office of Science and Technology (4305T), 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

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1 Executive Summary

In January 2001, EPA published ambient water quality criteria (AWQC) recommendations for methylmercury for the protection of people who eat fish and shellfish. This criterion, 0.3 mg methylmercury/kg fish tissue wet weight, marks EPA's first issuance of a water quality criterion expressed as a fish and shellfish tissue value rather than as an ambient water column value.

Research shows that exposure to mercury and its compounds can cause certain toxic effects in humans and wildlife (USEPA 1997c). As of 2004, 44 states, 1 territory, and 2 tribes have issued fish consumption advisories for mercury covering 13.2 million lake acres and 765,000 river miles (USEPA 2005a). Mercury is widely distributed in the environment and originates from both natural and anthropogenic processes, including combustion and volcanoes. Methylmercury is highly bioaccumulative and is the form of mercury that bioaccumulates most efficiently in the food web.

Under section 303(c) of the Clean Water Act (CWA), states and authorized tribes must adopt water quality criteria that protect designated uses. This document provides technical guidance to states and authorized tribes exercising responsibility under section CWA 303(c) on how to use the new fish tissue-based criterion recommendation as they develop their own water quality standards for methylmercury. One approach that States and authorized tribes may decide to use is to translate the tissue residue value to a water column value through use of methylmercury bioaccumulation factors (BAFs). If a state or authorized tribe decides to use this approach, EPA recommends three potential approaches for relating a concentration of methylmercury in fish tissue to a concentration of mercury in ambient water. The approaches are:

- Deriving site-specific methylmercury BAFs
- Using bioaccumulation models
- Using EPA's draft default methylmercury BAFs

All three approaches have limitations, especially in the amount of data necessary to develop a BAF. This guidance discusses the advantages and limitations of each approach. States and authorized tribes may also consider calculating their own fish tissue criteria or adopting site-specific criteria for methylmercury to reflect local or regional fish consumption rates or relative source contributions. EPA encourages states and authorized tribes to develop a water quality criterion for methylmercury using local or regional data rather than the default values if they believe that such a water quality criterion would be more appropriate for their target population. This guidance also discusses variances and use attainability analyses (UAAs) relating to methylmercury.

This document describes methods for measuring mercury and methylmercury in both tissue and water. These methods can analyze mercury and methylmercury in tissue and water at very low levels—well below the previous criterion for mercury in water and the current criterion of methylmercury in fish tissue. This document also provides guidance for field sampling plans, laboratory analysis protocols, and data interpretation on the basis of previously published EPA guidance on sampling strategies for contaminant

monitoring. This document also describes how states can assess the attainment of water quality criteria and protection of designated uses by comparing sampling data to water quality criteria.

EPA expects that, as states and authorized tribes adopt the methylmercury criterion, the number of waterbodies states report as impaired due to mercury contamination might increase. EPA expects this to occur because the number of river miles and lake acres under fish consumption advisories due to methylmercury in fish tissue greatly exceeds the number of waters listed by states as impaired. EPA expects that, as a result of this revised methylmercury water quality criterion, together with a more sensitive method for detecting mercury in effluent and the water column, and increased monitoring of previously unmonitored waterbodies, the number of waterbodies that states report on CWA section 303(d) lists as impaired due to mercury contamination may increase. Thus, this guidance also discusses approaches for managing the development of Total Maximum Daily Loads (TMDLs) for waterbodies impaired by mercury. This includes approaches for addressing waterbodies where much of the mercury is from atmospheric sources and how TMDLs can take into account ongoing efforts to address sources of mercury, such as programs under the Clean Air Act (CAA) and pollution prevention activities. This guidance also includes a recommended approach for directly incorporating the methylmercury tissue criterion in National Pollutant Discharge Elimination System (NPDES) permits.

2 Introduction

2.1 What is the interest in mercury?

Mercury occurs naturally in the earth's crust and cycles in the environment as part of both natural and human-induced activities. The amount of mercury mobilized and released into the biosphere has increased since the beginning of the industrial age. Most of the mercury in the atmosphere is elemental mercury vapor, which circulates in the atmosphere for up to a year, and hence can be widely dispersed and transported thousands of miles from sources of emission. Most of the mercury in water, soil, sediments, plants, and animals is in the form of inorganic mercury salts and organic forms of mercury (e.g., methylmercury). Divalent mercury, when bound to airborne particles, is readily removed from the atmosphere by precipitation and is also dry deposited. Even after it deposits, mercury commonly returns to the atmosphere either as a gas or associated with particles, and redeposits elsewhere. As it cycles between the atmosphere, land, and water, mercury undergoes a series of complex chemical and physical transformations, many of which are not completely understood.

This guidance focuses on an organic mercury compound known as methylmercury. Methylmercury most often results from microbial activity in wetlands, the water column, and sediments and is the form of mercury that presents the greatest risks to human health. The methylation process and methylmercury bioaccumulative patterns are discussed in more detail in section 2.3.

2.1.1 What are the health effects of mercury?

Exposure to methylmercury can result in a variety of health effects in humans. Children who are exposed to low concentrations of methylmercury prenatally might be at risk of poor performance on neurobehavioral tests, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory. (NRC 2000, USEPA 2002e, USEPA 2005b). In 2000, the National Academy of Sciences (NAS)/National Research Council (NRC) reviewed the health studies on mercury (NRC 2000). EPA's current assessment of the methylmercury reference dose (RfD) relied on the quantitative analyses performed by the NRC (USEPA 2002e). The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 2002e). In its review of the literature, NRC found neurodevelopmental effects to be the most sensitive endpoints and appropriate for establishing a methylmercury RfD (NRC 2000). On the basis of the NRC report, EPA established an RfD of 0.0001 mg/kg per day (0.1 microgram of methylmercury per day for each kilogram of a person's body mass) in 2001 (USEPA 2002e). EPA believes that exposures at or below the RfD are unlikely to be associated with appreciable risk of deleterious effects. It is important to note, however, that the RfD does not define an exposure level corresponding to zero risk; mercury exposure near or below the RfD could pose a very low level of risk that EPA deems to be non-appreciable. It is also important to note that the RfD does not define a bright line, above which individuals are at risk of adverse effects (USEPA 2005b).

The primary route by which the U.S. population is exposed to methylmercury is through the consumption of fish containing methylmercury. The exposure levels at which neurological effects have been observed in children can occur via maternal consumption of fish (rather than high-dose poisoning episodes) (USEPA 2005b). In 2005, the National Health and Nutrition Examination Survey (NHANES) published results of a study of blood mercury levels in a representative sample of U.S. women of childbearing age (CDC 2005). The report data for the period 1999–2002 show that all women of childbearing age had blood mercury levels below 58 µg/L, a concentration associated with neurologic effects in the fetus. These data show that 5.7 percent of women of childbearing age had blood mercury levels between 5.8 and 58 µg/L; that is, levels within an order of magnitude of those associated with neurological effects. Typical exposures for women of childbearing age were generally within two orders of magnitude of exposures associated with these effects, according to data from NHANES (CDC 2005, USEPA 2005b).

With regard to other health effects of methylmercury, some recent epidemiological studies in men suggest that methylmercury is associated with a higher risk of acute myocardial infarction, coronary heart disease, and cardiovascular disease in some populations. Other recent studies have not observed this association. The studies that have observed an association suggest that the exposure to methylmercury might attenuate the beneficial effects of fish consumption (USEPA 2005b). There also is some recent evidence that exposures of methylmercury might result in genotoxic or immunotoxic effects. Other research with less corroboration suggests that reproductive, renal, and hematological impacts could be of concern. There are insufficient human data to evaluate whether these effects are consistent with methylmercury exposure levels in the U.S. population (USEPA 2005b).

Deposition of mercury to waterbodies can also have an adverse impact on ecosystems and wildlife. Plant and aquatic life, as well as fish, birds, and mammalian wildlife, can be affected by mercury exposure; however, overarching conclusions about ecosystem health and population effects are difficult to make. Mercury contamination is present in all environmental media with aquatic systems experiencing the greatest exposures due to bioaccumulation. Bioaccumulation refers to the net uptake of a contaminant from all possible pathways and includes the accumulation that might occur by direct exposure to contaminated media as well as uptake from food. Elimination of methylmercury from fish is so slow that long-term reductions of mercury concentrations in fish are often due to growth of the fish (“growth dilution”), whereas other mercury compounds are eliminated relatively quickly. Piscivorous avian and mammalian wildlife are exposed to mercury mainly through the consumption of contaminated fish and, as a result, accumulate mercury to levels greater than those in their prey (USEPA 1997c). The *Regulatory Impact Analysis of the Clean Air Mercury Rule* (USEPA 2005b) provides a full discussion of potential ecosystem effects updated since publication of the 1997 *Mercury Study Report to Congress* (USEPA 1997c). Thus, the approach outlined in the Clean Air Mercury Rule provides states an alternative methodology for designing their site-specific TMDL analyses.

2.1.2 How frequent are the environmental problems?

As of 2004, 42 states reported at least one waterbody as being impaired due to mercury, and over 8,500 specific waterbodies were listed as being impaired due to mercury, either solely or in combination with other pollutants. In 2001, EPA mapped concentrations of mercury in fish tissue from fish collected from waterbodies all over the country (i.e., not limited to the 595 waters identified by the states) and compared these to the 2001 national recommended water quality criterion of 0.3 mg methylmercury/kg fish tissue wet weight (see Figure 1). These data were not randomly or systematically collected, but rather reflect fish tissue information that states had collected as part of their fish consumption advisory programs. Approximately 40 percent of the watershed-averaged fish tissue concentrations exceeded 0.3 mg methylmercury/kg fish tissue wet weight (USEPA 2001d).

A statistical comparison of the data presented in Figure 1 (from the National Listing of Fish Advisories (NLFA) fish tissue database), versus data from the National Lake Fish Tissue Study (NLFTS), a national random sample of fish tissue in 500 lakes and reservoirs throughout the United States, showed the NLFA data to be biased high (USEPA 2005b). The bias was found to be the result of sampling bias in the NLFA toward fish of species and sizes that tended to bioaccumulate more mercury. When data from the NLFA and NLFTS were normalized to a set of standard species and lengths, the bias was removed. (See USEPA 2005b, Figure 4-11, page 5-16 which shows fish tissue data averaged by watershed (i.e., hydrologic unit codes, or HUCs.) As a result, the NLFA data suggest that fewer watersheds contain fish with methylmercury that exceed the criterion.

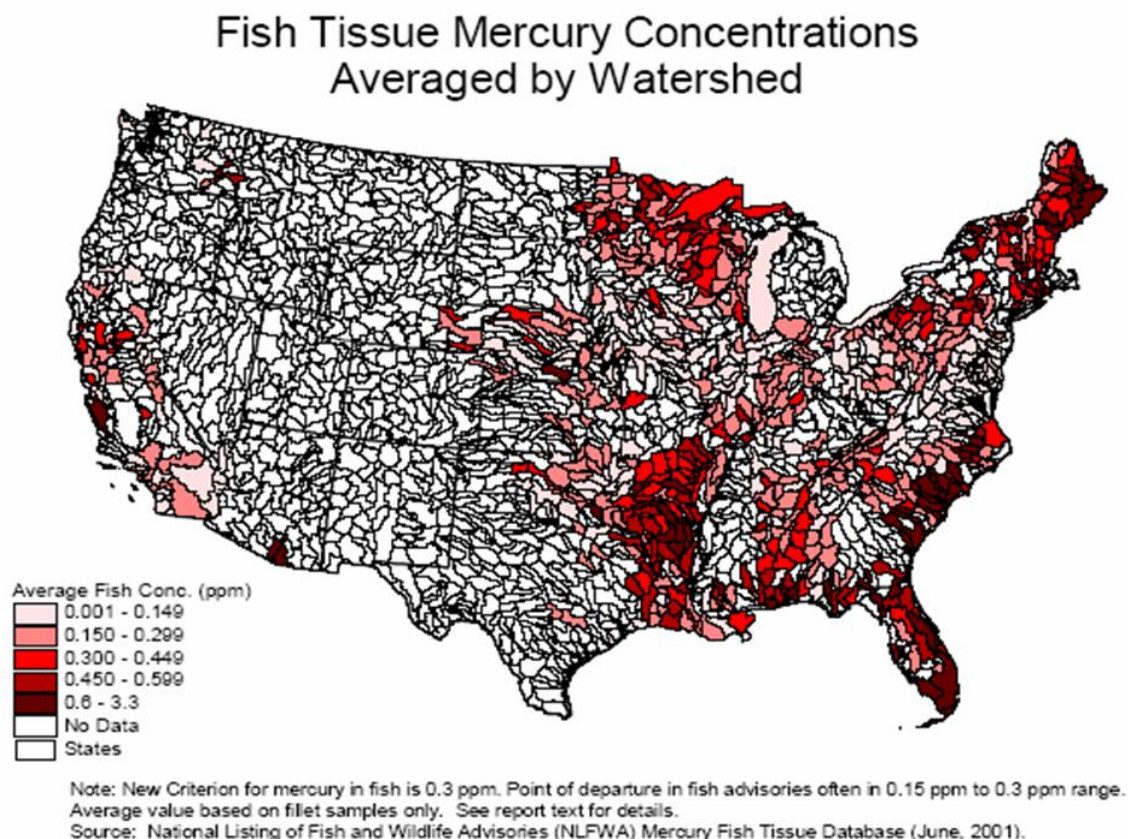


Figure 1. Fish Tissue Mercury Concentrations Averaged by Watershed (USEPA 2001d)

As of December 2004, 44 states, 1 territory, and 2 tribes have issued fish consumption advisories¹ for mercury covering 13.2 million lake acres and 765,000 river miles (see Figure 2). Twenty-one states have issued advisories for mercury in all freshwater lakes and rivers in their state, and 12 states have statewide advisories for mercury in their coastal waters (USEPA 2005a). EPA believes that the increase in advisories is primarily due to increased sampling of previously untested waters and not necessarily due to increased levels or frequency of contamination. Although states, territories, tribes, and local governments also continue to issue new fish advisories, most new fish advisories involve mercury and are a result of increased monitoring and assessment rather than increased domestic releases of mercury. In fact, U.S. mercury emissions have declined by more than 45 percent since 1990 (USEPA 2005a).

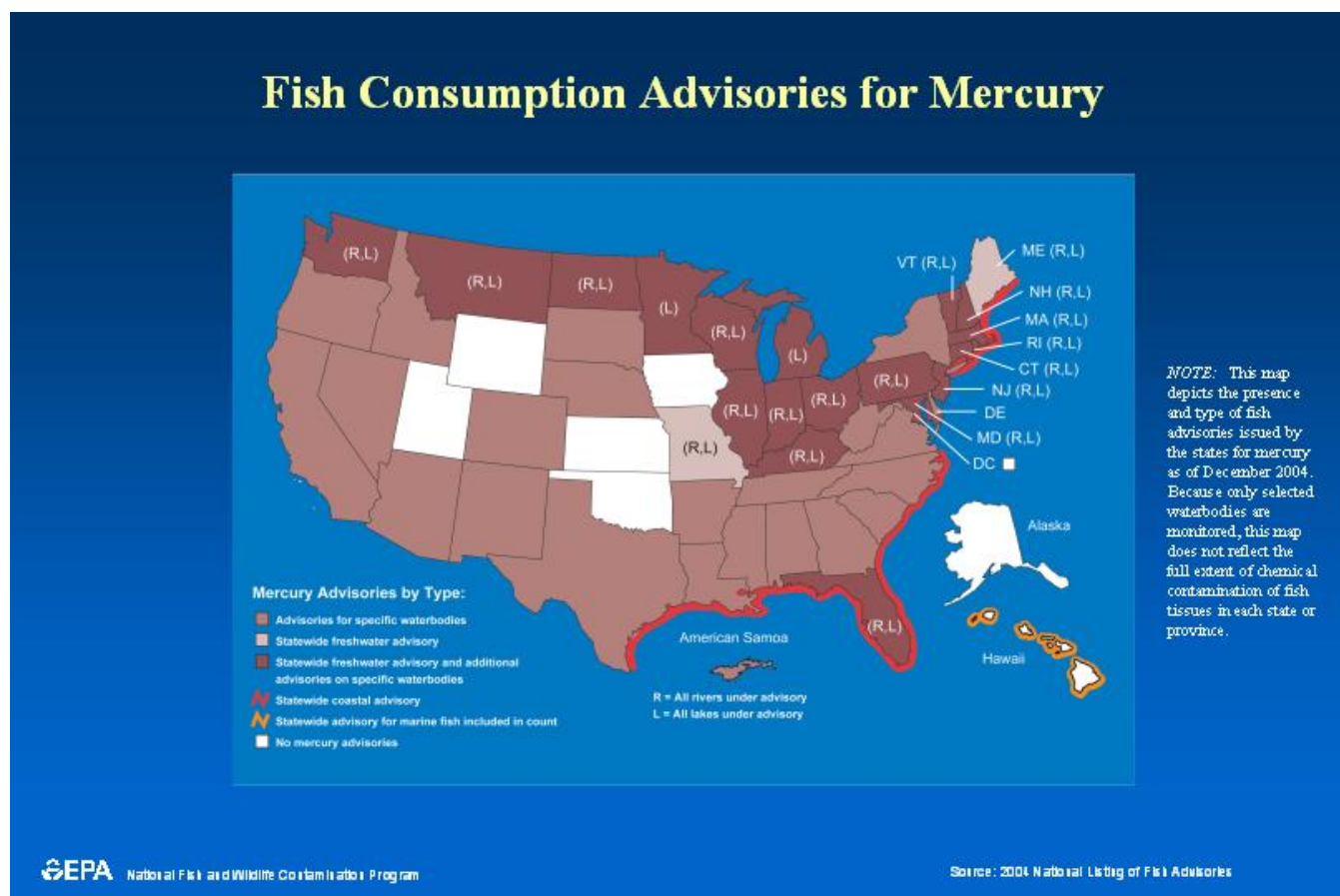


Figure 2. Total Number of State Mercury Fish Consumption Advisories 2004

2.2 What are the sources of mercury in fish?

Mercury is emitted from both natural and anthropogenic sources. Mercury's residence time in the atmosphere is much longer than that of most metals, because mercury can

¹ States issue their advisories and guidelines voluntarily and have flexibility in what criteria they use and how the data are collected. As a result, there are significant variations in the numbers of waters tested, the pollutants tested for, and the threshold for issuing advisories. Based on self-reporting, the national trend is for states to monitor different waters each year, generally without retesting waters monitored in previous years.

circulate for up to a year (USEPA 1997a). Such mobility enables elemental mercury to disperse and be transported over thousands of miles from likely sources of emission, across regions, and around the globe. As a result, the mercury detected in fish in U.S. surface waters is derived from both U.S. and international sources. EPA estimates that approximately 83 percent of the atmospheric mercury deposited on land and water in the country is from a combination of sources outside the United States and Canada, as well as natural and re-emitted sources. EPA's current air quality modeling does indicate a substantial variation across the country, with domestic sources influencing mercury deposition much more in the east and global sources being a more significant contributor to mercury deposition in the west, where relatively few domestic sources exist. This estimate was based on the advanced, state-of-the-science modeling assessment of the atmospheric fate, transport, and deposition of mercury conducted by EPA for the Clean Air Mercury Rule (CAMR) (USEPA 2005d).

Natural sources of mercury include geothermal emissions from volcanoes and crustal degassing in the deep ocean, as well as dissolution of mercury from other geologic sources (Rasmussen 1994). Anthropogenic sources of mercury in the United States include combustion (e.g., utility boilers, municipal waste combustors, commercial/industrial boilers, MWIs), manufacturing sources (e.g., chlor-alkali, cement, pulp and paper manufacturing), and mining (USEPA 1997a).

U.S. anthropogenic emissions of mercury to the air have declined more than 45 percent since passage of the 1990 CAA Amendments. These amendments provided new authority to EPA to reduce emissions of mercury and other toxic pollutants to the air. In 1990, more than two-thirds of U.S. human-caused mercury emissions came from just three source categories: coal-fired power plants, municipal waste combustion, and medical waste incineration (see Figure 4). Regulations were issued in the 1990s to control mercury emissions from waste combustion. In addition, actions to limit the use of mercury, most notably congressional action to limit the use of mercury in batteries and EPA regulatory limits on the use of mercury in paint, contributed to the reduction of mercury emissions from waste combustion during the 1990s by reducing the mercury content of waste. More recent regulations, including regulation of mercury emissions from chlorine production facilities that use mercury cells and regulation of industrial boilers, will further reduce emissions of mercury.²

The largest single source of anthropogenic mercury emissions in the country currently is coal-fired power plants. Mercury emissions from U.S. power plants are estimated to account for about one percent of total global mercury emissions. In March 2005, EPA signed the CAMR to permanently cap and reduce mercury emissions from coal-fired power plants (USEPA 2005e). This rule makes the United States the first country in the world to regulate mercury emissions from utilities. CAMR builds on EPA's Clean Air

² EPA has issued several regulations pursuant to the CAA to address these air emissions, including recent regulations covering coal-fired power plants. For example, see Title 40 of the *Code of Federal Regulations* (CFR) Part Cb (standards for municipal waste combustors); 40 CFR Part 60, subpart Ce (standards for MWIs); 40 CFR Part 63 subpart IIIII (standards for chlor-alkali plants); 40 CFR 63.1203 (a)(2) and (b)(2) (standards for existing and new hazardous waste-burning incinerators), 40 CFR 63.1204 (a)(2) and (b)(2) (standards for existing and new hazardous waste-burning cement kilns), and § 63.1205 (a)(2) and (b)(2) (standards for existing and new hazardous waste-burning lightweight aggregate kilns); 40 CFR Part 63, Subpart DDDDD (standards for industrial boilers); and 70 *Federal Register* 28,606 (May 18, 2005) (codified at 40 CFR Parts 60, 72 and 75) (standards for power plants). See also section 8.2 of this document.

Interstate Rule (CAIR) to significantly reduce emissions from coal-fired power plants. When fully implemented, these rules will reduce utility emissions of mercury nearly 70 percent.

Point sources of mercury discharging into waters are also regulated by NPDES permits. Chlor-alkali facilities are subject to effluent guidelines that impose treatment levels reflective of the Best Available Technology Economically Achievable (40 CFR Part 415). All NPDES permits must assure that permitted discharges achieve water quality standards (40 CFR 122.42(d)). Nonpoint source discharges are not regulated under federal regulations, but to the extent that these sources cause a water to exceed its water quality standards, states will develop TMDLs that identify the necessary reductions in these sources for achieving the water quality standards.

Anthropogenic emissions are only one part of the mercury cycle, however. Releases from human activities today add to the mercury reservoirs that already exist in land, water, and air, both naturally and as a result of previous human activity.

2.3 How does methylmercury get into fish and shellfish?

Mercury is widely distributed in the environment. Understanding the distribution and cycling of mercury among the abiotic (nonliving) and biotic (living) compartments of aquatic ecosystems is essential to understanding the factors governing methylmercury uptake in fish and shellfish tissue. The following is a synopsis of the current understanding of mercury cycling in the environment as described in the *Regulatory Impact Analysis of the Clean Air Mercury Rule* (USEPA 2005b).

Mercury occurs naturally in the environment as several different chemical species. The majority of mercury in the atmosphere (95–97 percent) is present in a neutral, elemental state (Hg^0) (Lin and Pehkonen 1999), while in water, sediments, and soils, the majority of mercury is found in the oxidized, divalent state (Hg(II)) (Morel et al. 1998). A small fraction of this pool of divalent mercury is transformed by microbes into methylmercury ($\text{CH}_3\text{Hg(II)}$) (Jackson 1998). Methylmercury is retained in fish tissue and is the only form of mercury that biomagnifies in aquatic food webs (Kidd et al. 1995). Transformations among mercury species within and between environmental media result in a complicated chemical cycle.

The relative contributions of local, regional, and long-range sources of mercury to fish mercury levels in a given waterbody are strongly affected by the speciation of natural and anthropogenic emissions sources. Elemental mercury is oxidized in the atmosphere to form the more soluble mercuric ion (Hg(II)) (Schroeder et al. 1989). Particulate and reactive gaseous phases of Hg(II) are the principle forms of mercury deposited onto terrestrial and aquatic systems because they are more efficiently scavenged from the atmosphere through wet and dry deposition than Hg^0 (Lindberg and Stratton 1998). Because Hg(II) species or reactive gaseous mercury (RGM) and particulate mercury (Hg(p)) in the atmosphere tend to be deposited more locally than Hg^0 , differences in the species of mercury emitted affect whether it is deposited locally or travels longer distances in the atmosphere (Landis et al. 2004).

A portion of the mercury deposited in terrestrial systems is re-emitted to the atmosphere. On soil surfaces, sunlight might reduce deposited Hg(II) to Hg⁰, which might then evade back to the atmosphere (Carpi and Lindberg 1997, Frescholtz and Gustin 2004, Scholtz et al. 2003). Significant amounts of mercury can be codeposited to soil surfaces in throughfall and litterfall of forested ecosystems (St. Louis et al. 2001), and exchange of gaseous Hg⁰ by vegetation has been observed (e.g., Gustin et al. 2004). Hg(II) has a strong affinity for organic compounds such that inorganic mercury in soils and wetlands is predominantly bound to dissolved organic matter (Mierle and Ingram 1991). Concentrations of methylmercury in soils are generally very low. In contrast, wetlands are areas of enhanced methylmercury production and account for a significant fraction of the external methylmercury inputs to surface waters that have watersheds with a large portion of wetland coverage (e.g., St. Louis et al. 2001).

In the water column and sediments, Hg(II) partitions strongly to silts and biotic solids, sorbs weakly to sands, and complexes strongly with dissolved and particulate organic material. Hg(II) and methylmercury sorbed to solids settle out of the water column and accumulate on the surface of the benthic sediment layer. Surficial sediments interact with the water column via resuspension and bioturbation. The amount of bioavailable methylmercury in water and sediments of aquatic systems is a function of the relative rates of mercury methylation and demethylation. In the water, methylmercury is degraded by two microbial processes and sunlight (Barkay et al. 2003, Sellers et al. 1996). Mass balances for a variety of lakes and coastal ecosystems show that *in situ* production of methylmercury is often one of the main sources of methylmercury in the water and sediments (Benoit et al. 1998, Biggam and Vandal 1994, Gbundgo-Tugbawa and Driscoll 1998, Gilmour et al. 1998, Mason et al. 1999). Changes in the bioavailability of inorganic mercury and the activity of methylating microbes as a function of sulfur, carbon, and ecosystem specific characteristics mean that ecosystem changes and anthropogenic “stresses” that do not result in a direct increase in mercury loading to the ecosystem, but alter the rate of methylmercury formation, might also affect mercury levels in organisms (e.g., Grieb et al. 1990).

Dissolved Hg(II) and methylmercury accumulate in aquatic vegetation, phytoplankton, and benthic invertebrates. Unlike Hg(II), methylmercury biomagnifies through each successive trophic level in both benthic and pelagic food chains such that mercury in predatory, freshwater fish is found almost exclusively as methylmercury (Bloom 1992, Watras et al. 1998). In fish, methylmercury bioaccumulation is a function of several uptake (diet, gills) and elimination pathways (excretion, growth dilution) (Gilmour et al. 1998, Greenfield et al. 2001). Factors such as pH, length of the aquatic food chain, temperature, and dissolved organic carbon (DOC) can affect bioaccumulation (Ullrich et al. 2001). As a result, the highest mercury concentrations for a given fish species correspond to smaller, long-lived fish that accumulate methylmercury over their life span with minimal growth dilution (e.g., Doyon et al. 1998). In general, higher mercury concentrations are expected in top predators, which are often large fish relative to other species in a waterbody.

2.4 Why is EPA publishing this document?

In a January 8, 2001, *Federal Register* notice (66 FR 1344), EPA announced the availability of its recommended water quality criterion for methylmercury. In that notice, EPA also stated that development of the associated implementation procedures and guidance documents would begin by the end of 2001. As such, EPA makes this guidance available to fulfill that commitment to enable states and authorized tribes to adopt the recommendations set forth in *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001c), or other water quality criteria for methylmercury on the basis of scientifically defensible methods, into their water quality standards.

This nontraditional approach in developing a water quality criterion as a fish and shellfish tissue value raises several implementation questions on both technical and programmatic fronts. Development of water quality standards, NPDES permits, and TMDLs present many challenges because these activities have usually been based on a water concentration (e.g., as a measure of mercury levels in effluent). This guidance addresses issues associated with states and authorized tribes adopting the new water quality criterion into their water quality standards programs and implementation of the revised water quality criterion in TMDLs and NPDES permits. Further, because atmospheric deposition serves as a large source of mercury for many waterbodies, implementation of this criterion involves coordination across various media and program areas.

EPA expects that, as a result of this revised methylmercury water quality criterion, together with a more sensitive method for detecting mercury in effluent and the water column, and increased monitoring of previously unmonitored waterbodies, the number of waterbodies that states report on CWA section 303(d) lists as impaired due to mercury contamination might increase. This guidance discusses approaches for managing the development of TMDLs for waterbodies impaired by mercury. This includes approaches for addressing waterbodies where much of the mercury comes from atmospheric sources and how TMDLs can take into account ongoing efforts to address sources of mercury, such as programs under the CAA and pollution prevention activities. This guidance also includes a recommended approach for directly incorporating the methylmercury tissue criterion in NPDES permits.

2.5 What is the effect of this document?

This guidance document presents suggested approaches, but not the only technically defensible approaches, to criteria adoption and implementation. The guidance does not substitute for applicable sections of the CWA or EPA's regulations; nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, states, authorized tribes, or the regulated community and may not apply to a particular situation. EPA, state, territorial, and tribal decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. EPA may change this guidance in the future.

DISCLAIMER

This guidance provides advice on how to implement the water quality criterion recommendation for methylmercury that the U.S. Environmental Protection Agency (EPA) published in January 2001. This guidance does not impose legally binding requirements on EPA, states, tribes, other regulatory authorities, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA, state, tribal, and other decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from those in the guidance where appropriate. EPA may update this guidance in the future as better information becomes available.

The Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency has approved this guidance for publication. Mention of trade names, products, or services does not convey and should not be interpreted as conveying official EPA approval, endorsement, or recommendation for use

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3 Water Quality Criteria and Standards Adoption

3.1 What must states and authorized tribes include as they adopt the methylmercury criterion?

3.1.1 What do the CWA and EPA's regulations require?

The CWA and EPA's regulations specify the requirements for adoption of water quality criteria. States and authorized tribes must adopt water quality criteria³ that protect designated uses (see CWA section 303(c)(2)(A)). Water quality criteria must be based on a sound scientific rationale and must contain sufficient parameters or components to protect the designated uses (see 40 CFR 131.11). States and authorized tribes must adopt criteria for all toxic pollutants for which EPA has established AWQC where the discharge or presence of these pollutants could reasonably interfere with the designated uses (see CWA 303(c)(2)(B)). EPA issued guidance on how states and authorized tribes may comply with section 303(c)(2)(B), which is now contained in the *Water Quality Standards Handbook: Second Edition* (USEPA 1994). This document provides three options for compliance:

Option 1—states and authorized tribes may adopt statewide or reservation-wide numeric chemical-specific criteria for all toxic pollutants⁴ for which EPA has issued CWA section 304(a) criteria guidance.

Option 2—states and authorized tribes may adopt numeric chemical-specific criteria for those stream segments where the state or tribe determines that the priority toxic pollutants for which EPA has issued CWA section 304(a) criteria guidance are present and can reasonably be expected to interfere with designated uses.

Option 3—states or authorized tribes may adopt a chemical-specific translator procedure⁵ that can be used to develop numeric criteria as needed.

To protect human health from contaminants in fish, EPA considers the 2001 methylmercury criterion a sound, scientifically based approach for meeting human health designated uses. Thus, EPA strongly encourages states and authorized tribes to adopt the 2001 methylmercury criterion or any sound, scientifically based approach into their water quality standards to fulfill the requirements of 40 CFR Part 131.

³ The term “water quality criteria” has two different definitions under the CWA. Under section 304(a), EPA publishes water quality criteria that consist of scientific information regarding concentrations of specific chemicals or levels of parameters in water that protect aquatic life and human health. The 2001 methylmercury criterion is an example of a section 304(a) criterion. States may use these criteria as the basis for developing water quality standards. Water quality criteria are also elements of state water quality standards adopted under CWA section 303(c).

⁴ CWA section 307(a) identifies a list of toxic pollutants that EPA has published at 40 CFR 401.16.

⁵ A translator procedure is simply the detailed process, published by a state or authorized tribe that explains how the state or authorized tribe will interpret its narrative criteria for toxics so that a quantifiable term can be used in assessment, permitting, and TMDL development. For example, a state or tribe could use EPA's water quality criteria as the means for interpreting its narrative criteria.

Water quality criteria generally consist of three components: magnitude, duration, and frequency (USEPA 1994). Water quality criteria for human health are typically expressed as an allowable magnitude. A criterion is calculated to protect against long-term chronic, human health effects. Thus, the duration of exposure assumed in deriving the criterion is a lifetime exposure even though the criterion is expressed as a magnitude of contaminant per day (USEPA 1991).

3.1.2 What is the recommended form of the methylmercury criterion?

EPA's current recommended 304(a) water quality criterion for methylmercury is expressed as a fish⁶ tissue concentration value (0.3 milligram methylmercury per kilogram of wet-weight fish tissue, or 0.3 mg/kg). With the publication of this 304(a) criterion, EPA withdrew the previous ambient human health water quality criterion for mercury as the recommended section 304(a) water quality criterion for states and authorized tribes to use as guidance in adopting water quality standards (USEPA 2001b). States and authorized tribes that decide to use the recommended criterion as the basis for new or revised methylmercury water quality standards have the option of adopting the criterion as a fish tissue residue concentration into their water quality standards, or adopting it as a traditional water column concentration. However, if states and authorized tribes choose to use both approaches, they should clearly describe how each will be used for specific applications in their standards and describe applicable implementation procedures. States and authorized tribes remain free not to use EPA's current recommendations, provided that their new or revised water quality criteria for methylmercury protect the designated uses and are based on a scientifically defensible methodology. In doing this, states and authorized tribes should consider bioaccumulation, local or statewide fish consumption, and exposure to mercury from other sources (relative source contribution (RSC)). EPA will evaluate criteria submitted by states and authorized tribes on a case-by-case basis.

3.1.2.1 Why is the fish tissue concentration criterion recommended?

EPA recommends that states and authorized tribes adopt new or revised methylmercury water quality criteria in the form of a fish tissue methylmercury concentration. The following reasons make this the preferred form:

- A fish tissue concentration value water quality criterion is closely tied to the “fishable” designated use goal applied to nearly all waterbodies in the United States.
- A fish tissue concentration value is expressed in the same form (fish tissue) that humans are exposed to methylmercury.
- A fish tissue concentration value is more consistent with how fish advisories are issued.

⁶ The criterion applies to both finfish and shellfish. For purposes of simplifying language in this document, the term “fish” means both finfish and shellfish.

- A fish tissue sample is currently easier to analyze for methylmercury and analysts are more experienced in analyzing methylmercury in fish tissue than in water samples.
- A fish tissue concentration avoids the need for BAFs⁷ that are necessary to translate between a tissue concentration and water concentration when deriving a water concentration-based criterion. This is significant because bioaccumulation of methylmercury by aquatic organisms is temporally and spatially variable such that site-specific BAFs, which can be costly to develop, are the preferred approach for translating tissue concentrations into water concentrations.

3.1.2.2 How is the fish tissue concentration criterion calculated?

The derivation of a methylmercury water quality criterion uses a human health toxicological risk assessment (e.g., a reference dose (RfD)), exposure data (e.g., the amount of pollutant ingested, inhaled, or absorbed per day), and data about the target population to be protected. The methylmercury fish tissue criterion for the protection of human health is calculated as:

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^4 FI} \quad (\text{Equation 1})$$

Where:

- TRC* = Fish tissue residue criterion (mg methylmercury/kg fish tissue) for freshwater and estuarine fish and shellfish.
- RfD* = Reference Dose (based on noncancer human health effects). For methylmercury it is 0.1 µg/kg body weight/day.
- RSC* = Relative source contribution (subtracted from the RfD to account for methylmercury in marine fish consumed⁸) estimated to be 0.027 µg/kg body weight/day.
- BW* = Human body weight (default value of 70 kg for adults).
- FI* = Fish intake at trophic level (TL) *i* (*i* = 2, 3, 4); total default intake of uncooked freshwater and estuarine fish is 17.5 g fish/day for the general U.S. adult population.⁹

This equation and all values used in the equation are described in *Water Quality Criterion for the Protection of Human Health, Methylmercury* (USEPA 2001c). This equation is

⁷ A BAF is a ratio (in milligrams/kilogram per milligrams/liter, or liters per kilogram) that relates the expected concentration of a chemical in commonly consumed aquatic organisms in a specified trophic level to the concentration of the chemical in water (USEPA 2001c).

⁸ The RSC accounts for exposures from all anticipated sources so that the entire RfD is not apportioned to freshwater/estuarine fish and shellfish consumption alone. In the assessment of human exposure in the methylmercury water quality criterion document, EPA found that human exposures to methylmercury were negligible except from freshwater/estuarine and marine fish. Therefore, in developing the criterion on the basis of consumption of freshwater/estuarine fish, EPA subtracted the exposure due to consumption of marine fish. See 66 *Federal Register* 1354-1355.

⁹ The value of 17.5 grams uncooked fish per day is the 90th percentile of freshwater and estuarine fish consumed by the public according to the 1994–96 *Continuing Survey of Food Intakes by Individuals* (USEPA 2000i). EPA uses this value as the default consumption rate in development of water quality criteria. The default trophic level values for the general population are 3.8 g fish/day for TL2, 8.0 g fish/day for TL3, and 5.7 g fish/day for TL4. The rationale behind the selection of this value is described in the Human Health Methodology (USEPA 2000e).

essentially the same equation used in the 2000 Human Health Methodology to calculate a water quality criterion for a pollutant that may cause noncancerous health effects. Here, it is rearranged to solve for a protective concentration in fish tissue rather than in water. Thus, it does not include a BAF or drinking water intake value (methylmercury exposure from drinking water is negligible (USEPA 2001b)). When all the numeric values are put into the generalized equation, the TRC of 0.3 mg methylmercury/kg fish is the concentration in fish tissue that should not be exceeded on the basis of a consumption of 17.5 g fish/day of freshwater or estuarine fish. EPA encourages states and authorized tribes to develop a water quality criterion for methylmercury using local or regional data rather than the default values if they believe that such a water quality criterion would be more appropriate for their target population.

The TRC value is not based on any default breakout of fish consumption by trophic level. The trophic levels assigned to the fish consumption value should reflect those that each target population consumes. For assessing impairment or attainment of the TRC, a state or authorized tribe may choose to assign the TRC value to only trophic level 4 or to the highest trophic level consumed. This will result in a conservative assumption, thereby protecting most, if not all, populations at an uncooked freshwater or estuarine fish consumption rate of 17.5 grams/day. If a state or authorized tribe wishes to calculate the TRC value on the basis of consumption at each trophic level for monitoring and compliance purposes, it would first determine consumption patterns at each trophic level for the target population(s). (For guidance on determining consumption patterns see section 4.)

EPA acknowledges that implementation of a TRC entails more technical steps than implementation of a water column criterion. Although water quality standards programs traditionally use water column values, states and authorized tribes may not find it necessary to translate this fish tissue based-criterion into a water column value for all implementation methodologies. Later chapters on TMDLs and NPDES permits in this guidance offer some methodologies that use the fish tissue value without translating from fish tissue to water column values.

3.1.3 Can states or authorized tribes adopt a water column concentration criterion?

EPA recognizes that a fish tissue residue water quality criterion is new to states and authorized tribes and might pose implementation challenges for traditional water quality standards programs. Water quality standards, water quality-based effluent limits (WQBELs), TMDLs, and other activities generally employ a water column value. If states and authorized tribes decide to adopt the tissue criterion expressed as fish tissue concentration, per EPA recommendation, without translating to a traditional water column concentration, they will make a choice on how to implement the tissue criterion. A state or authorized tribe could decide to directly develop TMDLs and to calculate WQBELs¹⁰ in NPDES permits without first measuring or calculating a BAF. This guidance provides some options for such approaches in sections 6 and 7.

¹⁰ A WQBEL is a requirement in an NPDES permit that is derived from, and complies with, all applicable water quality standards and is consistent with the assumptions and requirements of any approved wasteload allocation (see 40 CFR 122.44(d)(1)(vii)).

Alternatively, a state or authorized tribe may decide to adopt a tissue concentration-based standard with a site-specific procedure for translating the tissue concentration-based standard to a water column concentration. Because methylmercury bioaccumulation can vary substantially from one location to another, this option allows for the tissue concentration-based standard to be translated to water concentration-based standards using site-specific information on methylmercury bioaccumulation (i.e., site-specific BAFs) while ensuring that a water-expressed standard is ultimately developed for the waterbodies of interest. Administratively, this option might be more efficient when compared to adopting a water concentration-based standard for an entire state or tribal jurisdiction adopting or approving site-specific standards on an individual waterbody basis. Approaches for translating a tissue concentration-based criterion to a water concentration-based criterion are provided in the following section.

States or authorized tribes may also choose to adopt a standard that is expressed as a water column concentration. Conversion of the tissue concentration-based criterion to a water concentration-based criterion may be desirable for various reasons, such as achieving consistency with traditional water column-based AWQCs and/or regulatory simplicity. However, note that this approach requires assessment of methylmercury bioaccumulation on a state or tribal geographic scale. Thus, the uncertainty associated with differential bioaccumulation of methylmercury across sites within a state or authorized tribe will be embedded in the state or tribal water-based criterion. Reducing such uncertainty is one of the primary reasons EPA chose to express its national AWQC for methylmercury as a tissue concentration rather than as a water concentration.

To express the methylmercury concentration-based criterion as a water concentration, a state or authorized tribe would translate the methylmercury concentrations in fish tissue to methylmercury concentrations in the water column. To accomplish this, the state or authorized tribe will develop BAFs. In the Federal Register notice of the methylmercury criterion, EPA identified three possible different approaches for developing a BAF. These approaches are discussed in more detail in section 3.1.3.1. The basic equations used in developing a water column criterion are presented below, and additional discussion of calculating BAFs is presented in the following section.

States and authorized tribes would translate the tissue concentration-based human health AWQC to a water concentration-based methylmercury criterion using a BAF as

$$AWQC = TRC \times BAF \quad (\text{Equation 2})$$

Where:

- $AWQC$ = Water concentration-based ambient water quality criterion for methylmercury in mg/L
- TRC = Tissue concentration (residue)-based ambient water quality criterion for methylmercury in mg/kg
- BAF = Bioaccumulation factor for trophic levels 2, 3, and 4, weighted on the basis of fish consumption rates for each trophic level in L/kg

The BAF is the ratio of the concentration of the chemical in the appropriate tissue of the aquatic organism and the concentration of the chemical in ambient water at the site of

sampling. BAFs are trophic level-specific. EPA recommends that they be derived from site-specific, field-measured data as

$$BAF = \frac{C_t}{C_w} \quad (\text{Equation 3})$$

Where:

- BAF = Bioaccumulation factor, derived from site-specific field-collected samples of tissue and water in L/kg fish
- C_t = Concentration of methylmercury in fish tissue in mg/kg (wet tissue weight)
- C_w = Concentration of methylmercury in water in mg/L

When such data are unavailable, other approaches for deriving BAFs may be used, as outlined in the following section.

In the calculation to derive an AWQC as a water column concentration, the BAFs for the different trophic levels are combined to provide a weighted BAF value. For example, if a state wants to protect a population that eats on average 17.5 grams per day of uncooked fish from a waterbody, and 75 percent of the fish eaten are in trophic level 4 and 25 percent of the fish eaten are in trophic level 3, the weighted BAF would be the sum of 0.25 times the trophic level 3 BAF and 0.75 times the trophic level 4 BAF. Section 3.2.1.2 provides guidance on estimating fish intake rates.

3.1.3.1 How is the methylmercury fish tissue concentration translated to a methylmercury water concentration?

Should a state or authorized tribe decide to translate the methylmercury fish tissue criterion into a water column concentration, it would assess the extent to which methylmercury is expected to bioaccumulate in fish tissue for the site(s) of interest. Assessing and predicting methylmercury bioaccumulation in fish is complicated by a number of factors that influence bioaccumulation. Some of these factors include the age or size of the organism; food web structure; water quality parameters such as pH, DOC, sulfate, alkalinity, and dissolved oxygen; mercury loadings history; proximity to wetlands; watershed land use characteristics; and waterbody productivity, morphology, and hydrology. In combination, these factors influence the rates of mercury bioaccumulation in various—and sometimes competing—ways. For example, these factors might act to increase or decrease the delivery of mercury to a waterbody, alter the net production of methylmercury in a waterbody (i.e., via changes in methylation and/or demethylation rates), or influence the bioavailability of methylmercury to aquatic organisms. Although bioaccumulation models have been developed to address these and other factors for mercury, their broad application can be limited by the site- or species-specific nature of many of the factors and by limitations in the data parameters necessary to run the models.

The bioaccumulation of nonionic organic chemicals can also be affected by a number of these same physico-chemical factors (e.g., loading history, food web structure, dissolved oxygen, DOC). However, a substantial portion of the variability in bioaccumulation for

nonionic organic chemicals can be reduced by accounting for lipid content in tissues, and organic carbon content in water, and “normalizing” BAFs using these factors (Burkhard et al. 2003, USEPA 2003b). Normalizing to the age or size (length, weight) of fish has been shown to reduce variability in measures of bioaccumulation (Sorensen et al. 1990, Glass et al. 2001, Brumbaugh et al. 2001, Sonesten 2003, Wentz 2004). The United States Geological Survey (USGS) developed a procedure called the National Descriptive Model of Mercury and Fish Tissue (Wentz 2004). This model provides a translation factor to convert a mercury concentration taken from one species/size/sample method to an estimated concentration for any other user predefined species/size/sample method; EPA used this model to normalize national data sets of fish tissue for analysis supporting the CAMR (USEPA 2005a).

Taking into account the previous discussion, EPA recommends three different approaches for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water:

1. Use site-specific methylmercury BAFs derived from field studies.
2. Use a scientifically defensible bioaccumulation model.
3. When derivation of site-specific field-measured BAFs or use of a model are not feasible, use national methylmercury BAFs derived from empirical data.

Of these approaches, 1 and 2 are preferred over 3 for reasons discussed below. However, the hierarchy assigned to the approaches is not intended to be inflexible. Some situations might indicate that greater uncertainty is likely to occur when applying a BAF derived from a “more highly preferred” approach (e.g., a field-measure BAF) than with a “less preferred” approach, for example, when data from the more preferred method have less representativeness, quantity, or quality relative to the less preferred approach. In these situations, data from the less preferred, but less uncertain, approach would be used to derive BAFs.

3.1.3.1.1 Site-specific bioaccumulation factors derived from field studies

The use of site-specific BAFs based on data obtained from field-collected samples of tissue from aquatic organisms that people eat and water from the waterbody of concern—referred to as a “field-measured site-specific BAF”—is the most direct and most relevant measure of bioaccumulation. This approach is consistent with EPA’s bioaccumulation guidance contained in the 2000 Human Health Methodology (USEPA 2000e) and its Technical Support Document for developing national BAFs (USEPA 2003b). Although a BAF is actually a simplified form of a bioaccumulation model, the field-measured site-specific BAF approach is discussed separately here because of its widespread use and application. A field-measured site-specific BAF is derived from measurements of methylmercury concentrations in tissues of aquatic organisms and the ambient water that they inhabit. Because the data are collected from a natural aquatic ecosystem, a field-measured BAF reflects an organism’s exposure to a chemical through all relevant exposure routes (e.g., water, sediment, diet). The BAF can be measured for the aggregate of fish in a location or specific to each trophic level. A field-measured site-specific BAF also reflects biotic and abiotic factors at a location that influence the bioavailability and metabolism of a chemical that might occur in the aquatic organism or its food web.

However, states should exercise caution in developing a site-specific BAF for a migratory fish because its exposure to methylmercury reflects areas other than where the fish was caught. By incorporating these factors, field-measured site-specific BAFs account for the uptake and accumulation of the chemical.

For the purposes of developing a human health water quality criterion, states and tribes should calculate the BAF as the ratio of the concentration of methylmercury in the tissue of aquatic organisms that people eat to the concentration of methylmercury in water (Equation 3). To predict the corresponding methylmercury concentration in water for a site, the tissue-based methylmercury criterion would then be divided by the site-specific BAF. Using the site-specific BAF approach assumes that at steady state, the accumulation of methylmercury by the aquatic organism varies in proportion to the methylmercury concentration in the water column (specifically methylmercury) and that the site-specific BAF is independent of water column concentration.

As an example, the State of California is currently employing a site-specific BAF approach in its Central Valley Region. In this approach, California evaluated graphs of average concentrations of methylmercury in water and the corresponding concentrations in fish at multiple sites in a watershed. Researchers found statistically significant, positive relationships between concentrations of unfiltered methylmercury in water and in various trophic levels of the aquatic food chain (Slotton, 2004). California linearly regressed fish tissue methylmercury concentrations for specific trophic level 3 and 4 fish against aqueous methylmercury concentrations ($P < 0.001$, $R^2 = 0.98$, and $P < 0.01$, $R^2 = 0.9$, respectively), and determined methylmercury concentrations in unfiltered water that correspond to the fish tissue criteria (0.15 ng/l for TL3 fish and 0.14 ng/l for TL4 fish) that were used in the TMDL analyses. (Central Valley Water Board, 2005). California assumed that sites that fit in a statistically significant regression have similar processes controlling methylmercury accumulation. In other words, site-specific BAFs are nearly identical.

Strengths associated with using a site-specific BAF approach include simplicity, widespread applicability (i.e., site-specific BAFs can be derived for any waterbody, fish species, and the like), and that the net effects of biotic and abiotic factors that affect bioaccumulation are incorporated within the measurements used to derive the BAF. Specifically, it is not required that the exact relationship between methylmercury accumulation and the factors that can influence it be understood or quantified to derive a site-specific BAF. By measuring the methylmercury concentrations empirically, such factors have been incorporated such that site-specific BAFs provide an accounting of the uptake and accumulation of methylmercury for an organism in a specific location and point in time.

Limitations to the site-specific BAF approach relate primarily to its cost and empirical nature. For example, the level of effort and associated costs of developing site-specific BAFs increases as the spatial scale of the site of interest increases. Furthermore, the amount of data necessary to obtain a representative characterization of methylmercury in the water and fish might take considerable time to gather. (For a discussion on sampling considerations for developing a site-specific BAF see section 3.1.3.2.) The strictly empirical nature of this approach is also a barrier to extrapolating BAFs among species,

across space, and over time because the site-specific factors that might influence bioaccumulation are integrated within the tissue concentration measurement and thus, cannot be individually adjusted to extrapolate to other conditions.

3.1.3.1.2 Bioaccumulation models

Bioaccumulation models for mercury vary in the technical foundation on which they are based (empirically or mechanistically based), spatial scale of application (specific to waterbodies, watersheds or regions, and species of fish), and level of detail in which they represent critical bioaccumulation processes (simple, mid-level, or highly detailed representations). Thus, it is critical that states and tribes use a model that is appropriately developed, validated, and calibrated for the species and sites of concern.

Empirical bioaccumulation models that explicitly incorporate organism-, water chemistry-, waterbody/watershed-specific factors that might affect methylmercury bioaccumulation (e.g., fish species, age, length, pH, DOC, sulfate, alkalinity, sediment acid volatile sulfide concentration, proximity to wetlands, land use, morphology, hydrology, productivity) usually take the form of multivariate regression models. Many examples of such models are available in the literature (e.g., Sorensen et al. 1990, Kamman et al. 2004, Brumbaugh et al. 2001). The model developed by Brumbaugh et al. (2001) is based on a national pilot study of mercury in 20 watersheds throughout the United States. Specifically, Brumbaugh et al. (2001) developed a multiple regression relationship between five factors: length-normalized mercury concentration in fish, methylmercury concentration in water, percent wetland area in the watershed, pH, and acid volatile sulfide concentration in sediments ($r^2 = 0.45$; all fish species). When data were restricted to a single species (e.g., largemouth bass) and a single explanatory variable (e.g., methylmercury in water), a highly significant relationship was found ($p < 0.001$) with a similar degree of correlation ($r^2 = 0.50$). This demonstrates the importance of species specificity on the strength of such regression relationships and, in this case, methylmercury in water as an explanatory variable.

States and tribes should consider several important issues when using regression-based bioaccumulation models for translating from a tissue concentration to a water column concentration. First, a number of such regression models have been developed without explicitly incorporating methylmercury (or mercury) concentrations in the water column. Instead, the models relate fish tissue methylmercury concentrations to variables that serve as proxies for methylmercury exposure (e.g., atmospheric deposition rates, ratio of the watershed drainage to the wetland area, pH, lake trophic status) often due to the costs associated with obtaining accurate measurements of mercury in the water column. Obviously, such models cannot be directly solved for the parameter of interest (methylmercury in water). Second, correlation among independent or explanatory variables in these multiple regressions is common and expected (e.g., pH and methylmercury concentration in water). Such correlations among explanatory variables can cause bias and erroneous estimates of an explanatory variable (in this case, methylmercury concentration in water) when back-calculated from the regression equation (Neter et al. 1996). In such cases, use of the underlying data set to develop a separate regression model with methylmercury concentration in water as the dependent variable is more appropriate. Last, because these regression models are based on

empirical data, uncertainty is introduced when the results are extrapolated to aquatic ecosystems with different conditions. Only in a few cases have such models been tested using independent data sets (e.g., Kamman et al. 2004).

Mechanistic bioaccumulation models are mathematical representations of the natural processes that influence bioaccumulation. Three examples of mechanistic type bioaccumulation models are: the Dynamic Mercury Cycling Model (D-MCM) (EPRI 2002), BA (BASS) (Barber 2002), and the Quantitative Environmental Analysis Food Chain model (QEA FDCHN) (QEA 2000). The conceptual advantage of mechanistically based bioaccumulation models is that predictions of methylmercury bioaccumulation can be made under different conditions (e.g., different growth rates of fish, different water chemistry conditions, different mercury loading scenarios), because the models include mathematical representations of the various processes that affect bioaccumulation. This advantage comes at the cost of additional input data necessary to run the model. Notably, only a few models have been used to predict methylmercury bioaccumulation. Such models have not been widely used and have been applied only to mercury in a few aquatic ecosystems under specific environmental conditions. Of the examples listed above, only the D-MCM was developed specifically for mercury. The D-MCM has not yet been applied to lotic systems. The other models have been developed more generally, for nonionic organic chemicals that bioaccumulate and that require substantial modification and validation for application to mercury.

Most mechanistic bioaccumulation models use a chemical mass balance approach to calculate bioaccumulation into fish or other aquatic organisms. This approach requires considerable understanding of mercury loadings to and cycling within the environment. None of the example models presented can predict bioaccumulation without considerable site-specific information, at least some degree of calibration to the waterbody of interest, and in some cases, considerable modification of the model. The amount and quality of data necessary for proper model application may equal or exceed that necessary to develop site-specific methylmercury BAFs, although these models might also help in determining BAFs if the kinetic condition in the waterbody is not steady-state.

Regardless of the type of model used, states' and authorized tribes' methodologies should be consistent with the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (section 5.6: National Bioaccumulation Factors for Inorganic and Organometallic Chemicals; USEPA 2000e) and *Technical Support Document Volume 2: Derivation of National Bioaccumulation Factors* (USEPA 2003b). These documents provide detailed discussion of topics such as BAF derivation procedures, bioavailability, and the steps involved in Procedures 5 and 6 of the Human Health Methodology. States and tribes should document how they derive site-specific parameters used in the bioaccumulation models, and should describe the uncertainty associated with the BAFs derived using any of the models.

3.1.3.1.3 Draft national bioaccumulation factors

EPA acknowledges that using site-specific BAFs or model-derived BAFs might not be feasible in all situations. Without site-specific methylmercury bioaccumulation data or an appropriate bioaccumulation model, another approach is to use EPA's empirically derived draft national methylmercury BAFs. EPA used the BAF guidance in the 2000 Human

Health Methodology (USEPA 2000e, 2003b) and the BAF methods in Volume III, Appendix D of the *Mercury Study Report to Congress* (USEPA 1997b) to derive draft methylmercury BAFs as part of its initial efforts to derive a water column-based recommended section 304(a) ambient water quality criterion for methylmercury. These draft national BAFs were developed from field data collected from across the United States and reported in the published literature. These draft national BAFs and the uncertainties associated with them are discussed in Appendix A, section I of *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001c). The draft national BAFs (50th percentile values) are listed by trophic level in Table 1. The 5th and 95th percentile values are also provided to show the distribution of national BAF values.

Table 1. National draft BAFs for dissolved methylmercury

	BAF trophic level 2 (L/kg)	BAF trophic level 3 (L/kg)	BAF trophic level 4 (L/kg)
5 th Percentile	18,000	74,300	250,000
50 th Percentile (Geometric mean)	117,000	680,000	2,670,000
95 th Percentile	770,000	6,230,000	28,400,000

(USEPA 2001c)

(mg methylmercury/kg fish tissue per mg methylmercury/L water)

To develop the national BAFs for each trophic level, EPA calculated the geometric mean of the field-measured BAFs obtained from the published literature. EPA believes the geometric mean BAFs are the best available central tendency estimates of the magnitude of BAFs nationally, understanding that the environmental and biological conditions of the waters of the United States are highly variable. EPA generally does not recommend basing an AWQC on BAF values near the extremes of the distribution (e.g., 10th or 90th percentile) because such values might introduce an unacceptable level of uncertainty into the calculation of a water column-based AWQC.

When states and authorized tribes calculate a water column-based criterion using draft national BAFs that differ greatly from the BAFs for the waterbody of concern, the resulting water column-based criterion will be either over- or under-protective. As a result, evaluation of the results of the analysis of water samples might result in the false conclusion that a fish tissue concentration has been exceeded (when it actually has not) or a false conclusion that a fish tissue concentration has not been exceeded (when it actually has). The following examples illustrate the potential impact of calculating a water quality criterion using a BAF that is substantially different from the actual BAF.

Underprotective scenario

A state uses the draft national BAF of 2,670,000 L/kg for trophic level 4 fish, but the BAF based on site-specific data for the trophic level 4 fish in the waterbody is three times that, or 8,100,000 L/kg. In using the draft national BAF, a state would consider water column concentrations up to 0.11 nanogram per liter (ng/L) (0.3 mg/kg) 2,670,000 L/kg) to indicate attainment of the water quality column criterion. However, using the BAF based on site-specific data, a water column criterion of 0.11 ng/L would correspond to a fish tissue concentration of 0.9 mg/kg, which is three times the 0.3 mg/kg criterion recommended to protect

human health. Thus, load reduction or permits using the national BAF of 2,670,000 L/kg would be under-protective.

Overprotective scenario

A state uses the draft national BAF of 2,670,000 L/kg for trophic level 4 fish, but the BAF based on site-specific data for the trophic level 4 fish in the waterbody is one third of that, or 900,000 L/kg. As a result, a state would consider water column concentrations up to 0.11 ng/L (0.3 mg/kg / 2,670,000 L/kg) to indicate attainment of the water quality criterion. However, using the BAF based on site-specific data, attainment of the water quality criterion could be achieved at a higher water column concentration of 0.33 ng/L. Thus, load reductions or permits using the national BAF of 2,670,000 L/kg would be over-protective.

EPA cautions water quality managers that methylmercury bioaccumulation is generally viewed as a site-specific process and that BAFs can vary greatly across ecosystems. The uncertainty in the estimates of a draft national BAF comes from uncertainty arising from natural variability, such as size of individual fish, and from uncertainty due to measurement error, such as error in measurements of mercury in water or lack of knowledge of the true variance of a process (e.g., methylation). Users of the draft national BAFs are encouraged to review Appendix A of *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001c) that describes the uncertainties inherent in these values. The following is a synopsis of the discussion of uncertainty in that Appendix.

- Uncertainty due to sampling and chemical analysis: In many cases, water methylmercury concentrations reported in the available studies incorporated limited or no cross-seasonal variability, incorporated little or no spatial variability, and were often based on a single sampling event. Because fish integrate exposure of mercury over a lifetime, comparing fish concentrations to a single sample or mean annual concentrations introduces bias to the estimates. The geographic range represented by the waterbodies was also limited.
- Uncertainty due to estimation method: The approaches used to estimate the draft national BAFs have their own inherent uncertainties. The approaches assume that the underlying process and mechanisms of mercury bioaccumulation are the same for all species in a given trophic level and for all waterbodies. They are also based on a limited set of data.
- Uncertainty due to biological factors: With the exception of deriving BAFs on the basis of river or lake waterbody type, there were no distinctions in the BAFs as to the size or age of fish, waterbody trophic status, or underlying mercury uptake processes. In reality, methylmercury bioaccumulation for a given species can vary as a function of the ages (body size) of the organisms examined.
- Uncertainty due to universal application of BAFs: There is uncertainty introduced by failure of a single trophic level-specific BAF to represent significant real-world processes that vary from waterbody to waterbody. The simple linear BAF model relating methylmercury in fish to total mercury in water simplifies a number of nonlinear processes that lead to the formation of bioavailable methylmercury in the

water column and subsequent accumulation. Much of the variability in field data applicable to the estimation of mercury BAFs can be attributed to differences in biotic factors (e.g., food chain, organism age or size, primary production, methylation or demethylation rates), and abiotic factors (e.g., pH, organic matter, mercury loadings, nutrients, watershed type or size) between aquatic systems. Unfortunately, while the concentration of methylmercury in fish tissue is presumably a function of these varying concentrations, published BAFs are generally estimated from a small number of measured water values whose representativeness of long-term exposure is not completely understood. Furthermore, although it is known that biotic and abiotic factors control mercury exposure and bioaccumulation, the processes are not well understood, and the science is not yet available to accurately model bioaccumulation on a broad scale.

The peer reviewers of the draft national BAFs expressed concerns about the use of the draft national BAFs to predict bioaccumulation across all ecosystems and about using them to derive a national recommended section 304(a) water quality criterion for methylmercury that would suitably apply to waterbodies across the nation. EPA recognized the peer reviewers' concerns and acknowledges that these national BAF values might significantly over- or underestimate site-specific bioaccumulation. As a result, EPA decided not to use the draft national BAFs to develop a national water column-based AWQC for methylmercury. Furthermore, the draft national BAFs are EPA's least preferred means for assessing the BAF. However, EPA may revise its guidance should significant new information become available to support developing a final national BAF.

EPA believes that the draft national methylmercury BAFs in Table 1 sufficiently represent bioaccumulation such that they may be used to implement a fish tissue-based methylmercury water quality criterion in a state's or authorized tribe's water quality standards in the absence of any other site-specific bioaccumulation data. Thus, EPA is likely to approve water quality standards for mercury on the basis of these draft national BAFs in the absence of information indicating that the water quality criteria do not protect human health in the waters to which the standards apply. Risk managers should also understand that in using the draft national BAFs, one assumes that the biotic and abiotic processes affecting mercury fate and bioaccumulation are similar across different waterbodies, and therefore using the draft national BAFs does not address site-specific factors that might increase or decrease methylation and bioaccumulation. The decision to allow the use of the draft national BAFs is a risk management decision. It reflects judgment that human health is better protected if the water quality criteria reflect the new science associated with methylmercury, even if that means using a draft national BAF value, rather than not adopting a criterion because the state or authorized tribe lacks resources to conduct site-specific studies or to run an appropriate bioaccumulation model.

3.1.3.2 What are the sampling considerations for deriving site-specific field-measured BAFs?

For both fish tissue and water, states and authorized tribes should analyze for methylmercury when deriving site-specific BAFs. EPA has not yet published analytical methods to measure methylmercury in either water or fish in 40 CFR Part 136. However,

for fish tissue, states and authorized tribes can measure methylmercury concentrations using the same analytical method used to measure for total mercury at least for upper trophic level fish (i.e., levels 3 and 4). This is because 80 to 100 percent of the mercury found in the edible portions of freshwater fish greater than 3 years of age from these two trophic levels is in the form of methylmercury (USEPA 2000c). In fish greater than approximately 3 years of age, mercury has had sufficient time to bioaccumulate to roughly steady levels in the fish. Appendix E summarizes seven studies of the relative proportion of the mercury concentration in North American freshwater fish that is in the form of methylmercury. In six of the seven studies, methylmercury on average accounted for more than 90 percent of the mercury concentration in fish tissue.

States and tribes should consider a number of issues when sampling aquatic organism tissue and water to derive a site-specific BAF. The goal of deriving site-specific methylmercury BAFs is to reflect or approximate the long-term bioaccumulation of methylmercury in commonly consumed aquatic organisms of a specified trophic level. Hence, an important sample design consideration is how to obtain samples of tissue and water that represent long-term, average accumulation of methylmercury. Methylmercury is often slowly eliminated from fish tissue. Therefore, concentrations of methylmercury in fish tissue tend to fluctuate much less than the concentration of methylmercury in water. Thus, for calculating representative site-specific BAFs, states and tribes should consider how to integrate spatial and temporal variability in methylmercury concentrations in both water and tissue. States and tribes should address the variability in methylmercury concentrations in fish tissue with age or size of the organism either by restricting sample collection to organisms of similar age or size classes or through appropriate normalization techniques. EPA's fish sampling guidance recommends that fish should be of similar size so that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual (USEPA 2000c). One way of normalizing data is by use of the National Descriptive Model for Mercury in Fish Tissue (NDMMF) (Wente 2004). The NDMMF is a statistical model that normalizes Hg fish tissue concentration data to control for species, size, and sample type variability. An example use of the NDMMF is in the combination of mercury fish tissue data from two databases (USEPA 2005b).

States and tribes should assess the fish consumption patterns of the exposed human population when designing a site-specific sampling plan. Because the age and size of aquatic organisms is correlated with the magnitude of methylmercury accumulation, the types and sizes of aquatic organisms being consumed should be considered when determining what fish to sample for deriving BAFs. This information should also guide the decision on whether the site-specific BAF should be based on a single trophic level (e.g., trophic level 4) or on multiple trophic levels.

States and tribes should review site-specific data used to calculate a field-measured BAFs, and thoroughly assess the quality of the data and the overall uncertainty in the BAF values. Consider the following general factors when determining the acceptability of field-measured BAFs reported in the published scientific literature. Address the same general issues and questions also when designing a field study to generate site-specific field-measured BAFs.

- Calculate a field-measured BAF using aquatic organisms that are representative of those aquatic organisms that are commonly consumed at the site of interest (e.g., river, lake, ecoregion, state). Review information on the ecology, physiology, and biology of the target organisms when assessing whether an organism is a reasonable surrogate of a commonly consumed organism.
- Determine the trophic level of the study organism by taking into account its life stage, diet, and the food web structure at the study location. Information from the study site (or similar sites) is preferred when evaluating trophic status. If such information is lacking, states and authorized tribes can find general information for assessing trophic status of aquatic organisms in *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1: Fish Sampling and Analysis* (USEPA 2000c).
- Collect length, weight, and age data for any fish used in deriving a field-measured BAF because current information suggests that variability in methylmercury accumulation is dependent on fish age and size (USEPA 2001c). This information helps normalize the BAF to a standardized fish size within the range of fish sizes and species known to be consumed by the human population of interest.
- Verify that the study used to derive the field-measured BAF contains sufficient supporting information from which to determine that tissue and water samples were collected and analyzed using appropriate, sensitive, accurate, and precise analytical methods.
- Verify that the water concentrations used to derive a BAF reflect the average exposure of the aquatic organism of concern that resulted in the concentration measured in its tissue. Concentrations of methylmercury in a waterbody vary seasonally and diurnally (Cleckner et al. 1995) due to a variety of biological and physical factors.
- Attempt to design a field sampling program that addresses potential temporal and spatial variability and that allows estimation of average exposure conditions. The study should be designed to sample an area large enough to capture the more mobile organisms and also to sample across seasons or multiple years when methylmercury concentrations in waters are expected to have large fluctuations. Longer sampling durations are necessary for waters experiencing reductions in mercury loadings, changes in water chemistry that affect methylation, and changes in the composition of the food web.

Volume I of the *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c) provides additional guidance on selecting target species to sample, specific sampling design procedures, analytical measurement procedures, and quality assurance guidance. Chapter 10 of EPA's *Exposure Factors Handbook* provides additional guidance on collecting information about local species (USEPA 1997e). Additional guidance on evaluating existing site-specific bioaccumulation studies for use in deriving trophic level-specific BAFs and designing sampling plans for obtaining data for deriving site-specific BAFs is provided in *Technical Support Document—Volume 2: Developing National Bioaccumulation Factors* (USEPA 2003b). In addition, EPA

expects to publish specific guidance for deriving site-specific BAFs from field studies in the future. Until then, the EPA guidance cited above and a recent publication by Burkhard (2003) are good sources of information on the design of BAF field studies and on deriving field-measured site-specific BAFs.

3.2 What options are available to address for site-specific conditions and concerns?

3.2.1 How can the methylmercury water quality criterion be modified for site-specific conditions?

The 2000 Human Health Methodology (USEPA 2000e) describes how states and authorized tribes can adopt site-specific modifications of a 304(a) criterion to reflect local environmental conditions and human exposure patterns. “Local” may refer to any appropriate geographic area where common aquatic environmental or exposure patterns exist. Thus, local may signify a statewide or regional area, a river reach, or an entire river. Such site-specific criteria may be developed as long as the site-specific data, either toxicological or exposure-related, is justifiable. For example, when using a site-specific fish consumption rate, a state or authorized tribe should use a value that represents at least the central tendency of the population surveyed (either sport or subsistence, or both) to eat fish from the local area. When a state or authorized tribe develops a site-specific criterion on the basis of local fish consumption, site-specific BAFs, or a site-specific RSC, EPA will likely review the data supporting the site-specific criterion when EPA approves or disapproves state or tribal water quality standards under section 303(c).

States and authorized tribes may modify EPA’s recommended 304(a) criteria for methylmercury by using other scientifically defensible methods, or by using different assumptions for certain components of EPA’s criterion to derive a criterion that maintains and protects the designated uses. For example:

- Use an alternative RSC factor
- Use a daily uncooked freshwater and estuarine fish consumption rate that is more reflective of local or regional consumption patterns than the 17.5 grams/day default value. EPA encourages states and authorized tribes to consider using local or regional consumption rates instead of the default values if these would better reflect the target population.

If a state or authorized tribe intends to modify both the RSC and fish consumption rate, it may find it advantageous to collect the data at the same time.

3.2.1.1 How does one modify the RSC?

Section 5 of the methylmercury criterion document (USEPA 2001c) provides detailed discussions on how EPA assessed exposure to methylmercury and how EPA derived the RSC factor used in calculating the criterion. The methylmercury RSC is an exposure, subtracted from the reference dose to account for exposure to methylmercury from sources other than freshwater or estuarine fish. By accounting for other known exposures, the RSC seeks to ensure that methylmercury exposures do not exceed the RfD. To change the RSC used by EPA, states and authorized tribes should review section 5 of the

methylmercury criterion document and modify the media specific exposure estimates found in Table 5-30 using local data that reflect the exposure patterns of their populations. Of the six exposure media presented in Table 5-30, the exposure from ingestion of marine fish comprised greater than 99.9 percent of the total exposure to methylmercury, and thus ingestion of fish would be the focus of any modification to the RSC. To modify this factor, states and authorized tribes should review the amount of marine fish and shellfish estimated to be consumed (Table 5-1; USEPA 2001c) and the concentration of methylmercury in the commonly consumed marine species (Table 5-14; USEPA 2001c). States and authorized tribes should document the modifications with data supporting the modifications, and ideally should share the proposed modifications to the RSC with EPA prior to recalculating the criterion. See Appendix B for the tables included from the methylmercury criterion document.

3.2.1.2 How does one modify the daily fish intake rate?

EPA derived the recommended methylmercury water quality criterion on the basis of a default fish intake rate for the general population (consumers and nonconsumers) of 17.5 grams/day¹¹ (uncooked) (USEPA 2001c). States and authorized Tribes can choose to apportion an intake rate to the highest trophic level consumed for their population or use a different intake rate based on local or regional consumption patterns. The fish consumption value in the TRC equation can be changed if the target population eats a higher or lower amount of fish. For example, if the 90th percentile of a target population eats approximately 15 grams/day of freshwater and estuarine fish of various trophic levels, the fish intake value in the above equation would simply be 15 grams/day, rather than the national default value of 17.5 grams/day used in calculating the 0.3 mg/kg TRC.

EPA encourages states and authorized tribes to develop a water quality criterion for methylmercury using local or regional fish consumption data rather than the default values, if they believe that such a water quality criterion would be more appropriate for their target population. However, states and authorized tribes should consider whether the consumption rates reflect existing public concern about contamination of fish when collecting survey data, rather than local preference for fish consumption. In this instance, the state or authorized tribe should not use the survey data because it does not represent what the local population would eat if the fish was not already contaminated.

EPA suggests that states and authorized tribes follow a hierarchy when deriving fish intake estimates (USEPA 2000e). From highest preferred to lowest preferred, this hierarchy is as follows (1) use local data when available, (2) use data reflecting similar geography or population groups, (3) use data from national surveys, and (4) use EPA's default fish intake rates. Additional discussion of these four preferences is provided below.

¹¹ This value represents the 90th percentile of freshwater and estuarine finfish and shellfish consumption reported by the 1994–96 *Continuing Survey of Food Intakes by Individuals*. For more information, see *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000e).

3.2.1.2.1 Use local data

EPA's first preference is that states and authorized tribes modify the water quality criterion using fish intake rates derived from studies of consumption of local fish, such as results of surveys designed to obtain information on the consumption of freshwater or estuarine species caught from local watersheds within the state or tribal jurisdiction. EPA recognizes that states and authorized tribes may choose to develop a fish intake rate for highly exposed subpopulations (e.g., sport anglers, subsistence fishers), and if this is the case, the states and authorized tribes should collect the intake rates from these subpopulations.

States and authorized tribes might wish to conduct their own surveys of fish intake. *Guidance for Conducting Fish and Wildlife Consumption Surveys* (USEPA 1998a) provides EPA guidance on methods for conducting such studies. States and authorized tribes should take care to ensure that the local data are of sufficient quality and scope to support development of a criterion and are representative of the population of people who eat local fish. EPA's consumption survey guidance offers recommendations on how to develop appropriate quality assurance and control procedures to help assure the quality of the survey. Results of studies of broader geographic regions in which the state or authorized tribe is located can also be used, but might not be as applicable as study results for local watersheds. Because such studies would ultimately form the basis of a state or authorized tribe's methylmercury criterion, EPA would review any surveys of fish intake for consistency with the principles of EPA's guidance as part of the Agency's review of water quality standards under CWA section 303(c).

States and authorized tribes may use either high-end (such as 90th or 95th percentile) or central tendency (such as median or mean) consumption values for the population of interest (e.g., subsistence fishers, sport fishers, or the general population). EPA generally recommends that a central tendency value be the lowest value states or authorized tribes should use when deriving a criterion. When considering median values from fish consumption studies, states and authorized tribes should ensure that the distribution is based on survey respondents who reported consuming fish because surveys of both consumers and nonconsumers can often result in median values of zero. EPA believes the approach described above is a reasonable procedure and is also consistent with the recent Great Lakes Water Quality Initiative (known as the "GLI") (USEPA 1995a).

3.2.1.2.2 Use similar geography or population groups

If surveys conducted in the geographic area of the state or authorized tribe are not available, EPA's second preference is that states and authorized tribes consider results from existing surveys of fish intake in similar geographic areas and population groups (e.g., from a neighboring state or authorized tribe or a similar watershed type) and follow the method described above regarding target values to derive a fish intake rate. For instance, states or tribes with subsistence fisher populations might wish to use consumption rates from studies that focus specifically on these groups, or, at a minimum, use rates that represent high-end values from studies that measured consumption rates for a range of types of fishers (e.g., recreational or sport fishers, subsistence, minority populations). A state or tribe in a region of the country might consider using rates from studies that surveyed the same region; for example, a state or tribe that has a climate that

allows year-round fishing may underestimate consumption if rates are used from studies taken in regions where individuals fish for only one or two seasons per year. A state or tribe that has a high percentage of an age group (such as elderly individuals, who have been shown to have higher rates in certain surveys) may wish to use age-specific consumption rates, which are available from some surveys. EPA has published guidance for selecting a study from a similar geographic area or population group (USEPA 1998c). Again, EPA recommends that states and tribes use only uncooked weight intake values and freshwater or estuarine species data.

3.2.1.2.3 Use national surveys

If applicable consumption rates are not available from local, state, or regional surveys, EPA's third preference is that states and authorized tribes select intake rate assumptions for different population groups from national food consumption surveys. EPA has analyzed two such national surveys, the 1994–96 and 1998 Continuing Survey of Food Intakes by Individuals (CSFII). These surveys, conducted by the U.S. Department of Agriculture (USDA), include food consumption information from a probability sample of the population of all 50 states. Respondents to the survey provided 2 days of dietary recall data. A separate EPA report provides a detailed description of the combined 1994–96 and 1998 CSFII surveys, the statistical methodology, and the results and uncertainties of the EPA analyses (USEPA 2002f). The estimated fish consumption rates in the CSFII report are by fish habitat (i.e., freshwater or estuarine, marine, and all habitats) for the following population groups (1) all individuals, (2) individuals age 18 and over, (3) women ages 15–44, and (4) children age 14 and under. Three kinds of estimated fish consumption rates are provided (1) per capita rates (i.e., rates based on consumers and nonconsumers of fish from the survey period), (2) by consumers-only rates (i.e., rates based on respondents who reported consuming finfish or shellfish during the 2-day reporting period), and (3) per capita consumption by body weight (i.e., per capita rates reported as milligrams of fish per kilogram of body weight per day). For purposes of revising the fish consumption rate in the methylmercury criterion, EPA recommends using the rates for freshwater and estuarine fish and shellfish.

Table 2. Estimates of freshwater and estuarine combined finfish and shellfish consumption from the combined 1994–96 and 1998 CSFII surveys

	Mean	Median	90 th	95 th	99 th
All Ages	6.30	N/a	11.65	41.08	123.94
Age 18 and Over	7.50	0.00 ¹²	17.37	49.59	143.35
Women Ages 15–44	5.78	N/a	6.31	32.37	109.79
Children Ages 14 and Under	2.64	0.00	0.00	13.10	73.70

Note: (all values as g/day for uncooked fish)

The CSFII surveys have advantages and limitations for estimating per capita fish consumption. The primary advantage of the CSFII surveys is that USDA designed and conducted them to support unbiased estimation of food consumption across the

¹² The median value of 0 grams/day may reflect the portion of individuals in the population who never eat fish as well as the limited reporting period (2 days) during which intake was measured.

population in the United States and the District of Columbia. One limitation of the CSFII surveys is that individual food consumption data were collected for only 2 days—a brief period that does not necessarily depict “usual intake.” Usual dietary intake is defined as “the long-run average of daily intakes by an individual.” Upper percentile estimates might differ for short-term and long-term data because short-term food consumption data tend to be inherently more variable. It is important to note, however, that variability due to duration of the survey does not result in bias of estimates of overall mean consumption levels. Also, the multistage survey design does not support interval estimates for many of the subpopulations because of sparse representation in the sample. Subpopulations with sparse representation include Native Americans on reservations and certain ethnic groups. While these individuals were participants in the survey, they were not present in sufficient numbers to support fish consumption estimates. The survey does support interval estimates for the U.S. population and some large subpopulations (USEPA 2002f).

3.2.1.2.4 Use EPA default fish intake rates

EPA’s fourth preference is that states and authorized tribes use as fish intake assumptions the following default rates, on the basis of the 1994–96 CSFII data, which EPA believes are representative of freshwater and estuarine fish and shellfish intake for different population groups: 17.5 grams/day for the 90th percentile of the general adult population, an average of 17.5 grams/day for sport fishers, and an average of 142.4 grams/day for subsistence fishers. EPA has made these risk management decisions after evaluating numerous fish intake surveys. These values represent the uncooked weight intake of freshwater and estuarine finfish and shellfish. As with the other preferences, EPA requests that states and authorized tribes routinely consider whether a substantial population of sport fishers or subsistence fishers exists in the area when establishing water quality criteria rather than automatically using data for the general population.

The CSFII surveys also provide data on marine species, but EPA considered only freshwater and estuarine fish intake values for determining default fish consumption rates, because EPA considered exposure from marine species of fish in calculating an RSC for dietary intake.¹³ States and tribes should ensure that when evaluating overall exposure to a contaminant, marine fish intake is not double-counted with the other dietary intake estimate used. Coastal states and authorized tribes that believe accounting for total fish consumption (i.e., fresh or estuarine *and* marine species) is more appropriate for protecting the population of concern may do so, provided that the marine intake component is not double-counted with the RSC estimate (USEPA 2000e).

Because the combined 1994–96 CSFII survey is national in scope, EPA uses the results from it to estimate fish intake for deriving national criteria. The estimated mean of freshwater and estuarine uncooked fish intake for adults from the CSFII study is 7.5 grams/day, and the median is 0 grams/day. The estimated 90th percentile is 17.53 grams/day; the estimated 95th percentile is 49.59 grams/day; and the estimated 99th percentile is 142.41 grams/day. The median value of 0 grams/day reflects the portion of individuals in the population who never eat fish as well as the limited reporting period (2

¹³ See the discussion of the RSC in sections 3.1.2.2. and 3.2.1.1.

days) during which intake was measured. By applying as a default 17.5 grams/day for the general adult population, EPA selected an intake rate that is protective of a majority of the population (again, the 90th percentile of consumers and nonconsumers according to the 1994–96 CSFII survey data). In apportioning the default consumption rate to fish in different trophic levels, EPA uses the following breakout: TL2 = 3.8 grams/day; TL3 = 8.0 grams/day; and TL4 = 5.7 grams/day (USEPA 2000e)

Similarly, EPA believes that the 99th percentile of 142.4 grams/day is within the range of consumption estimates for subsistence fishers according to the studies reviewed, and represents an average rate for subsistence fishers. EPA knows that some local and regional studies indicate greater consumption among Native American, Pacific Asian American, and other subsistence consumers, and recommends the use of those studies in appropriate cases, as indicated by the first and second preferences. Again, states and authorized tribes have the flexibility to choose intake rates higher than average values for these population groups. If a state or authorized tribe has not identified a separate well-defined population of exposed consumers and believes that the national data from the 1994–96 CSFII are representative, they may choose these recommended rates.

3.2.2 How do water quality variances apply?

A state or authorized tribe may provide NPDES dischargers temporary relief from a water quality standard by granting a temporary variance to that standard. The variance would then, in effect, serve as a substitute standard for a point source, and the WQBEL contained in an NPDES permit would then be based on the variance. As a change to the otherwise applicable water quality standard (designated use and criteria), water quality variances must be supported by one of the six justifications¹⁴ under 40 CFR 131.10(g) where a state or authorized tribe believes the standard cannot be attained in the immediate future. Variances are tied to the discharger's ability to meet a WQBEL and, therefore, are considered after an evaluation of controls necessary to implement water quality standards. Typically, variances apply to specific pollutants and facilities, which means that a water quality standard variance for mercury would apply only to the new human health methylmercury criterion in a stated waterbody and specifically to the discharger requesting the variance, but the State may provide justification for more than one discharger or for an entire waterbody or segment to receive a variance (as discussed in section 3.2.2.3 of this document).

3.2.2.1 When is a variance appropriate?

Typically, variances provide a bridge when a state or authorized tribe needs additional data or analyses before making a determination of whether the designated use is

¹⁴ These six justifications are the ones allowed for use attainability analyses (1) Naturally occurring pollutant concentrations prevent the attainment of the use; (2) Natural, ephemeral, intermittent or low-flow conditions or water levels prevent the attainment of the use, unless these conditions may be compensated for by the discharge of sufficient volume of effluent discharges without violating state water conservation requirements to enable uses to be met; (3) Human caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place; (4) Dams, diversions or other types of hydrologic modifications preclude the attainment of the use, and it is not feasible to restore the waterbody to its original condition or to operate such modification in a way that would result in the attainment of the use; (5) Physical conditions related to the natural features of the waterbody, such as the lack of a proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, preclude attainment of aquatic life protection uses; or (6) Controls more stringent than those required by sections 301(b) and 306 of the CWA would result in substantial and widespread economic and social impact.

attainable and when the state or authorized tribe adopts an alternative use on the basis of a determination under 40 CFR 131.10(g). In the case of methylmercury, such a variance might also be appropriate where implementation tools are not available or feasible, particularly where a state or authorized tribe has not yet developed a TMDL. With EPA's belief that a number of waterbodies will be added to CWA section 303(d) listings for mercury following adoption of the new methylmercury criterion, variances could provide a short-term solution until development of the TMDL. Further, given limited resources, a state or authorized tribe might decide to focus on controlling significant mercury sources one at a time, beginning with a source other than effluent discharges (e.g., sediment, atmospheric deposition) and employing variances in the interim.

EPA believes that a large number of regulated point sources discharging mercury may apply for variances because they discharge into impaired waters where the largest source of mercury comes from atmospheric deposition, and expects there to be commonality in the grounds for these variances. The most likely scenarios to prompt a variance request are listed below. Many point source dischargers contribute a relatively small percentage of the mercury in an aquatic system. These scenarios are examples of demonstrations that could satisfy the requirements under 40 CFR 131.10(g). These demonstrations are more thoroughly explained below and in the *Water Quality Standards Handbook* (USEPA 1994).

Economic or social impacts—Demonstrate that, in the short term, the costs of constructing controls necessary to meet the methylmercury criterion (beyond those required by sections 301(b)(1)(A) and (B) and 306 of the CWA) would result in substantial and widespread economic and social impact.

Human caused conditions that cannot be remedied—Demonstrate that, in the short term, none of the present technologies for improving the quality of an effluent are capable of bringing methylmercury levels down to the criterion (i.e., no technological remedy or it is technologically infeasible). For example, atmospheric deposition originating overseas could be the source of elevated mercury levels in a local stream, yet the lack of an international agreement or treaty to cut mercury emissions worldwide prevents attainment of the mercury criterion, despite local efforts of reduction. In this instance, if air deposition modeling shows that the atmospheric deposition from outside the United States was a substantial cause of the impairment, the variance may be warranted.

Natural conditions preclude attainment—Demonstrate that local conditions of an aquatic system result in high methylmercury levels. This could result from two conditions. The first is that elevated mercury concentrations occur naturally. The second is that conditions of the area or the waterbody itself—whether it be the soil or sediment composition, microbial community, or the aquatic biota interactions—might favor a high level of methylation such that low levels of atmospherically-derived or ambient water column levels of mercury can amplify into high concentrations in fish tissues. In other words, bioaccumulation might occur at a higher rate under certain natural conditions and prevent the criterion from being attained.

3.2.2.2 What considerations should a state or tribe consider before granting a variance?¹⁵

In general, the temporary standard established by a variance is set as close as possible to the numerical criterion for the designated use and is always retained at the level needed to preserve the existing use. This is done to protect the existing uses, and to ensure progress toward ultimate attainment of the designated use. Regarding procedural considerations, the same requirements apply for a variance as for a new or revised standard (e.g., public review and comment, EPA approval or disapproval) because a variance is a change in the water quality standards. In addition, the following describes more specific issues that states and authorized tribes should take into account when considering granting a variance.

Performance-based approach—Unlike the typical numeric chemical criterion, EPA based the recommended methylmercury criterion on a fish tissue concentration, thus requiring a nontraditional expression of the criterion. States and authorized tribes have flexibility in how a variance is expressed in their water quality standard regulations. One approach is to incorporate the temporary fish tissue-based criterion established by the variance directly in the standards, and another is to use a performance-based approach. In the performance-based approach, the state or authorized tribe adopts into its water quality standards the procedure for calculating a new criterion on the basis of the variance. Such a procedure should fully lay out the calculations and default values necessary to derive an alternative fish tissue criterion using more site-specific numbers. To implement a performance-based approach, a state or tribe would maintain a publicly available, comprehensive list of all site-by-site decisions made using the procedures; however, such decisions would not, as a federal matter, have to be codified in state or tribal regulations. In addition, the public notice requirements for adopting variances could be satisfied through the process of issuing the NPDES permit that incorporates such temporary limits.

States and authorized tribes may find a performance-based approach advantageous in the case of variances to the methylmercury criterion because once the state or authorized tribe has submitted—and EPA has approved—these procedures, performance-based variances could be issued without subsequent individual approvals. The key advantage of this approach is that adoption of sufficiently detailed implementation procedures, with suitable safeguards, does not require EPA approval of every application of the variance.

Time frames—A variance is typically a time-limited change in the water quality standards. Although EPA regulations do not specify a time limit for variances, EPA regulations at 40 CFR 131.20 provide an opportunity to consider new information every three years for the purpose of reviewing water quality standards and, as appropriate, modifying and adopting standards. For this reason, states typically limit the time frame of a variance to 3 to 5 years, with renewals

¹⁵ Federal or state regulations also govern the granting of a variance. For example, regulations promulgated under 40 CFR Part 132, Appendix F, Procedure 2 specifies the conditions for granting variances in the Great Lakes, and prohibits the granting of variances to new dischargers or recommencing Great Lakes dischargers.

possible following a sufficient demonstration that the variance is still necessary. Variances that extend longer than 3 years are traditionally revisited in the context of a triennial review to justify their continuation. While the discharger makes this demonstration, the discharger also shows that it made reasonable progress to control mercury in the discharge during the period of the previous variance. In terms of methylmercury, there will likely be a time lag between implementing controls and seeing results (i.e., there may be unaddressed sources, continual leaching of mercury from sediments and so on). EPA modeled the response in fish tissue to a 50 percent reduction in mercury loadings to four lakes as part of the analysis supporting the CAMR and estimated that it would take between 1 to 56 years for the lakes to reach 90 percent of the estimated steady state fish tissue methylmercury concentration (USEPA 2005b). To address this issue, states and authorized tribes could develop an expedited variance adoption process, especially if legislative deliberations or administrative procedures are necessary to adopt variances into water quality standards. Namely, a specific provision within a variance for methylmercury could describe a less comprehensive demonstration for renewals by making use of information already available.

Another perspective regarding the life span of a variance is that a 3-year timeframe is mainly associated with a triennial review; there is no specific federal regulatory requirement for a variance to expire in 3 years. Regardless, as with any other revision to the water quality standards, the permit and permit conditions implementing the variance do not automatically change back to the previous permit conditions if the variance expires, unless that is a condition of a variance and permit. Although water quality standards can change with every triennial review, states and authorized tribes are not obliged to reopen and modify permits immediately to reflect those changes before issuance of a new permit.

Antidegradation—Permits with effluent limits based on a variance for methylmercury must conform to the state or authorized tribe's antidegradation policy.

Pollutant Minimization Plans—Pollution Minimization Plans (PMPs) may serve as a pollution prevention measure that states and authorized tribes could require of dischargers receiving a variance. By reducing mercury sources up front, as opposed to traditional reliance of treatment at the end-of-pipe, PMPs might partially counter the effects of a variance by improving the water quality.

3.2.2.3 What is involved in granting a variance on a larger scale?

Traditionally, variances are specific to a pollutant and a facility. However, for situations where a number of NPDES dischargers are located in the same area or watershed and the circumstances for granting a variance are the same, EPA encourages states and authorized tribes to consider administering a multiple-discharger variance for a group of dischargers collectively. Such a group variance can be based on various scales and may depend largely on the rationale for adopting a variance for methylmercury. Possible applications of a group variance may include any or some combination of the following:

Case study: Ohio statewide variance for mercury

Ohio adopted a statewide mercury variance applicable to any point source dischargers in the state that meet several criteria. Specifically, Ohio adopted, and EPA approved, a rule that finds complying with a mercury WQBEL on the basis of the Great Lakes Guidance criteria applied at the end-of-pipe (i.e., without a mixing zone) would result in widespread adverse social and economic impacts, relieving individual permittees of the burden of making this demonstration on an individual basis. However, to obtain individual coverage under the Ohio group variance, a permittee must do the following:

1. Demonstrate that it can (or will within 5 years) achieve an average annual effluent concentration no greater than 12 ng/L mercury
2. Document that it is currently unable to comply with what would be the WQBEL for mercury in the absence of a variance (based on the guidance wildlife criterion of 1.3 ng/L)
3. Provide a plan of study to document known and suspected sources of mercury
4. Describe control measures taken to date as well as planned future measures to reduce or eliminate mercury from the discharger's effluent
5. Explain why there are not readily available means of complying with the WQBEL for mercury without construction of end-of-pipe controls

As a condition for receiving the variance, the discharger must accept permit conditions needed to implement the plan of study regarding the identification and evaluation of mercury sources and potential control measures. Further, the rule requires public notice of the preliminary decision and the supporting materials (including the plan of study). Ohio also requires monitoring as necessary to assess the impacts of the variance on public health, safety, and welfare. If the discharger still cannot meet the standard following completion of actions addressed in the plan of study and in the PMP, Ohio may take action (through permit modification or permit reissuance) to delete the variance or impose additional pollutant minimization steps (after consideration of public comment). Ohio also retains the right to request that a discharger submit an individual variance application.

Similar costs, discharge processes —A type of industry or effluent treatment process may be targeted on the basis of the associated costs or available technology (i.e., publicly owned treatment works (POTWs), mining operations, and so on). A state or authorized tribe can choose to adopt a variance with tiered requirements, depending on the type of industry requesting coverage. For example, due to the differing cost implications, one industry would be required to meet a variance of 10 parts per billion (ppb) above the criterion, whereas another industry would be required to meet a variance of 20 ppb above the criterion.

Case study: Michigan's mercury multiple discharger variance

Until recently, analytical methods for detecting mercury in effluents at levels below the

water quality criterion (1.3 ng/L for the protection of wildlife) were lacking. Due to the inability to quantify effluent mercury concentrations at low levels, most monitoring resulted in no detects. Because of these monitoring results, facilities did not receive effluent limits for mercury or were considered in compliance with effluent limits. EPA's new method (1631) makes possible quantification of effluent mercury concentrations to levels less than the criterion (quantification level = 0.5 ng/L).

Application of EPA's new method is expected to result in additional permit limits for mercury and better detection of noncompliance with permit limits. Michigan expects that many facilities with mercury limits will be unable to comply with the limits. No known, demonstrated treatment technologies for removing mercury from effluents at low nanogram per liter levels exist. Consequently, efforts intended to achieve compliance with water quality-based effluent limits for mercury focus on the identification and reduction of sources of mercury to a wastewater treatment system. Often, it is difficult to identify such sources and to quantify the expected effects of source controls on effluent mercury concentrations. Given the uncertainty in the ability to comply and the timing of compliance, Michigan invoked a provision of this water quality standards (R 323.1103(9)) that authorizes multiple-discharger variances where the Michigan Department of Environmental Quality determines, "that a multiple discharger variance is necessary to address widespread UQS compliance issues, including the presence of ubiquitous pollutants or naturally high background levels of pollutants in a watershed" for mercury.

Where the available data indicate that a limit on mercury is needed, Michigan imposes a limit that reflects the level currently achievable (10 ng/L expressed as a rolling 12 month average). The permit requires reasonable progress towards achieving the limit on the basis of the water quality criterion over the course of the permit. The permit requires the permittee to develop and implement a pollutant minimization plan to identify and eliminate sources of mercury. Effluent data will be generated using Method 1631. The variance is not available to new dischargers.

Rather than having each of these individual facilities apply for and receive an individual variance, the multiple discharger variance allows Michigan to respond to this issue consistently and efficiently and to get in place permits that require pollutant minimization plans that produce reductions in mercury effluent concentrations.

Watershed basis—A variance on a watershed scale might be a sensible approach, particularly for those states that issue NPDES permits on a watershed basis. As with other pollutants, methylmercury concentrations can be monitored to gain site-specific information (perhaps for calculating site specific BAFs) in key watersheds for a given year. A state or authorized tribe using a watershed approach to permitting will be collecting data from a watershed in 1 year for the purpose of issuing NPDES permits in a subsequent year. The state or authorized tribe could use these data for the purpose of revising a previously issued water quality variance. Meanwhile, variances for other watersheds remain the same or are renewed with unchanged variance requirements until monitoring occurs, with variance time frames coinciding with the permitting cycle. This way, the WQBELs will reflect a more "real-time" variance limit.

Statewide—Analogous to a general NPDES permit, a statewide variance is made available by the state or authorized tribe. Individual dischargers may apply for coverage under the variance upon fulfillment of certain conditions. One example

of this approach is Ohio's statewide variance for mercury, which is described below.

It is important to note that, despite the coverage of a multiple source variance, an individual discharger must still demonstrate that the underlying criterion is not attainable with the technology-based controls identified by CWA sections 301(b) and 306 and with cost effective and reasonable best management practices (BMPs) for nonpoint sources (40 CFR 131.10(h)(2)).

3.2.3 How are use attainability analyses conducted?

3.2.3.1 What is a use attainability analysis?

A UAA is defined in 40 CFR 131.3(g) as a structured scientific assessment of the factors affecting the attainment of a use, which may include physical, chemical, biological, and economic factors that must be conducted whenever a state wishes to remove a designated use specified in section 101(a)(2) of the CWA, or to adopt subcategories of uses specified in section 101(a)(2) of the CWA, which require less stringent criteria (see 40 CFR 131.3 and 40 CFR 131.10(g)).

3.2.3.2 What is EPA's interpretation of CWA section 101(a)?

CWA section 101(a)(2) establishes as a national goal "water quality [that] provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water," wherever attainable. These goals are commonly referred to as the "fishable/swimmable" goals of the CWA. EPA interprets fishable/swimmable as providing for the protection of aquatic communities and human health related to consumption of fish and shellfish. In other words, EPA views fishable/swimmable to mean that fish and shellfish can thrive in a waterbody, and when caught, can also be safely eaten by humans. This interpretation also satisfies the CWA section 303(c)(2)(A) requirement that water quality standards protect public health. Including human consumption of fish and shellfish as the appropriate interpretation of the definition of section 101(a)(2) fishable/swimmable uses is not new. For example, in the National Toxics Rule, all waters designated for even minimal aquatic life protection (and therefore a potential fish and shellfish consumption exposure route) are protected for human health (57 FR 60859, December 22, 1992).

3.2.3.3 What is the rebuttable presumption of CWA section 101(a)?

EPA regulations effectively establish a rebuttable presumption that fishable/swimmable uses are attainable and therefore should apply to a waterbody unless it is affirmatively demonstrated that such uses are not attainable. The rebuttable presumption approach preserves states' and authorized tribes' paramount role in establishing water quality standards in weighing any available evidence regarding the attainable uses of a waterbody. If the water quality goals articulated by Congress cannot be met in a waterbody, the regulations simply require that such a determination be based upon a credible structured scientific assessment (e.g., a UAA). EPA believes that the rebuttable presumption policy reflected in the federal regulations is an essential foundation for effective implementation of the CWA as a whole. The use of a waterbody is the most

fundamental articulation of its role in the aquatic and human environments, and all the water quality protections established by the CWA follow from the water's designated use. If a use lower than a fishable/swimmable use is designated on the basis of inadequate information or superficial analysis, water quality-based protections that might have enabled the water to achieve the goals articulated by Congress in section 101(a) may not be put in place.

3.2.3.4 When is a UAA needed for a fishable use?

Under 40 CFR 131.10(j) of the Water Quality Standards Regulation, states and authorized tribes are required to conduct a UAA whenever the state or authorized tribe designates or has designated uses that do not include the fishable/swimmable use specified in CWA section 101(a)(2); or the state or authorized tribe wishes to remove a designated use that is specified in CWA section 101(a)(2), or adopt subcategories of the uses specified in that section that require less stringent criteria. An important caveat to the process of removing a designated use is that states and authorized tribes may not remove an "existing use" as defined by the Water Quality Standards Regulation. Existing uses are defined in 40 CFR 131.3(c) as any use that has been actually attained on or after November 28, 1975, when the CWA regulations regarding use designation were originally established. In practical terms, waters widely used for recreational fishing would not be good candidates for removing a "fishable" use, especially if the associated water quality supports, or has until recently supported, the fishable use, on the basis, in part, of the "existing use" provisions of EPA's regulations. In addition, designated uses are considered by EPA to be attainable, at a minimum, if the use can be achieved (1) through effluent limitations under CWA sections 301(b)(1)(A) and (B) and 306 and (2) through implementation of cost effective and reasonable BMPs on nonpoint sources. The federal regulation 40 CFR 131.10(g) further establishes the basis for finding that attaining the designated use is not feasible, as long as the designated use is not an existing use. EPA emphasizes that when adopting uses and appropriate criteria, states and authorized tribes must ensure that such standards provide for the attainment and maintenance of the downstream uses. States are not required to conduct UAAs when designating uses that include those specified in CWA section 101(a)(2), although they may conduct these or similar analyses when determining the appropriate subcategories of uses.

3.2.3.5 What conditions justify changing a designated use?

EPA's regulations at 40 CFR 131.10(g) lists the following six reasons for states or authorized tribes to use to support removal of a designated use or adoption of a subcategory of use that carries less stringent criteria:

- Naturally occurring pollutant concentrations prevent the attainment of the use
- Natural, ephemeral, intermittent, or low-flow conditions or water levels prevent the attainment of the use, unless these conditions may be compensated for by the discharge of sufficient volume of effluent discharges without violating state water conservation requirements to enable uses to be met
- Human caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place

- Dams, diversions, or other types of hydrologic modifications prevent the attainment of the use, and it is not feasible to restore the waterbody to its original condition or to operate such modification in a way that would result in attainment of the use
- Physical conditions related to the natural features of the waterbody, such as the lack of a proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, prevent attainment of aquatic protection uses
- Controls more stringent than those required by CWA sections 301(b) and 306 would result in substantial and widespread economic and social impact

In addition to citing one or more of these factors to support removal of a use, states and authorized tribes use the same six factors to serve the purpose of guiding analysis and decision making with respect to establishing an attainable use. Of the six factors above, it is most likely that human caused conditions that cannot be remedied, naturally occurring pollutant concentrations, or substantial and widespread social and economic impact resulting from additional controls would be the reason cited in a UAA addressing methylmercury impacted waters. In all cases, states and authorized tribes must obtain scientifically sound data and information to make a proper assessment. It is also recommended that they conduct pollutant source surveys to define the specific dominant source of mercury in the waterbody. Sources may include: point source loadings, air deposition, mining waste or runoff, legacy levels (e.g., mercury resulting from historical releases), and geologic “background levels.” This is similar to source assessments under the TDML program. Existing documents provide guidance on obtaining data and conducting analyses for the other components of a UAA. *The Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses* (USEPA 1983) covers the physical and chemical components of UAAs. Technical support for assessing economic and social impacts is offered through the *Interim Economic Guidance for Water Quality Standards Workbook* (USEPA 1995b).

4 Monitoring and Assessment

4.1 What are the analytical methods for detecting and measuring methylmercury concentrations in fish and water?

Over the last 2 decades, EPA and other organizations have developed several analytical methods for determining mercury and methylmercury concentrations in fish and water. In 2001, EPA conducted a literature review to assess the availability of different protocols and to determine which of these protocols would be most useful for implementing the new methylmercury criterion. After its review, EPA concluded that nearly all current research on low level concentrations of mercury and methylmercury is being performed using techniques that are based on procedures developed by Bloom and Crecelius (1983) and refined by Bloom and Fitzgerald (1988), Bloom (1989), Mason and Fitzgerald (1990), and Horvat et al. (1993).

EPA Methods 1630 and 1631, developed by EPA's Office of Water, reflect the techniques developed by these researchers for analyzing methylmercury and mercury in water, respectively. Appendix A to Method 1631 (64 FR 10596) details the researcher's techniques for determining total and dissolved mercury in tissue, sludge, and sediments. These methods, which are written in EPA Environmental Monitoring Management Council (EMMC) format, include all quality control elements that EPA's Office of Water considers necessary to adequately define data quality.

In Appendix C, Table C1 summarizes these and other methods that EPA knows have been used to analyze mercury and methylmercury in fish tissue, and Table C2 summarizes methods available for the analysis of mercury and methylmercury in water and other nontissue matrices. Each table identifies the forms and species targeted by each method, estimated or known sensitivity, the techniques employed in the method, and any known studies or literature references that use the techniques employed in the method.

Modifications to Method 1630 described in Table C1 (see Appendix C) and in Horvat et al. (1993) allow for measurement of methylmercury in tissue as low as 0.001 to 0.002 mg/kg, well below the water quality criterion for methylmercury in tissue (0.3 mg/kg). EPA recommends use of these techniques when direct measurements of methylmercury in tissue are desired.

Because researchers have found that nearly all mercury in fish tissue is in the form of methylmercury (USEPA 2000c), EPA also suggests that analysis of tissue for mercury, as a surrogate for methylmercury, is a useful means for implementing the methylmercury criterion. If mercury concentrations in tissue exceed the criterion, further investigation of the methylmercury component might be desired. Appendix A to Method 1631 allows for measurement of mercury in tissue at approximately 0.002 mg/kg, well below the tissue criterion.

Several options are also available for measuring mercury concentrations in water (Table D2). Because Method 1631 has already been promulgated for use in CWA applications,

EPA strongly recommends use of this method when measuring all species of mercury in water, especially when low-level measurements are expected. When measuring methylmercury in water, three options are Method 1631, developed by the Office of Water (USEPA 2002d); UW-Madison's SOP (Hurley et al. 1996), used by the Great Lakes National Program Office for its Lake Michigan Mass Balance Study; and a recently released USGS method (DeWild et al. 2002). All these procedures are based on the same techniques, and each can meet the most stringent (i.e., Great Lakes Guidance) mercury water quality criterion of 1.3 ng/L for wildlife protection in water. While any of these methods are acceptable, EPA recommends the use of Method 1631, which is documented in EMMC format and includes all quality control criteria considered necessary to define data quality.

In summary, on the basis of the available information, EPA believes that the most appropriate methods for measuring compliance with new or revised methylmercury criteria are Method 1631 (mercury in water by cold vapor atomic fluorescence spectrometry (CVAFS)), Method 1630 (methylmercury in water by CVAFS), Appendix A to Method 1631 (mercury in tissue by CVAFS), and modifications to Method 1630 for handling tissues (described in Table C1—see Appendix C). EPA recommends these procedures for the following reasons:

- Methods 1630 and 1631 were developed by EPA to support implementation of water quality criteria for mercury and methylmercury. Both are already in the appropriate EPA format and include all standardized quality control (QC) elements needed to demonstrate that results are reliable enough to support permitting and enforcement programs.
- Appendix A to Method 1631 was developed by EPA to support its National Study of Chemical Residues in Fish Tissue. Appendix A provides information on preparing a fish tissue sample for analysis using Method 1631. The method was validated by Brooks Rand (USEPA 1998b) and is currently being used by Battelle Marine Sciences to analyze more than a thousand tissue samples collected during EPA's National Fish Tissue Survey (USEPA 2000j). Successful use of these techniques also has been widely reported in the literature. This history, combined with the fact that Appendix A supplements the already well-characterized and approved Method 1631, makes this method a good candidate for use with the new fish tissue criterion.
- Method 1630 already has been used in several studies including EPA's Cook Inlet Contaminant Study (USEPA 2001g) and the Savannah River TMDL study (USEPA 2001e). The techniques described in the method and in the recommended method modifications also have been successfully applied in numerous studies described in the published literature. The procedures in Method 1630 also are nearly identical to those given in the USGS method and in the University of Wisconsin SOP, listed in Table D2 (Hurley et al. 1996). The University of Wisconsin SOP was used in EPA's Lake Michigan Mass Balance Study (USEPA 2001f).

4.1.1 What is Method 1631 for determination of mercury in water?

In May 1998, EPA proposed Method 1631 at 40 CFR Part 136 for use in determining mercury concentrations at AWQC levels in EPA's CWA programs, and subsequently published a Notice of Data Availability (64 FR 10596) that included additional data supporting application of the method to effluent matrices. On June 8, 1999, EPA responded to numerous public comments on the proposed method and promulgated EPA Method 1631, Revision B: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* at 40 CFR Part 136 for use in EPA's CWA monitoring programs. EPA promulgated the method on the basis of extensive validation of the procedures, including four single-laboratory studies and an interlaboratory validation involving 12 participating laboratories and 1 referee laboratory. The highest method detection limit (MDL) determined by all laboratories in reagent water was 0.18 ng/L, indicating that this method is capable of producing reliable measurements of mercury in aqueous matrices at AWQC levels.

EPA has revised Method 1631 after its promulgation to clarify method requirements, increase method flexibility, and address frequently asked questions. The current method (Method 1631, Revision E) includes recommendations for use of clean techniques contained in EPA's *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (USEPA 1996b). The benefits of using Method 1631 are that it is an approved method under EPA's CWA monitoring programs, has been fully validated, and numerous laboratories are routinely using this method. However, Method 1631 measures only mercury (total and dissolved) in aqueous samples and is not capable of measuring the methylmercury species.

Method 1631, Appendix A was developed for processing fish tissue samples to be analyzed for mercury using the previously validated and approved Method 1631 analytical procedures. The procedures are expected to be capable of measuring mercury in the range of 2 to 5,000 ng/g (0.002 to 5.0 mg/kg). The expected method detection limit for mercury in fish tissue is 0.002 mg/kg, well below the new water quality criterion for methylmercury. The procedures in the appendix are not published in the *Code of Federal Regulations*, but were implemented in EPA's National Study of Chemical Residues in Fish Tissue (USEPA 2000j). Although Appendix A of Method 1631 has not been fully validated (i.e., via an interlaboratory validation study), it was validated by EPA in a single laboratory study, and the techniques have been widely reported in the literature. Also, as discussed above, the analytical component of the method (Method 1631) has been fully validated and approved for measurement of total or dissolved mercury in aqueous matrices.

4.1.2 What analytical methods are available for determination of methylmercury?

EPA has not published an analytical method specifically for measuring methylmercury. As technical guidance to assist States and authorized tribes in their selection of an analytical method to use, Tables C1 and C2 in Appendix C include four methods that EPA has seen investigators successfully use for the determination of methylmercury. Other methods may be acceptable for use under the appropriate circumstances. As written, all four of the methods are specific to aqueous matrices and are based on almost

identical analytical procedures (i.e., distillation, ethylation, GC separation, and CVAFS detection). These methods have been or are being used in several national or regional studies, but none are yet published in 40 CFR Part 136. Modifications to adapt these procedures for fish tissue have been reported in the literature (e.g., Bloom 1989, and modified by Horvat et al. 1993) and used in EPA's Cook Inlet contaminant study (USEPA 2001g), the 4-year Lake Michigan Mass Balance study (USEPA 2001f), and an extensive study of the Everglades (USEPA 2000b).

Because the four methods are nearly identical, they are expected to produce very similar results with sensitivity as low as 0.002 mg/kg in tissue and 0.01 to 0.05 ng/L in water. These levels are well below the methylmercury criterion for fish and the most stringent (i.e., Great Lakes Guidance) mercury water quality criterion of 1.3 ng/L for wildlife protection in water.

4.2 What is the recommended guidance on field sampling plans for collecting fish for determining attainment of the water quality standard?

EPA has published guidance providing information on sampling strategies for a fish contaminant monitoring program in Volume 1: Fish Sampling and Analysis (2000c) of a document series, *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c). This guidance provides scientifically sound recommendations for obtaining a representative sample for issuing fish consumption advisories and, thus, offers EPA's current guidance for obtaining a representative sample for determining attainment. This guidance also includes recommendations for quality control and quality assurance considerations. In all cases, states should develop data quality objectives for determining the type, quantity, and quality of data to be collected (USEPA 2000h).

4.2.1 What fish species should be monitored?

EPA's fish sampling guidance (USEPA 2000c) provides recommendations for selecting finfish and shellfish species for monitoring to assess human consumption concerns. According to the guidance, the most important criterion is that the species are commonly eaten in the study area and have commercial, recreational, or subsistence fishing value. Fish creel data (from data gathered through surveying anglers) from state fisheries departments is one justifiable basis for estimating types and amounts of fish consumed from a given waterbody. States and authorized tribes should ensure that the creel data are of sufficient quality and are representative of the local population of people who eat fish.

The fish sampling guidance also identifies recommended target species for inland fresh waters and for Great Lakes waters. Seabass, walleye, king mackerel, tilefish, and largemouth bass have been identified as accumulating high levels of methylmercury. Reptiles such as turtle species and alligators are recommended as target species for mercury if they are part of the local diet. Larger reptiles can also bioaccumulate environmental contaminants in their tissues from exposure to contaminated sediments or via consumption of contaminated prey.

The fish sampling guidance recommends that the size range of the sampled fish ideally should include, from the species of fish that people in the area eat, the larger fish individuals harvested at each sampling site, because larger (older) fish within a population are generally the most contaminated with methylmercury (Phillips 1980, Voiland et al. 1991). This means that small fish such as minnows should be avoided as target species. In addition, the methylmercury concentrations in migratory species are likely to reflect exposures both inside and outside the study area, and the state or authorized tribe should take this into account when determining whether to sample these species. For migratory species, EPA's fish sampling guidance recommends, for migratory species, that neither spawning populations nor undersized juvenile stages be sampled in fish contaminant monitoring programs (USEPA 2000c). Sampling of target finfish species during their spawning period should be avoided as contaminant tissue concentrations may decrease during this time and because the spawning period is generally outside the legal harvest period.

If states and authorized tribes do not have local information about the types of fish present that people eat, the following two options provide an alternative for identifying which fish to sample:

Match assumed or known consumption pattern to sampled species—If the state has some knowledge of the fish species consumed by the general population, a monitoring sample could be composited to reflect this knowledge. For example, a state might decide that 75 percent of the fish consumed by the general population are trophic level 4 species, 20 percent are trophic level 3 species, and 5 percent are trophic level 2 species. A composite sample would reflect the determined trophic level breakout. Fish creel data (from data gathered through surveying anglers) from state fisheries departments is one justifiable basis for estimating types and amounts of fish consumed from a given waterbody. States and authorized tribes should ensure that the creel data are of sufficient quality and are representative of the local population of people who eat fish. The state or authorized tribe should decide which approach to use.

Trophic level 4 fish only—Predator species (e.g., trout, walleye, largemouth bass, smallmouth bass) are good indicators for mercury and other persistent pollutants that are biomagnified through several trophic levels of the food web. Increasing mercury concentrations correlate with an increase in fish age, with some variability, so that consumption of higher trophic level species correlates with greater risks to human health. (This correlation is less evident in estuarine and marine species.) Therefore, targeting trophic level 4 species should serve as a conservative approach (depending upon the species most frequently consumed by anglers) for addressing waterbodies with highly varying concentrations of methylmercury.

4.2.2 What sample types best represent exposure?

EPA recommends using composite samples of fish fillets from the types of fish people in the local area eat because methylmercury binds to proteins and is found primarily in fish muscle. Using skinless fillets is a more appropriate approach for addressing mercury

exposures for members of the general population and most recreational fishers because fish consumers generally eat the fillets. Because mercury is differentially concentrated in muscle tissue, leaving the skin on the fish fillet actually results in a lower mercury concentration per gram of skin-on fillet than per gram of skinless fillet (USEPA 2000c). Analysis of skinless fillets might also be more appropriate for some target species such as catfish and other scaleless finfish species. However, some fish consumers do eat fish with the skin on. In areas where the local population eats fish with the skin, the state or authorized tribe should consider including the skin in the sample.

Composite samples are homogeneous mixtures of samples from two or more individual organisms of the same species collected at a site and analyzed as a single sample. Because the costs of performing individual chemical analyses are usually higher than the costs of sample collection and preparation, composite samples are most cost effective for estimating average tissue concentrations in target species populations. Besides being cost effective, composite samples also ensure adequate sample mass to allow analyses for all recommended contaminants. In compositing samples, EPA recommends that composites be of the same species and of similar size so that the smallest individual in a composite is no less than 75 percent of the total length (size) of the largest individual (USEPA 2000c). Composite samples can also overcome the need to determine how nondetections will be factored into any arithmetical averaging because the composite represents a physical averaging of the samples. However, depending upon the objectives of a study, compositing might be a disadvantage because individual concentration values for individual organisms are lost. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1*, at sections 6.1.1.6 and 6.1.2.6 provides additional guidance for sampling recommendations.

4.2.3 What is the recommended study design for site selection?

To address spatial variability of methylmercury levels in fish, EPA recommends that states and tribes design a probabilistic sampling by randomly selecting sites or sampling locations. This approach allows statistically valid inferences to be drawn on an area as a whole.

Ideally, samples should be collected over a geographic area that represents the average exposure to those who eat fish from the waterbody. However, if there are smaller areas where people are known to concentrate fishing, these areas should be used as the sampling area. Fish sampled in locations with mercury point sources should be included in the average concentration if fishing occurs in these areas but not included if the area is not used for fishing.

4.2.4 How often should fish samples be collected?

EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1*, (USEPA 2000c) at section 6.1.1.5 provides recommendations for how frequently to sample fish tissue. If sufficient program resources exist, this guidance recommends biennial sampling of fish in waterbodies where recreational or subsistence harvesting is commonly practiced. If biennial screening is not possible, waterbodies

should be screened at least once every 5 years. Also, the state or authorized tribe should sample during the period when the target species is most frequently harvested or caught.

In fresh waters, the guidance recommends that the most desirable sampling period is from late summer to early fall (i.e., August to October). Water levels are typically lower during this time, thus simplifying collection procedures. Also, the fish lipid content is generally higher, thus allowing these data to also provide information for other contaminant levels. The guidance does not recommend the late summer to early fall sampling period if it does not coincide with the legal harvest season of the target species or if the target species spawns during this period. However, if the target species can be legally harvested during its spawning period, sampling to determine contaminant concentrations should be conducted during that time. In estuarine and coastal waters, the guidance recommends that the most appropriate sampling time is during the period when most fish are caught and consumed (usually summer for recreational and subsistence fishers).

EPA recommends that states and tribes sample consistently in a season to eliminate seasonal variability as a confounding factor when analyzing fish monitoring data. Additionally, focused seasonality studies could be used both to assess the impact of seasonal variability on fish concentrations and to normalize concentrations to a standard season(s). Several studies have measured seasonality in fish-fillet muscle mercury concentrations in estuaries and reservoirs (Kehrig et al. 1998, Park and Curtis 1997, Szefer et al. 2003). In these studies, concentrations were generally higher in cold seasons by as much as a factor of two to three times that in warm seasons. Slotten et. al. (1995) showed that the uptake of methylmercury in zooplankton and fish increased dramatically during the fall mixing of Davis Creek Reservoir, a California reservoir contaminated by mercury mining activities.

No studies of seasonality in fish mercury were found for rivers or natural lakes. On the basis of literature reported fish-mercury depuration rates, EPA does not expect seasonal fluctuations in fish mercury. Though reported mercury elimination half-lives cover a wide range of rates, from a few days to several years, the central tendency is 100–200 days (Giblin and Massaro 1973, Rodgers and Beamish 1982, Huckabee et al. 1979 [literature review], Burrows and Krenkel 1973, McKim et al. 1976). Such slow depuration rates are expected to dampen strongly any fluctuations in methylmercury concentrations in fish. Instead, season variations in fish tissue are likely linked to seasonal nutrition variability that impact fish body conditions but not mercury body burden.

EPA recommends that states and tribes routinely collect both weight and length data when assessing the potential influence of fish nutritional state on mercury concentration, and potentially for normalizing fish concentrations to a standard body condition. Greenfield et al. (2001), Cizdziel et al. (2002, 2003), and Hinnert (2004) reported a negative correlation between fish body condition (a ratio of weight to cubed length) and fish tissue mercury concentration. These studies support the concept of *starvation concentration*—whereby loss of muscle mass during periods of starvation occurs quicker than loss of mercury. Burrows and Krenkel (1973) found mercury elimination rate to be the same for fish that were starved relative to nonstarved fish. The converse phenomenon of *growth dilution*, where lower fish-mercury concentrations correlate with higher growth

rates, has been described by a number of researchers (Simoneau et al. 2005, Doyon et al. 1998, Park and Curtis 1997). The authors of the first two papers hypothesize that slower-growing fish allocate more energy towards maintenance and less to flesh production while faster growing fish add flesh at a lower energy cost and, thus, with proportionally less mercury intake. Park and Curtis (1997) proposed an alternative hypothesis that growth dilution occurs when high growth coincides with periods of low methylmercury concentration. Regardless of the exact mechanism, body condition offers a useful method to explain variability in fish mercury.

4.2.5 How many samples should be collected?

EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1*, (USEPA 2000c) at section 6.1.2.7.1 provides information to help determine the number of composite samples for comparing fish tissue information to a target value. This guidance does not recommend a single set of sample size requirements (e.g., number of replicate composite samples per site and the number of individuals per composite sample) for all fish contaminant monitoring studies, but rather presents a more general approach that is both scientifically defensible and cost effective. The guidance provides the means for determining an optimal sampling design that identifies the minimum number of composite samples and of individuals per composite necessary to detect a minimum difference between a target (in this case, the water quality criterion) and the mean concentration of composite samples at a site. Under optimal field and laboratory conditions, at least two composite samples are needed at each site to estimate the variance. To minimize the risk of a destroyed or contaminated composite sample preventing the site-specific statistical analysis, a minimum of three replicate composite samples should be collected at each site.

4.2.6 What form of mercury should be analyzed?

Because of the higher cost of methylmercury analysis (two to three times greater than for mercury analysis), states and authorized tribes should first measure mercury in fish tissue. This approach assumes that all mercury in fish tissue is methylmercury and is, thus, a conservative assessment. This approach does not pose a risk of a false positive decision (considering the tissue to exceed the criterion when it does not) where the measured mercury in fish tissue is less than the 0.3 mg/kg criterion (or a site-specific criterion adopted by a state) nor should it pose a realistic risk of a false positive when the measured mercury exceeds the criterion by 10 percent. Appendix E summarizes seven studies of the relative proportion of the mercury concentration in North American freshwater fish that is in the form of methylmercury. In six of the seven studies, methylmercury, on average, accounted for more than 90 percent of the mercury concentration in fish tissue. If the measured mercury level is within 10 percent of the methylmercury criterion, states might wish to repeat the sampling (if sufficient tissue is not left) and analyze for methylmercury.

4.3 How should waterbody impairment be assessed for listing decisions?

Section 303(d)(1) of the CWA requires states and authorized tribes to identify and establish priority ranking for waters that do not, or are not expected to, achieve or maintain water quality standards with existing or anticipated required controls. In accordance to this ranking, a TMDL for such waters must then be established. For purposes of determining impairment of a waterbody and whether to include it on section 303(d) lists, states and authorized tribes must consider all existing and readily available data and information (see 40 CFR 130.7).

States and authorized tribes determine attainment of water quality standards by comparing ambient concentrations to the numeric AWQC. EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1*, at section 6.1.2.7.1 recommends using the t-test to determine whether the mean concentration of mercury in composite fish tissue samples exceeds the screening value. This involves a statistical comparison of the mean of all fish tissue data to the criterion. If the t-test statistic of the mean exceeds the water quality standards, there is an exceedence. EPA recommends that this procedure also be used for determining impairment. States and authorized tribes might also want to consider the guidance in Appendices C and D of the *Consolidated Assessment and Listing Methodology, Toward a Compendium of Best Practices* (USEPA 2002b). Ultimately, the method that states choose depends on how they express their water quality standards.

4.3.1 How should nondetections be addressed?

When computing the mean of mercury in fish tissue, a state or authorized tribe might encounter a data set that includes analyzed values below the detection level. EPA does not expect this to occur frequently for two reasons. First, if the samples are physically composited (see section 4.2.2.), the composite itself provides the average, and there will be no need to mathematically compute an average. Second, the newer analytical Methods 1630 and 1631 are able to quantify mercury at 0.002 mg/kg, which should be lower than the observed mercury in fish tissue samples being analyzed.

However, if a state or authorized tribe is mathematically computing an average of a data set that does include several values below the detection level, the water quality standards and/or assessment methodology should discuss how it will evaluate these values. The convention recommended in EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1*, at section 9.1.2, is to use one-half of the method detection limit for nondetects in calculating mean values (USEPA 2000c). This guidance also recommends that measurements that fall between the method detection limit and the method quantitation limit be assigned a value of the detection limit plus one-half the difference between the detection limit and quantitation limit. EPA notes, however, that these conventions provide a biased estimate of the average concentration (Gilbert 1987), and where the computed average is close to the criterion, might suggest an impairment when one does not exist or, conversely, suggest no impairment when one does exist.

States or tribes can calculate the average of a data set that includes values below the detection level using other statistical methods (e.g., sample median and trimmed means)

(Gilbert 1987). EPA has published a review of several methods and analyzed the potential bias each can introduce into the calculation of the mean (USEPA 2001i).

One approach that a state or authorized tribe could take is to conduct a sensitivity analysis to ascertain the consequence of what value is used to quantify samples below the detection level. In a sensitivity analysis, the state or authorized tribe would compute the mean concentration using first the value of the detection level to quantify samples below the detection level and then again using a zero value for samples below the detection level. If both calculated means are either above or below the criterion, it is clear that the choice of how to quantify samples below the detection level does not affect the decision. However, if one calculated mean is below the criterion and the other is above, it is clear that the choice of how to quantify samples below the detection does affect the decision, and a more sophisticated approach such as the ones in *Robust Estimation of Mean and Variance Using Environmental Data Sets with Below Detection Limit Observations* (USEPA 2001i) should be used.

All methods have advantages and disadvantages. A state or authorized tribe should understand the consequences of which method it uses, especially if the choice makes a difference as to whether a waterbody is considered impaired or not. Furthermore, a state or authorized tribe should be clear about which approach it used.

4.3.2 How should data be averaged across trophic levels?

If target populations consume fish from different trophic levels, the state or authorized tribe should consider factoring the consumption by trophic level when computing the average methylmercury concentration in fish tissue. To take this approach, the state or authorized tribe would need some knowledge of the fish species consumed by the general population so that the state or authorized tribe performs the calculation using only data for fish species that people commonly eat. (For guidance on gathering this information see section 3.2.1.2) States and authorized tribes can choose to apportion all the fish consumption, either a value reflecting the local area or the 17.5 grams fish/day national value for freshwater and estuarine fish if a local value is not available, to the highest trophic level consumed for their population or modify it using local or regional consumption patterns. Fish creel data from state fisheries departments are one reasonable basis for estimating types and amounts of fish consumed from a given waterbody. The state or authorized tribe must decide which approach to use.

As an example of how to use consumption information to calculate a weighted average fish tissue concentration, see Table 3.

Table 3. Example data for calculating a weighted average fish tissue value

Species	Trophic Level	Number of Samples	Geometric Mean Methylmercury Concentration (mg/kg)
Cutthroat Trout	3	30	0.07
Kokanee	3	30	0.12
Yellow Perch	3	30	0.19
Smallmouth Bass	4	95	0.45
Pumpkinseed	3	30	0.13
Brown bullhead	3	13	0.39
Signal crayfish	2	45	0.07

These concentrations are used to compute a weighted average of tissue methylmercury concentrations for comparison to the 0.3 mg/kg criterion. All fish measured are classified as trophic level 3 except for signal crayfish, which are trophic level 2, and smallmouth bass, which are trophic level 4. The mean methylmercury concentration in trophic level 3 fish in this example is 0.15 mg/kg. This is calculated by weighting the geometric mean methylmercury concentration in each trophic level 3 species by the number of samples of each of the trophic level 3 species, and then averaging the weighted geometric means. Had the concentrations been averaged without weighting for the number of samples, the average concentration would be 0.18 mg/kg, and would have given more weight to the methylmercury concentrations in brown bullhead than the concentrations in the other species. (Note that this averaging approach does not consider that the trophic level 3 fish in this sample are of different sizes, or that some fish might be consumed more or less frequently than is represented by the number of samples.) Equation 4 shows how the total (all trophic levels) weighted concentration is calculated using the 0.15 mg/kg value as representative of trophic level 3 fish and the default consumption for each trophic level:

$$C_{\text{avg}} = \frac{3.8 * C_2 + 8.0 * C_3 + 5.7 * C_4}{(3.8 + 8.0 + 5.7)} = 0.23 \text{ mg/kg} \quad (\text{Equation 4})$$

Where:

- C_2 = average mercury concentration for trophic level 2
- C_3 = average mercury concentration for trophic level 3
- C_4 = average mercury concentration for trophic level 4

This calculation is based on apportioning the 17.5 grams/day national default consumption rate for freshwater and estuarine fish and shellfish by trophic level (5.7 grams/day of trophic level 4 fish, 8.0 grams/day of trophic level 3 fish, and 3.8 grams/day of trophic level 2 fish¹⁶). However, as noted throughout this document, the consumption pattern of the target population should be used if available

¹⁶ The values for each trophic level are the same as discussed in section 3.2.1.2., and are found in *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000e).

If fish tissue data from a trophic level are missing, one would drop the consumption factor for that trophic level from both the numerator and denominator. For example, if there were no data for trophic level 2 fish in the previous example, Equation 5 shows the revised calculation:

$$C_{\text{avg}} = \frac{8.0 * C_3 + 5.7 * C_4}{(8.0 + 5.7)} = 0.27 \text{ mg/kg} \quad (\text{Equation 5})$$

This revised calculation preserves the relative contribution of each trophic level to consumption patterns. However, this approach should not be used if there are no data for trophic level 4 fish, which is the type of fish that is most often eaten. Instead, the state or authorized tribe should collect information to determine the consumption rate for fish in trophic level 4. If the state or authorized tribe finds that no trophic level 4 fish are eaten, the approach can be applied to trophic level 4.

If the state or authorized tribe has developed a site-specific fish consumption rate for the criterion, then the state or authorized tribe should incorporate this site-specific rate in Equation 4 above. In this case, the state or authorized tribe would replace the values of 5.7 grams/day of trophic level 4 fish, 8.0 grams/day of trophic level 3 fish, and 3.8 grams/day of trophic level 2 fish with the values that the state or authorized tribe developed.

As an alternative approach, states or authorized tribes might wish to translate fish tissue sample data to a standard size, length, or species of fish that is more commonly consumed or are representative of the risk considerations of the state. Regression models have been developed for this purpose (Wente 2003, Rae 1997). An inherent assumption is that concentrations will differ between samples of two different species/lengths/sample cuts in a fixed equilibrium distribution relationship among all fish. If this relationship is known and at least one tissue sample concentration is measured from a species/length/sample cut that is accurately described by this relationship, fish consumption risk analyses could be performed for any species/lengths/sample cuts described by the relationship at this site.

Such regression models may include independent variables that account for species, aquatic environment (e.g., lotic vs. lentic, or other waterbody characteristics), sample cut (e.g., whole fish, skin-on fillet, skinless fillet), specific characteristics (e.g., age and retention time) of reservoirs, temporal trends, and fish length. The response variable is fish mercury concentration, which is typically assumed log-normally distributed. In a graphic sense, the model shows the covariance of each combination of nominal scale variables (e.g., whole fish, lentic waterbody) with fish length, with the slope representing the concentration/length ratio. Regression slopes can vary from lake to lake resulting in models that inappropriately retain some fish-size covariation (Soneston 2003).

EPA used the USGS National Descriptive Model of Mercury and Fish to analyze two data sets for use in analysis supporting the CAMR (USEPA 2005a). This model is a statistical model related to covariance and allows the prediction of methylmercury concentrations in different species, cuts, and lengths of fish for sampling events, even when those species, lengths, or cuts of fish were not sampled during those sampling

events. This model can also prove useful to states and authorized tribes in averaging fish tissue across trophic levels.

4.3.3 How should older data be assessed?

For purposes of determining waterbody impairment and inclusion on section 303(d) lists, states and authorized tribes must consider all existing and readily available water-quality related data and information (40 CFR 130.7). Ideally, a state or authorized tribe would have collected fish tissue information within the last 5 years, as recommended in section 4.2.4. However, such information might not be available, and states and authorized tribes will often consider mercury from samples collected and analyzed several years in the past. Although the state and authorized tribe should consider this information, they should also determine the reliability of this information and its accordance with applicable data collection or quality assurance/quality control (QA/QC) program requirements before using these data for listing assessments.

4.3.4 How should fish consumption advisories be used to determine impairment?

On October 24, 2000, EPA issued guidance on the use of fish advisories in CWA section 303(d) listing and 305(b) reporting decisions (USEPA 2000g). This guidance notes EPA's general interpretation that fish consumption advisories on the basis of waterbody specific information can demonstrate impairment of CWA section 101(a) "fishable" uses. Although the CWA does not explicitly direct the use of fish consumption advisories to determine attainment of water quality standards, states and authorized tribes must consider all existing and readily available data and information to identify impaired waterbodies on their section 303(d) lists. For purposes of determining waterbody impairment and inclusion on a section 303(d) list, EPA considers a fish consumption advisory and the supporting data as existing and readily available data and information.

A state or authorized tribe should include on its section 303(d) list, at a minimum, those waters where waterbody-specific data that was the basis of a fish or shellfish consumption advisory demonstrates nonattainment of water quality standards. EPA believes that a fish or shellfish advisory would demonstrate nonattainment when the advisory is based on tissue data, the data are from the specific waterbody in question, and the risk assessment parameters of the advisory or classification are cumulatively equal to or less protective than those in the water quality standards.¹⁷ For example, consider a state or authorized tribe that bases its water quality criterion on eating two fish meals a month. If the state or authorized tribe finds fish tissue information showing that the level of mercury is at a level where it decides to advise people to not eat more than one fish meal a month and all other risk assessment factors are the same, the advisory also may serve to demonstrate a water quality standard exceedence and that the waterbody should be placed on the 303(d) list. In contrast, if this same state or authorized tribe finds the level of mercury in fish in another waterbody is at a level where it would advise people to

¹⁷ The October 2000 EPA guidance assumes that the fish tissue monitoring that supports the advisory is sufficiently robust to provide a representative sample of mercury in fish tissue. EPA's fish tissue guidance (USEPA 2000c) provides recommendations on how public health officials can collect sufficient information about contaminants in fish.

eat no more than 8 meals a month, and all other risk assessment factors are the same, the advisory is not necessarily the same as an impairment, and the waterbody may not need to be listed.

When reporting water quality conditions under CWA sections 303(d) or 305(b) on the basis of a fish advisory for a migratory fish species, the state or authorized tribe should include the waters where the migratory fish are known to inhabit because these are the waters where the fish would become potentially exposed to mercury. In addition, a state or authorized tribe has the discretion to include any other water having a fish consumption advisory as impaired on its section 303(d) list if the state or authorized tribe believes it is appropriate.

5 Other Water Quality Standards Issues

5.1 How does this criterion relate to the criteria published as part of the Great Lakes Initiative?

As stated in the January 8, 2001, *Federal Register* notice, EPA encourages states and authorized tribes to adopt the fish tissue residue water quality criterion for methylmercury into their water quality standards to protect CWA section 101(a) designated uses related to human consumption of fish. With respect to waterbodies within the Great Lakes basin, a state or authorized tribe must also follow the requirements promulgated on March 23, 1995, at 40 CFR Part 132. Under these regulations, if a state or authorized tribe adopts the new methylmercury criterion, EPA, in its review of the new state or tribal criterion, must determine if it is as protective as the mercury criterion for human health protection published in Table 3 at 40 CFR 132.5(g)(1) or on the basis of improved science (40 CFR 132.4(h)).

The human health criterion for mercury established by the methodology contained at Part 132 and adopted by the Great Lakes states is 3.1 ng/L. This water column criterion for mercury is equivalent to a fish tissue residue value of 0.35 µg methylmercury/g fish tissue using the Great Lakes-specific BAFs for mercury of 27,900 L/kg for trophic level 3 and 140,000 L/kg for trophic level 4 as well as other Great Lakes-specific information (USEPA 1995c). Therefore, a state or authorized tribe would apply the site-specific modification procedures of Part 132 to show that the current, local BAF is lower than the one used to develop the criterion in Part 132 before it could adopt the new fish tissue-based criterion and methodology.

Also, EPA believes that if a state or authorized tribe adopts the new tissue-based criterion for protection of human health in the Great Lakes, this action may not always result in a change to TMDLs or NPDES permits. Part 132 also includes a 1.3 ng/L criterion for the protection of wildlife, and in some instances, this criterion may drive the calculation of TMDLs or NPDES permit limits.

5.2 What is the applicable flow for a water column-based criterion?

If a state or authorized tribe adopts new or revised methylmercury criteria based on a water column value rather than a fish tissue value, it should consider the dilution flow specified in a state's or tribe's water quality standards when applying the new mercury criterion. Where a state's or authorized tribe's water quality standards do not specify the appropriate flow for use with the mercury criterion, EPA recommends using a harmonic mean flow. EPA used this flow for application of the human health criteria for mercury in the Great Lakes (40 CFR Part 132). EPA also used this flow for application to the human health criteria in the California Toxics Rule (CTR) (40 CFR 131.38) and the National Toxics Rule (40 CFR 131.36). The Agency considers this flow to better reflect the exposure of fish to mercury. The technical means for calculating a harmonic mean is described in section 4.6.2.2.a of the *Technical Support Document for Water Quality-based Toxics Control* (USEPA 1991).

5.3 How are mixing zones used for mercury?

5.3.1 What is a mixing zone?

A mixing zone is the area beyond a point source outfall (e.g., a pipe) in which concentrations of a pollutant from a wastewater discharge mix with receiving waters. Under 40 CFR 131.13, states and authorized tribes may, at their discretion, include mixing zones in their water quality standards. Within a mixing zone, the water is allowed to exceed the concentration-based water quality criterion for a given pollutant. The theory of allowing mixing zones is based on the belief that by mixing with the receiving waters within the zone, the concentration of the pollutant being discharged will become sufficiently diluted to meet applicable water quality criteria beyond the borders of that zone. More information on mixing zones is available in the *Technical Support Document for Water Quality-based Toxics Control* (USEPA 1991) and the *Water Quality Standards Handbook* (USEPA 1994). States and authorized tribes often authorize mixing zone provisions and methodologies for calculating mixing zones in their water quality standards plans for later application to NPDES point sources discharge points.

5.3.2 How does a mixing zone apply for the fish tissue-based methylmercury criterion?

The question of mixing zones is not relevant when applying the fish tissue-based criterion, which refers to the level of mercury found in fish flesh. The criterion is fish tissue-based, not water column-based. The criterion reflects the exposure of the fish to mercury in both the water column and food over the life of the fish and, thus, reflects an integration of the exposure over time and over spatially varying water column concentrations. The total load of mercury in the waterbody, taking into account the methylation rate and bioaccumulation of mercury in fish, affects the level of methylmercury in the fish tissue.

However, some states and authorized tribes may choose to adopt a water column criterion based on the fish tissue criterion and, thus, have a criterion where a mixing zone may apply. In this situation, a state or authorized tribe should follow its existing procedures for mixing zones.

5.3.3 Does the guidance for the fish tissue-based criterion change the Great Lakes Initiative approach to mixing zones for bioaccumulative pollutants?

To reduce the adverse effects from bioaccumulative chemicals of concern (BCCs) in the Great Lakes, on November 13, 2000, EPA promulgated an amendment to the Final Water Quality Guidance for the Great Lakes System (40 CFR Part 132, Appendix F, Procedure 3). This regulation requires prohibition of mixing zones for bioaccumulative pollutants from existing discharges in the Great Lakes to the greatest extent technically and economically feasible. Specifically, existing discharges of BCCs are not eligible for a mixing zone after November 10, 2010 (although under certain circumstances, mixing zones may be authorized). For new BCC discharges, the rule essentially prohibits mixing zones of bioaccumulatives immediately upon commencing discharge. This means that NPDES permit limitations for mercury discharged to the Great Lakes system must not

exceed the water quality criterion. This also limits the flexibility that states and authorized tribes would otherwise have to adjust point source controls on the basis of nonpoint source contributions through the phased approach to TMDL development.

EPA reiterates that the new methylmercury criterion, and EPA's recommendations on its implementation, does not supersede the requirements applicable to the Great Lakes at 40 CFR Part 132. The criteria for the Great Lakes are water column-based and, thus, can be applied as an effluent requirement at the end of a pipe. EPA continues to view the prohibition of a mixing zone for mercury and other bioaccumulative pollutants for the Great Lakes as appropriately protective for water column-based water quality criteria applied to these waters.

If a state or authorized tribe adopts the new fish tissue-based criterion for a Great Lake or tributary to the Great Lake, the state or tribe would do this using the site-specific modification procedures of Part 132 (see section 5.1. of this document). The state or authorized tribe would have determined a site-specific BAF in this process and, thus, have the means for calculating a water column-based criterion. Under the Part 132 regulations, EPA in its review of the new state or tribal implementation procedures would determine if they are as protective as the Great Lakes procedures for human health protection (40 CFR 132.5(g)(3)). Specifically, EPA would determine if the implementation procedures are as protective as applying the Table 3 (in 40 CFR Part 132) criterion for protection of human health without a mixing zone, consistent with the prohibition on mixing zones for BCCs (40 CFR 132, Appendix F.3.c.). In addition, if the state's or authorized tribe's implementation procedures involve converting the fish tissue-based criterion into an equivalent water column-based number, the mixing zone prohibition requirements of 40 CFR Part 132 still apply.

5.4 How are fish consumption advisories and water quality standards harmonized?

5.4.1 What is the role of the Fish Advisory Program?

States and authorized tribes have the primary responsibility of estimating the human health risks from the consumption of chemically contaminated, noncommercially caught finfish and shellfish (e.g., where water quality standards are not attained). They do this by issuing consumption advisories for the general population, including recreational and subsistence fishers, and sensitive subpopulations (such as pregnant women, nursing mothers and their infants, and children). These advisories are nonregulatory and inform the public that high concentrations of chemical contaminants, such as mercury, have been found in local fish. The advisories recommend either limiting or avoiding consumption of certain fish from specific waterbodies or, in some cases, from specific waterbody types (e.g., all lakes). In the case of mercury, many states and authorized tribes have calculated a consumption limit to determine the maximum number of fish meals per unit of time that the target population can safely eat from a defined area.

5.4.2 How are consumption limits for consumption advisories determined?

EPA has published guidance for states and authorized tribes to use in deriving their recommended fish consumption limits, titled *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, Volume 1 and 2 (USEPA 2000c, 2000d). This guidance describes the two main equations necessary to derive meal consumption limits on the basis of the methylmercury RfD. Basically, a first equation is used to calculate the daily consumption limits of grams of edible fish (in grams per day (gd)); a second equation is used to convert daily consumption limits to meal consumption limits over a specified period of time. Variables used to calculate the advisory consumption limits include fish meal size and frequency, consumer body weight, contaminant concentration in the fish tissue, the time-averaging period selected, and the reference dose for methylmercury health endpoints.

As a default screening-level approach, EPA recommends basing fish consumption advisories on a consumption rate of 17.5 grams/day of fish (uncooked) eaten from the local water. This consumption rate equates to approximately two 8-ounce meals per month. Using this consumption rate, and assuming a 70 kg body weight (the same assumption used to derive the methylmercury criterion), the concentration of methylmercury in locally caught fish that would result in exposures that do not exceed the RfD (0.0001 mg/kg-day) is about 0.4 mg/kg and lower ($[0.0001 \text{ mg/kg-day} \times 70 \text{ kg bw}] / 0.0175 \text{ kg fish/day}$).

Advisory limits can differ from one state or tribe to another. This inconsistency is due to a host of reasons, some of which speak to the flexibility states and authorized tribes have to use different assumptions (i.e., chemical concentrations, exposure scenarios and assumptions) to determine the necessity for issuing an advisory. The nonregulatory nature of fish advisories allows such agencies to choose the risk level deemed appropriate to more accurately reflect local fishing habits or to safely protect certain subpopulations (e.g., subsistence fishers).

5.4.3 How does the criterion differ from the advisory level?

Although EPA derived its recommended screening value for a fish advisory limit for mercury and human health methylmercury criterion from virtually identical methodologies, it is important to clarify the distinctions between the two values. They are consistently derived, but because each value differs in purpose and scope, they diverge at the risk management level. Fish advisories are intended to inform the public about how much consumers should limit their intake of individual fish species from certain waterbodies. Alternatively, the Agency uses its methylmercury criterion, like other CWA section 304(a) criteria, as a basis for both nonregulatory and regulatory decisions. The criterion can serve as guidance to states and authorized tribes for use in establishing water quality standards, which, in turn, serve as a benchmark for attainment, compliance, and enforcement purposes.

The main risk management difference between EPA's recommended methylmercury water quality criterion and fish consumption limit for mercury is that the criterion

includes an RSC¹⁸ and EPA's recommended tissue value for a fish advisory does not. In deriving the criterion, EPA assumed an RSC value of 2.7×10^{-5} mg/kg-day to account for exposure from marine fish and shellfish. The guidance for setting fish consumption limits also discusses using an RSC to account for exposures other than noncommercially caught fish, but the guidance can be applied without using an RSC. The RSC guidance in the 2000 Human Health Methodology (USEPA 2000e) provides more detail and specific quantitative procedures to account for other exposure pathways. EPA's advisory guidance recommends that states and authorized tribes consider using an RSC to account for exposure from other sources of pollutants (such as mercury) when deriving a fish consumption limit and setting a fish advisory for mercury.

5.4.4 What if there is a difference between the attainment of a criterion and issuance of a fish consumption advisory?

In many states and authorized tribes, numeric water quality criteria and fish and shellfish consumption limits differ due to inherent differences in the technical and risk assumptions used to their development. As discussed in section 4.2, EPA considers a fish consumption advisory to demonstrate nonattainment of water quality standards when the advisory is based on tissue data, the data are from the specific waterbody in question, and the risk assessment parameters of the advisory or classification are cumulatively equal to or less protective than those in the water quality standards. Two situations where the presence of an advisory may not imply an exceedence of the water quality standard (USEPA 2000g) are as follows:

Statewide or regional advisory—States have issued statewide or regional warnings regarding fish tissue contaminated with mercury, on the basis of data from a subset of waterbodies as a precautionary measure. In these cases, fish consumption advisories may not demonstrate that a CWA section 101(a) “fishable” use is not being attained in an individual waterbody and may not be appropriate for determining attainment based on exceedence of water quality criteria.

Local advisory—States have issued local advisories using a higher fish consumption value than they use in establishing water quality criteria for protection of human health. Again, in this case the fish consumption advisories may not demonstrate that a section 101(a) “fishable” use is not being attained in an individual waterbody and may not as appropriate as water quality criteria as a basis for determining attainment.

For example, consider a state or authorized tribe that adopts EPA's methylmercury criterion of 0.3 mg/kg, which is based on eating approximately two fish meals a month. If the state or authorized tribe finds that a waterbody has fish with a mercury level of 0.2 mg/kg, this water would not be exceeding the water quality criterion. Yet, this mercury concentration is sufficient for the state or authorized tribe to issue a fish consumption advisory recommending that people eat no more than eight meals a month. In this case,

¹⁸ See discussion on the RSC in section 3.1.2.2.

because the fish consumption advisory uses a higher fish consumption value than was used to develop the water quality criterion (and the fish tissue concentration does not exceed the criterion), consistent with EPA's 2000 guidance, the waterbody is not necessarily impaired (USEPA 2000g).

In the case where a local advisory is based on a higher fish consumption value, the state or authorized tribe should consider whether it should adopt a site-specific criterion for the waterbody. A local advisory generally reflects actual contaminant monitoring data, local fish consumption patterns, and may identify more representative fish species. The information gathered in developing the advisory may provide valid grounds for revising the level of a numeric water quality criterion to match that of the advisory.

5.4.5 *Should existing advisories be revised to reflect the new criterion?*

Although EPA's screening value for a fish consumption limit and 304(a) criterion for mercury are based on similar methodologies and are intended to protect human health from consumption of mercury-contaminated fish, they do not necessarily have to be the same value. As explained above, each limit is predicated on different risk-management decisions and thus incorporates different assumptions. A state or tribe may choose to revise existing advisories to mirror the methylmercury criterion. Likewise, there is merit in adopting a site-specific methylmercury criterion on the basis of a local fish advisory, if that advisory is supported by sufficient data that are representative and of acceptable quality.

5.4.6 *How is the criterion related to FDA action levels?*

The Food and Drug Administration's (FDA's) mission is to protect the public health with respect to levels of chemical contaminants in all foods, including fish and shellfish, sold in interstate commerce. To address the levels of contamination in foods, FDA has developed both action levels and tolerances. An action level is an administrative guideline that defines the extent of contamination at which FDA may regard food as adulterated and represents the limit at or above which FDA may take legal action to remove products from the marketplace. It is important to emphasize that FDA's jurisdiction in setting action levels is limited to contaminants in food shipped and marketed in interstate commerce, not food that is caught locally by recreational or subsistence fishers.

The current FDA action level for mercury in fish is 1 mg/kg. Generally, an action level is different from a fish advisory limit—and even more different from a CWA section 304(a) criterion. FDA action levels are intended for the general population who consume fish and shellfish typically purchased in supermarkets or fish markets that sell products that are harvested from a wide geographic area. The underlying assumptions used in the FDA methodology were never intended, as local fish advisories are, to be protective of recreational, tribal, ethnic, and subsistence fishers who typically consume fish and shellfish from the same local waterbodies repeatedly over many years. EPA and FDA have agreed that the use of FDA action levels for the purposes of making local advisory determinations is inappropriate. Furthermore, it is EPA's belief that FDA action levels

and tolerances should not be used as a basis for establishing a state's methylmercury criterion.

5.5 What public participation is recommended for implementing the methylmercury criterion?

By applicable regulations, water quality standards, TMDL, and NPDES permit decisions require public notice and the opportunity for the public to comment on tentative decisions. Some public interest groups might have an interest in decisions related to mercury, especially in areas where local citizens are more reliant upon locally caught fish as a food source. EPA recommends that organizations with an interest in environmental justice issues be included in the public notice.

6 TMDLs

6.1 What is a TMDL?

Section 303(d)(1) of the CWA requires states and authorized tribes to identify and establish priority ranking for waters that do not, or are not expected to, achieve or maintain water quality standards with existing or anticipated required controls. This list is known as the state's or tribe's list of "impaired" waterbodies or 303(d) list. States and authorized tribes then must establish TMDLs for those impaired waterbodies.

A TMDL is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards. A TMDL also allocates the pollutant loads among the contributing sources, both point and nonpoint. The TMDL calculation must include a margin of safety to take into account any uncertainty in the TMDL calculation and must account for seasonal variation in water quality. The current statutory and regulatory framework governing TMDLs includes CWA section 303(d) and the TMDL regulations published in 1985 at 40 CFR 130.2 and 130.7 and amended in 1992 (see 50 FR 1774 (Jan. 11, 1985); 57 FR 33040 (July 24, 1992)).

As of 2004, 42 states reported at least one waterbody as being impaired due to mercury, and over 8,500 specific waterbodies were listed as being impaired due to mercury, either solely or in combination with other pollutants. With the implementation of the new methylmercury fish tissue criterion, EPA expects that the number of waterbodies listed as impaired due to mercury is likely to increase, although the waterbodies might also be impaired due to other contaminants.

6.2 How have states and tribes approached mercury TMDLs?

Developing TMDLs for waters impaired by mercury raises a number of technical and policy issues. For example, air deposition is the predominant source of mercury to many waterbodies, especially in the eastern United States. The mercury deposited from air comes from local, regional, and international sources, and identifying how each of these sources contributes to the mercury load in the waterbody is challenging. In other waterbodies, significant loadings might come from other sources, such as mining or geologic sources. Frequently, states and authorized tribes do not have the authority to address all the sources that contribute mercury to their waterbodies and rely on efforts conducted under a variety of programs, such as regulations under the CAA, pollution prevention programs, and international efforts to reduce releases and emissions from mercury sources. States and EPA have found that, in many cases, it is important to coordinate closely with programs other than those under the CWA to address these mercury sources.

Given these challenges, EPA is working with states, tribes, and stakeholders to determine how best to use TMDLs to provide a basis for reducing mercury releases to water, including through air deposition, to meet applicable water quality standards and Clean Water Act goals. In areas where large numbers of waterbodies are impaired due to

mercury derived from air deposition, some states have begun to explore ways to address mercury impairments efficiently, such as through development of TMDLs on various geographic scales. EPA plans to develop further information on approaches to listing mercury impaired waters and developing mercury TMDLs at a later date.

In the meantime, states continue to develop mercury TMDLs, with mercury TMDLs approved for over 280 waterbodies. This guidance provides examples of approaches that have been used in approved mercury TMDLs and examples of technical tools available to assist in mercury TMDL development. Note that there are examples beyond those cited in this document. Approaches in approved TMDLs range from waterbody-specific TMDLs to regional-scale approaches. Technical tools available to assist in the development of mercury TMDLs include screening level analyses of mercury loadings and sources using the Mercury Maps tool and more complex water and air models. Many of these tools are discussed in the sections below.

6.2.1 How have large-scale approaches been used for mercury TMDLs?

In areas of the country where many waterbodies are listed as impaired for mercury, some states have begun to explore the development of mercury TMDLs either as a group or on a larger geographic scale, such as statewide or regionally. One example of a regional or grouped approach is the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana, approved in June 2005. The TMDL covers six segments of coastal Louisiana. Due to the large extent of mercury from air deposition, the TMDL was developed on a regional rather than a waterbody-by-waterbody basis. The TMDL used air deposition modeling results to estimate wet and dry deposition of mercury for the six segments. Air deposition modeling results in turn were used to model runoff or nonpoint source mercury loadings. As described in the following section, mercury loadings can include direct deposition to waterbodies and deposition to the watershed, which is subsequently transported to the waterbody via runoff and erosion. Additional information on this TMDL can be found on EPA's detailed TMDL report at http://oaspub.epa.gov/pls/tmdl/waters_list.tmdl_report?p_tmdl_id=11642.

In New England, EPA is conducting a pilot project to test the feasibility of taking a regionwide approach to mercury contamination. Mercury contamination throughout New England has resulted in statewide fish consumption advisories and the inclusion of almost all fresh surface water on state lists of impaired waters. The pilot project will involve development of a system to show regionwide information on mercury levels in fish, loadings and sources of mercury, and mercury reductions needed to meet water quality standards. The New England pilot project will consist of two levels of analyses or models—fish tissue concentration predictions and mercury load reduction predictions. EPA will use the regional model to identify factors that contribute to high levels of mercury in fish and to predict the risk of mercury contamination for waterbodies with no fish tissue data. EPA will use the Mercury Maps system, described above, to estimate needed fish tissue concentration reductions.

6.2.2 What is the Mercury Maps screening analysis?

A simple screening level analysis of the mercury sources impacting a waterbody or waterbodies can assist in determining what type of approach to TMDLs is most appropriate. One tool available to help states with such an analysis is EPA's Mercury Maps (USEPA 2001d). Mercury Maps is a peer-reviewed geographic information system (GIS) based analysis with national data coverage for watersheds, fish tissue concentrations, and non-air deposition source locations. Mercury Maps uses a simplified form of the IEM-2M model applied in EPA's Mercury Study Report to Congress (USEPA 1997a). By simplifying the assumptions inherent in the freshwater ecosystem models that were described in the report to Congress, Mercury Maps showed that these models converge at a steady-state solution for methylmercury concentrations in fish that are proportional to changes in mercury inputs from atmospheric deposition (e.g., over the long term, fish concentrations are expected to decline proportionally to declines in atmospheric loading to a waterbody). This analytical approach applies only to situations where air deposition is the only significant source of mercury to a waterbody, and the physical, chemical, and biological characteristics of the ecosystem remain constant over time. To predict reductions in fish concentrations, Mercury Maps requires estimates of percent air deposition reductions by watershed, as generated from a regional air deposition model, and georeferenced measurements of mercury concentrations in fish.

Because Mercury Maps is a simplified approach, it has several limitations. First, Mercury Maps is based on the assumption of a linear, steady-state relationship between concentrations of methylmercury in fish and present day air deposition mercury inputs. This condition will likely not be met in many waterbodies because of recent changes in mercury inputs and other environmental variables that affect mercury bioaccumulation. For example, the United States has recently reduced human-caused emissions (see Figure 3).

A second limitation is that the Mercury Maps methodology inherently requires that environmental conditions remain constant over the time required to reach steady states. This methodology might not be met, especially in systems that respond slowly to changes in mercury inputs. For example, fish tissue data might not represent average, steady-state concentrations for two major reasons. Fish tissue and deposition rate data for the base period are not at steady state. Where deposition rates have recently changed, the watershed or waterbody might not have had sufficient time to fully respond. Also, fish tissue data do not represent average conditions (or conditions of interest for forecast fish levels). Methylation and bioaccumulation are variable and dynamic processes. If fish are sampled during a period of high or low methylation or bioaccumulation, they would not be representative of the average, steady-state or dynamic equilibrium conditions of the waterbody. Other examples include areas in which seasonal fluctuations in fish mercury levels are significant, for example due to seasonal runoff of contaminated soils from abandoned gold and mercury mines or areas geologically rich in mercury. In such a case, Mercury Maps predictions would be valid for similar conditions (e.g., wet year, dry year, or season) in the future, rather than typical or average conditions. Alternatively, sufficient fish tissue should be collected to get an average concentration that represents a baseline dynamic equilibrium.

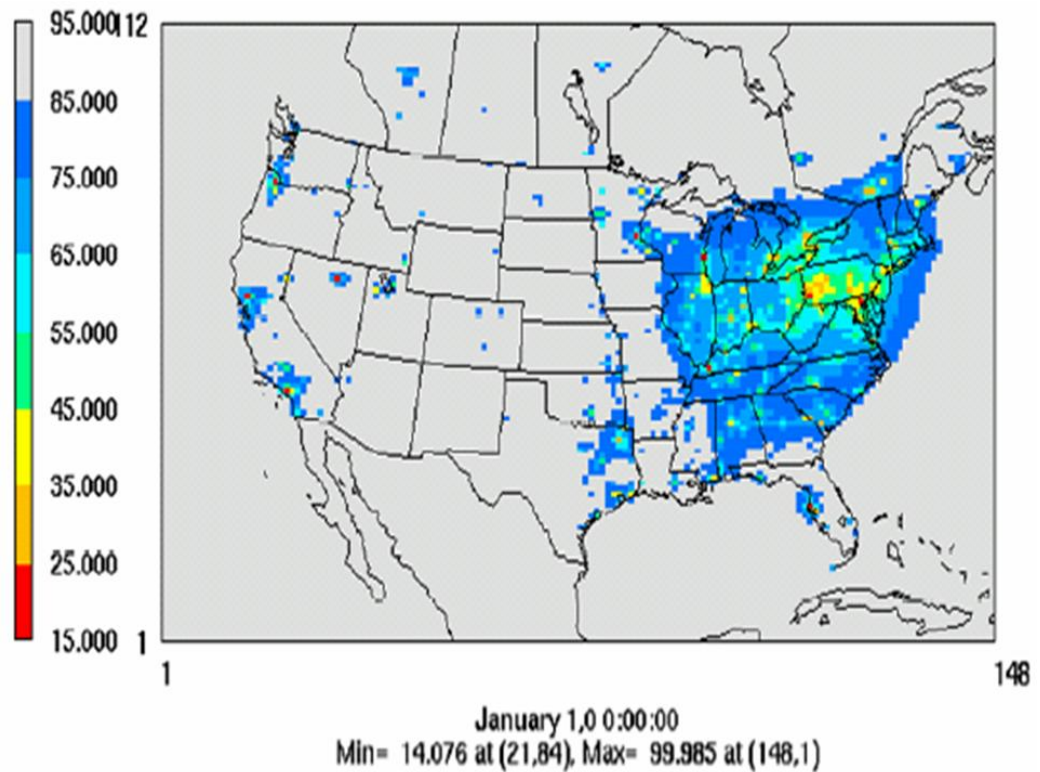


Figure 3. Percent of total mercury deposition attributable to global sources (USEPA 2005c)

Other ecosystem conditions might cause projections from the Mercury Maps approach to be inaccurate for a particular ecosystem. Watershed and waterbody conditions can undergo significant changes in capacity to transport, methylate, and bioaccumulate mercury. Examples of this include regions where sulfate or acid deposition rates are changing (in turn, affecting methylmercury production independently of mercury loading), and where the trophic status of a waterbody is changing. A number of other water quality parameters have been correlated with increased fish tissue concentrations (e.g., low pH, high DOC, lower algal concentrations), but these relationships are highly variable among different waterbodies. Mercury Maps will be biased when waterbody characteristics change between when fish were initially sampled and the new conditions of the waterbody.

Third, states should be aware that many waterbodies, particularly in areas of historic gold and mercury mining or areas with known natural mercury deposits, contain significant non-air sources of mercury. The Mercury Maps methodology cannot be applied to these waterbodies.

Fourth, Mercury Maps does not provide for a calculation of the time lag between a reduction in mercury deposition and a reduction in the methylmercury concentrations in fish. If a state or authorized tribe wants to know the time over which the methylmercury concentrations would change, they should use a dynamic model to estimate the recovery during the period in which waterbody response lags reductions in mercury loads. A dynamic model is also essential for understanding seasonal fluctuations and year-to-year fluctuations due to meteorological variability.

Finally, another source of uncertainty in the Mercury Maps forecasts are the atmospheric deposition rates used to forecast changes in fish mercury concentrations. In the analysis for the CAMR, EPA compared deposition rates in the Community Multiscale Air Quality (CMAQ) and Regulatory Modeling System for Aerosols and Deposition (REMSAD) grid cells to empirically derived loading rates (USEPA 2005b). At the locations chosen for the analysis, site-specific data suggest somewhat higher deposition rates than the CMAQ and REMSAD models. In evaluating the importance of differences in absolute deposition rates from air quality models and site-specific data, it is important to consider how the results will be applied. If the results from air quality models are used as inputs to ecosystem models such as the Dynamic Mercury Cycling Model and the BASS model then the absolute deposition rates are used and so differences in absolute deposition is important. However, if the results are used as inputs into models like Mercury Maps then relative changes in deposition are used. In the latter case, differences in absolute deposition rates are not directly relevant although such differences are important in model validation.

EPA recognizes that methylmercury concentrations in fish across all ecosystems might not reach steady state and that ecosystem conditions affecting mercury dynamics are unlikely to remain constant over time. EPA further recognizes that many waterbodies, especially in areas of historic gold and mercury mining in western states, contain significant non-air sources of mercury. Finally, EPA recognizes that Mercury Maps does not provide for a calculation of the time lag between a reduction in mercury deposition and a reduction in the methylmercury concentrations in fish. Despite the limitations of Mercury Maps, EPA is unaware of any other tool for performing a regional-scale assessment of the change in fish methylmercury concentrations resulting from reductions in atmospheric deposition of mercury. Mercury Maps can show the watersheds across a region where the current fish tissue concentration on average exceeds the new methylmercury fish tissue criterion and, thus, where mercury load reductions will be necessary to achieve the criterion. Mercury Maps also can group watersheds by their major mercury sources, such as those watersheds where air deposition of mercury predominates and those watersheds where other mercury sources besides air deposition (e.g., POTWs, mining, pulp and paper mills, chlor-alkali chemical plants) have significant impacts. For those watersheds where mercury comes almost exclusively from air deposition, Mercury Maps can estimate the atmospheric load reductions needed to meet the new criterion.

A state or authorized tribe can apply Mercury Maps on a state or watershed scale. For example, it could apply Mercury Maps on a statewide scale, using state- or tribal-defined watershed boundaries. The state may have its own data on point source effluent loads and more detailed information on other significant sources of mercury in their state, e.g., erosion of mine tailings or natural geology. Further information on Mercury Maps is available at <http://www.epa.gov/waterscience/maps>.

6.2.3 What are considerations in developing mercury TMDLs?

A TMDL must identify the applicable water quality standards for each listed segment and identify the loading capacity of a water (40 CFR 130.2). In addition, a TMDL must allocate the pollutant loads among the sources, both point and nonpoint sources (40 CFR

130.2(i)). EPA guidance further notes that a TMDL should identify the pollutant sources, both point and nonpoint sources, including the location of the sources and quantity of the loading. Some of the considerations in developing a mercury TMDL are described in more detail in the text below.

6.2.3.1 What are potential mercury sources to waterbodies?

Some of the potential sources of mercury to waterbodies include direct discharges of mercury from water point sources, including industrial dischargers and wastewater treatment plants; atmospheric deposition, including direct deposition to the waterbody surface and deposition to the watershed, which subsequently is transported to the waterbody via runoff and erosion; runoff, ground water flow, acid mine drainage, and erosion from mining sites or mining wastes, and other waste disposal sites such as landfills and land application units; sediments, which might have mercury contamination or hot spots resulting from past discharges; and “naturally occurring” mercury in soils and geologic materials. Sediments containing mercury from past discharges might continue to contribute mercury to the overlying waterbody. Below is further discussion of examples of TMDLs involving each of these types of sources.

Point sources—Point source discharges of mercury include POTWs, electric utilities, and other industrial facilities. Sources of data on point source discharges of mercury include the Permit Compliance System (PCS) as well as a study of domestic mercury sources by the National Association of Clean Water Agencies (NACWA), formerly known as the Association of Metropolitan Sewerage Agencies (AMSA 2000). Without accurate discharge data, a sample of a representative portion of dischargers has been used in mercury TMDLs to estimate the mercury discharges from point sources. In addition, some point source dischargers such as chlor-alkali plants and POTWs might have permits requiring monitoring for mercury, although most dischargers, especially smaller dischargers, are not likely to have such monitoring requirements.

Atmospheric deposition—Deposition of mercury from the air can be a significant source of mercury in many waterbodies. Some waterbodies have been identified as receiving as much as 99 percent of the total loadings from atmospheric deposition, either directly or indirectly via runoff and erosion. (See various mercury TMDLs developed by EPA Region 4 at <http://www.epa.gov/region4/water/tmdl/georgia/index.htm>.) The mercury in atmospheric deposition originates from natural sources and from facilities such as medical and waste incinerators, electric utilities, and chlor-alkali plants, among others. Mercury is emitted to the air in several chemical forms or species. Some chemical forms of mercury emissions to air deposit relatively close to their sources, while others are transported over longer distances and even globally. The mix of chemical forms or species emitted from a given source will determine what fraction of the mercury from that source is depositing locally and what proportion is transported over longer distances, making the task of identifying sources of deposition to a waterbody challenging. At any given location, the mercury deposited from air can originate from several sources. Figure 3 depicts the current understanding of deposition from U.S. and international sources, showing that in many parts of the United States the source of deposited mercury is not from a U.S. source.

In approved mercury TMDLs involving atmospheric loadings, most have characterized the contributions from air deposition in terms of total or aggregate loadings. Atmospheric mercury loadings include both direct deposition to the waterbody surface and indirect deposition to the watershed. Indirect deposition is that which is deposited to the watershed and then transported to the waterbody via runoff and erosion. Atmospheric mercury loadings include both wet and dry deposition of mercury.

It is important to use the most current information about deposition because U.S. mercury emissions into the air have decreased over time. Older data on deposition might not reflect current deposition conditions. For example, Figure 4 depicts a summary of U.S. mercury air emissions between 1990 and 1999 and shows a 45 percent overall decrease. Additional decreases in mercury air emissions have occurred since 1999 as the result of EPA's regulatory efforts under the CAA. At the same time, global emissions might have increased.

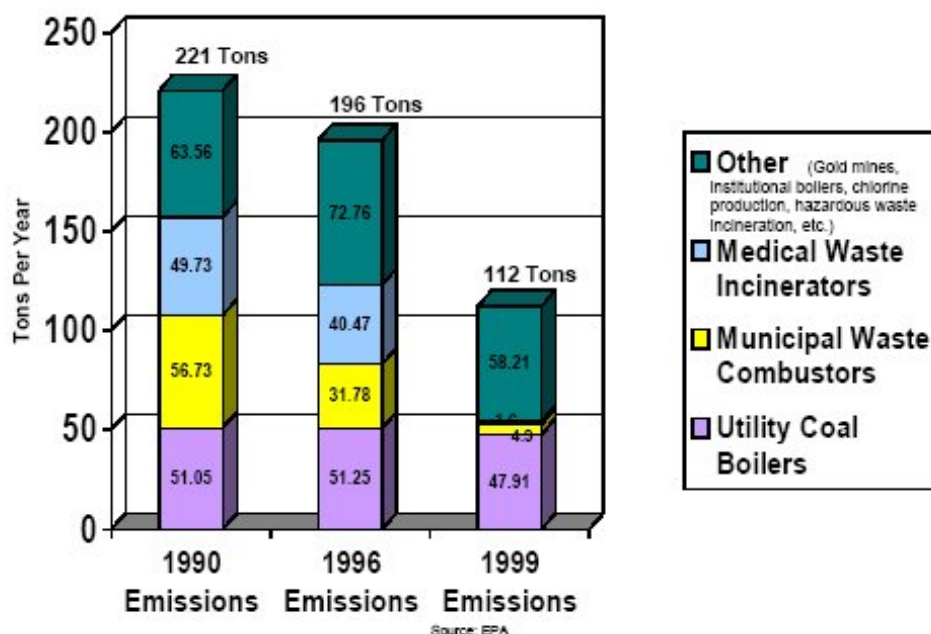


Figure 4. Trends in mercury air emissions between 1990 and 1999

The 2002 National Emissions Inventory (NEI) is EPA's latest comprehensive national emission inventory. It contains emission measurements and estimates for 7 criteria pollutants and 188 hazardous air pollutants (HAPs). The NEI contains emissions for all major contributors to air pollution including point sources (large industrial sources such as electric utilities and petroleum refineries), mobile sources (both onroad sources such as cars and trucks, and nonroad engines such as construction equipment, agricultural equipment, and so on), and nonpoint sources (small stationary sources such as residential fuel use and various types of fires). The NEI includes emission estimates for the entire United States. For point sources, the NEI inventories emissions for each individual process at an industrial facility. For mobile and nonpoint sources, the NEI contains county-level emission estimates. The NEI is developed using the latest data and best estimation methods including data from Continuous Emissions Monitors, data collected from all 50 states, as well as many local and tribal air agencies, and data using EPA's

latest models such as the MOBILE and NONROAD models. More information on the 2002 NEI is at <http://www.epa.gov/ttn/chief/net/2002inventory.html>.

Some approved mercury TMDLs have identified the types or categories of sources likely to contribute to mercury deposition in a waterbody. An example of this type of source analysis is included in the Savannah River mercury TMDLs issued February 28, 2001, and a series of mercury TMDLs issued February 28, 2002, for a number of watersheds in middle and south Georgia (see <http://www.epa.gov/region4/water/tmdl/georgia/index.htm>). These TMDLs included an analysis of the categories of air sources contributing deposition to the waterbodies and the reductions in loadings expected from controls in place when the TMDL was approved.

EPA has evaluated water and air deposition modeling approaches as part of two mercury TMDL pilot projects in Wisconsin and Florida. The Florida pilot report is complete (see <ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf>) (Atkeson et al. 2002). In the Wisconsin pilot project, EPA evaluated modeling tools such as the REMSAD model for identifying the sources or categories of sources contributing mercury deposition to a waterbody.¹⁹ The modeling and peer review for the Wisconsin pilot are completed, and a final report is expected in 2006. The Agency also plans to provide each state or authorized tribe with modeled estimates of mercury deposition from sources within the state or on the tribal land and contributions from sources outside the state or tribe. The modeling results will help EPA and the states and authorized tribes determine the appropriate strategies for addressing mercury deposition from sources within their jurisdictions.

Air quality modeling for the CAMR was conducted using the CMAQ. The CMAQ modeling system is a comprehensive three-dimensional grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales (Dennis et al. 1996, Byun and Ching 1999, Byun and Schere 2006). The CMAQ model is a publicly available, peer-reviewed, state-of-the-science model consisting of a number of science attributes that are critical for simulating the oxidant precursors and nonlinear chemical relationships associated with the formation of mercury. Version 4.3 of CMAQ (Byun and Schere 2006, Bullock and Brehme 2002) was used for CAMR. This version reflects updates to earlier versions in a number of areas to improve the underlying science and address comments from peer review. The updates in mercury chemistry used for CAMR from that described in (Bullock and Brehme 2002) are as follows:

1. The elemental mercury (Hg⁰) reaction with H₂O₂ assumes the formation of 100 percent RGM rather than 100 percent particulate mercury (HgP).
2. The Hg⁰ reaction with ozone assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP.
3. The Hg⁰ reaction with OH assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP.

¹⁹ The air deposition modeling using REMSAD used an older emissions inventory than was used in CMAQ modeling conducted as part of the CAMR analysis.

4. The rate constant for the $\text{Hg}^0 + \text{OH}$ reaction was lowered from 8.7 to $7.7 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.

CMAQ simulates every hour of every day of the year and requires a variety of input files that contain information pertaining to the modeling domain and simulation period. These include hourly emissions estimates and meteorological data in every grid cell and a set of pollutant concentrations to initialize the model and to specify concentrations along the modeling domain boundaries.

Meteorological data, such as temperature, wind, stability parameters, and atmospheric moisture contents influence the formation, transport, and removal of air pollution. The CMAQ model requires a specific suite of meteorological input files to simulate these physical and chemical processes. For the CAMR CMAQ modeling, meteorological input files were derived from a simulation of Pennsylvania State University's National Center for Atmospheric Research Mesoscale Model (Grell et al. 1994) for the entire year of 2001. This model, commonly referred to as MM5, is a limited-area, nonhydrostatic, terrain-following system that solves for the full set of physical and thermodynamic equations that govern atmospheric motions. For this analysis, version 3.6.1 of MM5 was used. A complete description of the configuration and evaluation of the 2001 meteorological modeling is in McNally (2003).

These initial and boundary concentrations were obtained from output of a global chemistry model, Harvard's GEOS-CHEM model (Yantosca 2004), to provide the boundary concentrations and initial concentrations. The global GEOS-CHEM model simulates atmospheric chemical and physical processes driven by assimilated meteorological observations from the NASA's Goddard Earth Observing System (GEOS). This model was run for 2001 with a grid resolution of 2 degree x 2.5 degree (latitude-longitude) and 20 vertical layers.

The CMAQ modeling domain encompasses all the lower 48 states and extends from 126 degrees west longitude to 66 degrees west longitude and from 24 degrees north latitude to 52 degrees north latitude. The modeling domain is segmented into rectangular blocks referred to as grid squares. The model predicts pollutant concentrations and depositions for each of these grid cells. For this application the horizontal domain consisted of 16,576 grid cells that are roughly 36 km by 36 km. The modeling domain contains 14 vertical layers with the top of the modeling domain at about 16,200 meters, or 100 millibar. The height of the surface layer is 38 meters.

As with any analysis based on limited data, there is inherent uncertainty in the estimates of all analytical outputs of modeling. Model uncertainty results from the fact that models and their mathematical expressions are simplifications of reality that are used to approximate real-world conditions, processes, and their relationships. Models do not include all parameters or equations necessary to express real-world conditions because of the inherent complexity of the natural environment and the lack of sufficient data to describe the natural environment. Consequently, models are based on numerous assumptions and simplifications and reflect an incomplete understanding of natural processes. As a result, there will be some uncertainty when using models to quantify the sources of air deposited mercury.

Other tools available to help states characterize mercury deposition include existing national monitoring networks and modeling tools, such as the Mercury Deposition Network (MDN). Examples of these are provided in Appendix D. Published results of national modeling studies could also be available to help estimate atmospheric deposition loadings. Further information on tools and approaches for characterizing atmospheric deposition to waterbodies can be found in the Frequently Asked Questions about Atmospheric Deposition section at <http://www.epa.gov/owow/oceans/airdep/air7.html>.

Mining activity—Loadings from mining activities might include both historical and recent mining activity within the watershed. Mining areas of interest are those involving “placer” deposits in which mercury itself is present in the ore, or those deposits for which mercury is used to extract other metals (e.g., gold). For example, sulfide replacement deposits are often associated with mercury. Locations at mining sites that might serve as sources of mercury include direct seeps, as well as leachate from tailings or spoil piles. In the Clear Lake TMDL (see Appendix A), ground water from an abandoned mining site was reported to contain mercury that is readily methylated. In Clear Lake, acid mine drainage was found to contain high sulfate concentrations, which may enhance methylation by sulfate-reducing bacteria. Sources of data on potential mercury deposits associated with mining activity include USGS, the U.S. Bureau of Mines (for a list of major deposits of gold and silver), the State Inactive Mine Inventory, and the EPA Superfund program. Examples of TMDLs involving mercury associated with mining are provided in Appendix A.

Sediments—A TMDL analysis should account for any mercury present in sediments as a result of current or past mercury loadings. Data on levels of mercury in sediments are important in determining the extent to which controls on other sources will be effective and how long it will take to achieve water quality standards. An examination of past industrial practices in the watershed could include whether sediments may serve as a reservoir for mercury. Various national databases, such as the National Sediments Database (USEPA 2002c) and data collected by USGS might also identify isolated locations of elevated mercury in sediments. In the absence of sediment data for a waterbody, site-specific monitoring might be needed to confirm the levels of mercury in sediments to use as input to water quality models. In the sediment TMDL for Bellingham Bay, Washington, site-specific sediment analyses for mercury and other pollutants were conducted, including sediment sampling and toxicity analyses. Two kinds of modeling were also conducted

- Modeling of contaminant transport and mixing to determine if loadings from a location were contribution to water quality standards violations
- Screening modeling to determine other potential sources of sediment contamination (see the TMDL at http://www.epa.gov/waters/tmdl/docs/1991_Bellingham%20Bay%20TMDL.pdf)

Natural or “background” levels of mercury in soils—Soils and sediments can include mercury of geologic origin or mercury produced by the weathering of geological materials, together with mercury of anthropogenic origin (i.e., mercury emitted over time from human sources and then deposited on soils). Mercury in soils can also re-emit and subsequently redeposit to soils. Local studies have been used in some TMDLs to estimate

the geologic contributions of mercury to waterbodies. For example, a TMDL developed for the Ouachita watershed in Arkansas relied on a study of mercury concentrations in the rocks of the Ouachita Mountains (FTN 2002). The mercury concentration estimated to be of geologic origin was then subtracted from the total concentration of mercury measured in soils to estimate the nongeologic concentration of mercury in soils.

6.2.3.2 What modeling tools are available to link mercury sources and water quality?

When developing a TMDL states or tribes should characterize the association between the concentration of methylmercury in fish tissue and the identified sources of mercury in a watershed. The association is defined as the cause and effect relationship between the selected targets, in this case the fish tissue-based criterion and the sources. The association provides the basis for estimating the total assimilative capacity of the waterbody and any needed load reductions. TMDLs for mercury will typically link together models of atmospheric deposition, watershed loading, and mercury cycling with bioaccumulation. This enables a translation between the endpoint for the TMDL (expressed as a fish tissue concentration of methylmercury) and the mercury loads to the water. The analysis determines the loading capacity as a mercury loading rate consistent with meeting the endpoint fish tissue concentration.

When selecting a model or models for developing a mercury TMDL, states and authorized tribes should first consider whether the models will effectively simulate the management action(s) under consideration. If a percent reduction in mercury load to the waterbody is the sole action considered, a simple model may suffice. To answer more complex questions, a more complex or detailed model might be needed. Some questions decision makers should address include:

- How much do specific mercury loads need to be reduced to meet the criterion?
- What are the relative sources of the mercury load to the segment?
- Are mercury loads to the waterbody from sediments and watershed runoff and concentrations in fish at equilibrium with respect to current deposition levels? If not, how much will an equilibrium assumption affect accuracy of predicted future fish concentrations?
- Could other pollution control activities reduce mercury loads to the waterbody or affect the mercury bioaccumulation rate?
- After implementing regulatory controls, how long will it take for fish tissue levels to meet the criterion?

Depending on the types of questions states and tribes ask and the management approaches they consider, appropriate models could range from a very simple steady state model to a comprehensive dynamic simulation model, as described below. For more information on the specific models described below, see <http://www.epa.gov/athens> and <http://www.epa.gov/crem>.

6.2.3.2.1 Steady state models

Steady state modeling describes the dynamic equilibrium between environmental media established in response to constant loads over the long term. As such, complex mercury cycling processes can be compressed into simple equations. One such approach, discussed in the Mermentau/Vermillion Mercury TMDL (USEPA 2001h), assumes that a ratio of current to future fish tissue concentration equals the ratio of current to future mercury loads to the waterbody. This approach, derived in detail in the Mercury Maps report (USEPA 2001a), assumes that where air deposition is the sole significant source, the ratio of current to future fish tissue concentrations equals the ratio of current to future air deposition loads. For the Clean Air Mercury Rule the assumptions of the Mercury Maps steady state model were implemented. CMAQ modeled percentage changes in air deposition under the rule were used to predict changes in fish tissue concentrations. For example, if the air deposition model showed that the rule would result in a 10 percent reduction air mercury deposition at a given fish tissue sample location, that sample concentration was reduced by 10 percent. An advantage of this method is the ability to use measured fish tissue concentrations which, by default, reflect potential variability in bioaccumulation rates between ecosystems. Examples of the application of the Mercury Maps assumptions can be found in the Clean Air Mercury Rule (USEPA 2005b and USEPA 2005c).

Mass balance models are somewhat more complex implementations of the steady state modeling approach. In place of a simple ratio, the model would describe fluxes of mercury in and out of the model domain (e.g., impaired segment), and optionally, balancing fluxes (e.g., methylation and demethylation) within the model domain. The advantage of this approach is that individual fate processes, which could additionally be controlled in a management setting, can also be simulated. For example, if soil erosion and sediment runoff are modeled, decreased mercury soil erosion load can be related to decreased fish tissue concentrations (AZDEQ 1999). Where all other aspects of the watershed and waterbody remain unchanged, steady state models can produce as accurate an estimate of the necessary load reductions as a dynamic model at a fraction of the cost. Additionally, simple approaches, such as those discussed above, are less prone to calculation errors and much easier to communicate to the public.

6.2.3.2.2 Continuous simulation and dynamic models

Continuous simulation or dynamic models take into account time varying effects such as variable pollutant inputs, precipitation, hydrologic response, seasonal ecosystem changes, and other effects on fish tissue concentrations. They might also include a variety of physical and chemical fate and transport processes such as methylation, demethylation, volatilization, sedimentation, resuspension, adsorption and desorption and so on. Such dynamic models are important in establishing cause and effect relationships. They assemble all available scientific knowledge on mercury fate and transport into a single picture. Thus, they have been used to demonstrate how mercury moves from air emissions to deposition to watershed runoff to subsequent bioaccumulation in fish at observed levels in remote waterbodies (USEPA 1997b).

Dynamic models could be used to describe waterbodies in dis-equilibrium (e.g., a recent surface water impoundment with elevated methylation rates). The Everglades Mercury

TMDL pilot project (USEPA 2000b) simulated the amount of time necessary to attain equilibrium in response to reduced mercury loads using the Everglades Mercury Cycling Model. The model results showed sediments continued to supply as much as 5 percent of the mercury load 100 years after air deposition reductions occurred. The D-MCM was used in the mercury TMDLs for McPhee and Narraguinnep Reservoirs in Colorado and the TMDLs for Arivaca and Pena Blanca Lakes in Arizona (see Appendix A) (Tetra Tech 2001).

The SERAFM model incorporates more recent advances in scientific understanding described above and implements an updated set of the IEM-2M solids and mercury fate algorithms that were described in the 1997 *Mercury Study Report to Congress* (USEPA 1997b). This model was also used in the watershed characterizations to support the CAMR (USEPA 2005b).

Dynamic models can also describe how fish tissue concentrations are expected to respond to environmental variability, such as seasonal or year-to-year changes in meteorology. Thus, they can be used to better interpret how samples collected in a specific season of a specific year would be expected to vary relative to other seasons or years with mercury loads being constant.

6.2.3.2.3 Spatially detailed models

Spatially detailed models, such as that used in the Savannah River TMDL (USEPA 2001a), can demonstrate how mercury fish tissue concentrations are expected to vary with distance downstream of the impaired segment(s). For the Savannah River, EPA used the WASP (Water Quality Analysis Simulation Program) model. WASP is a dynamic, mass balance framework for modeling contaminant fate and transport in surface water systems. This model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. Another model used for both mercury TMDLs and watershed characterization in the CAMR is the EPA Region 4 Watershed Characterization System (WCS). This is a GIS-based modeling system for calculating soil particle transport and pollutant fate in watersheds (Greenfield et al. 2002).

As with the steady state mass balance model, including additional processes can allow the modeler to determine the impact of different environmental regulatory or management controls on mercury fish tissue concentrations. For example, where mercury transport to a waterbody is predominantly through soil erosion, erosion control might be identified as a valid nonpoint source control on mercury to waterbodies (Balogh et al. 1998).

Additionally, controls on acid deposition and, thus, changes in lake pH and its effect on fish tissue mercury concentrations, might also be modeled (Gilmour and Henry 1991, Hrabik and Watras 2002). Finally, spatially detailed models can be used to reflect the local effects of wetlands, which produce significantly more methylmercury per unit area than other types of land use.

6.2.3.2.4 Model selection

When selecting a model, the state or authorized tribe should be aware of the assumptions inherent in each type of model and consider what effect that assumption has on determining the relationship between loadings and fish tissue levels or water quality. The

first consideration is methylation. Several factors including pH, redox, sulfide concentrations, temperature, DOC concentrations, salinity, and microbial populations influence the speciation of mercury (Ullrich et al. 2001). If these factors vary seasonally or around an average condition, the waterbody could be at a dynamic equilibrium and the steady state assumption still apply. If these factors change with time such that they may have a significant impact on fish tissue concentrations, the equilibrium assumptions inherent in steady state modeling might not hold, and a dynamic model such as the D-MCM (EPRI 1999) should be used. In using this model, the state or authorized tribe should consider the amount of environmental media concentration data needed to initialize the model to represent its out of equilibrium state.

The second consideration is the BAF. As discussed in section 3.1.2.2., the BAF assumes a constant proportionality between fish tissue methylmercury concentrations, water column methylmercury concentrations, and water column mercury concentrations. Mercury in a waterbody might not be at a steady state due to ongoing reductions in mercury emissions, changes in water chemistry that affect methylation, changes in aquatic ecosystem makeup, or changes in fish biomass. If these factors change with time, the equilibrium assumptions inherent in steady state modeling might not hold, and a dynamic model should be used.

The third consideration is the relative importance of the mercury in aquatic sediments to the concentrations in fish tissue. Depending on previous loadings to the watershed, the deposition pattern of solids, and the chemistry in the aquatic sediments, the mercury in sediments can significantly influence the mercury concentrations in fish tissue. Sediments are repositories, and the loading that caused sediment mercury could be a legacy source. If so, a simplified steady state approach cannot simulate changes in mercury concentrations in fish tissue due to external loading reductions, and a dynamic model should be used.

6.2.3.2.5 *Model limitations*

To effectively estimate fish methylmercury concentrations in an ecosystem, it is important to understand that the behavior of mercury in aquatic ecosystems is a complex function of the chemistry, biology, and physical dynamics of different ecosystems. The majority (95 to 97 percent) of the mercury that enters lakes, rivers, and estuaries from direct atmospheric deposition is in the inorganic form (Lin and Pehkonen 1999). Microbes convert a small fraction of the pool of inorganic mercury in the water and sediments of these ecosystems into methylmercury. Methylmercury is the only form of mercury that biomagnifies in organisms (Bloom 1992). Ecosystem-specific factors that affect both the bioavailability of inorganic mercury to methylating microbes (e.g., sulfide, DOC) and the activity of the microbes themselves (e.g., temperature, organic carbon, redox status) determine the rate of methylmercury production and subsequent accumulation in fish (Benoit et al. 2003). The extent of methylmercury bioaccumulation is also affected by the number of trophic levels in the food web (e.g., piscivorous fish populations) because methylmercury biomagnifies as large piscivorous fish eat smaller organisms (Watras and Bloom 1992, Wren and MacCrimmon 1986). These and other factors can result in considerable variability in fish methylmercury levels among ecosystems at the regional and local scale.

The lack of complete knowledge about key mercury process variables, such as the functional form of equations used to quantify methylation rate constants, is a major contributor to overall uncertainty in models that cannot be quantified at this time. In addition, the expected effect of land-use changes on fish mercury concentrations for a watershed dominated system illustrates changes like urbanization within a watershed can alter the magnitude and timing of fish mercury concentrations.

6.2.3.3 What are the allocation approaches in mercury TMDLs?

A requirement for an approvable TMDL is that the state or tribe allocate the pollutant load necessary to achieve water quality standards among point and nonpoint sources. However, EPA's regulations leave the decision regarding how to allocate loadings to the state or authorized tribe developing the TMDL. States and authorized tribes may use any method or system for allocating pollutant loads among sources, provided that the allocations will result in attainment of water quality standards represented by the loading capacity (40 CFR 130.2). States and authorized tribes could reasonably consider the relative contribution of each source as one factor in developing allocations. Other factors may include cost-effectiveness, technical and programmatic feasibility, previous experience with the approach being considered, likelihood of implementation, and past commitments to load reductions. These same considerations apply to mercury TMDLs.

A number of pollutant loading scenarios have occurred in mercury TMDLs, each with a different mix of point and nonpoint sources. These scenarios have included the following:

- Point source loadings are small compared to loadings from nonpoint sources (e.g., atmospheric deposition), but the expected load reductions in the nonpoint sources, together with modest reductions from the point sources, are sufficient to achieve water quality standards.
- Point source loadings are small compared to nonpoint sources, but the expected nonpoint source reductions are not adequate to achieve water quality standards even if point sources cease to discharge.
- Point source loadings are not small compared to nonpoint source loadings.

Point source loadings small; nonpoint sources expected to achieve WQS—The Savannah River mercury TMDL provides an example of the first scenario. On the basis of an analysis of air loadings for the Savannah TMDL, CAA regulations in place when the TMDL was developed are expected to achieve the reductions from air loadings needed to achieve the water quality target in the TMDL. The TMDL determined that a 44 percent reduction in mercury loadings would be needed to reach the water quality target, and a 38–48 percent reduction in mercury loadings from air sources is expected by 2010 under air regulations in existence at that time. The air regulations identified in the TMDL address mercury emissions from medical, municipal, and hazardous waste incinerators. The TMDL identifies only one point source on the Georgia side of the river that has a permit to discharge mercury to the Savannah River. It identifies 28 point sources in Georgia that may have the potential to discharge larger amounts of mercury in their effluent according to the nature of the discharge or on mercury levels that have been found in their effluents above the water quality standard level.

The TMDL provides specific wasteload allocations for these sources on the basis of meeting the water quality criterion at the end of pipe or alternatively implementing a pollutant minimization program. In addition, the TMDL identifies about 50 other point sources expected, according to their size and nature, to either discharge mercury below the water quality standard or not add mercury in concentrations above the concentrations in their intake water. Individual wasteload allocations are given to these point sources on the basis of them holding their effluents at current levels. The wasteload allocations are expressed in the TMDL by their sum. This TMDL can be found at <http://www.epa.gov/region4/water/tmdl/georgia/index.htm>.

Note: After the Savannah River mercury TMDL was issued, Georgia adopted a new interpretation of its narrative water quality criteria that used EPA's new recommended fish tissue criterion for methylmercury. On the basis of the new interpretation, Georgia determined, and EPA agreed, that the Savannah River was meeting water quality standards for mercury. EPA therefore withdrew the TMDL. However, EPA believes that the decisions, policies, and interpretations set forth in the TMDL are still valid and serve as one example of an approach to mercury TMDLs.

Point source loadings small; nonpoint sources not expected to achieve WQS under current regulations—The series of mercury TMDLs issued February 28, 2002 for watersheds in middle and south Georgia illustrate the second scenario. In these basins, point source loadings contribute very little to the mercury loadings (cumulative loading of mercury from all point sources is less than 1 percent of the total estimated current loading), with the vast majority of loading to the basins as air deposition. In five out of seven basins where load reductions are needed to meet the water quality target, the analysis indicates that CAA air regulations in place at the time the TMDL was developed will not achieve sufficient load reductions in the air sources to achieve the target. In the Ochlockonee Basin, for example, a 76 percent reduction in mercury loadings is needed to achieve the water quality target, but an analysis conducted for the TMDL indicated that a 31–41 percent reduction in air loadings would likely be achieved under air regulations in place at that time (USEPA 2002a). In comparison, the aggregate of point sources is only 1 percent of the total load to the basin. The TMDL anticipates that there would be additional reductions in mercury loadings due to current and planned activities. However, as provided for under section 303(d), the TMDL quantifies the reductions needed to meet the water quality standards.

Although point sources collectively contributed a very minute share of the mercury load, the Ochlockonee and other mercury TMDLs for middle and south Georgia included wasteload allocations for the point sources. The TMDLs include wasteload allocations for each facility identified as a significant discharger of mercury, with the remainder of the allocation assigned collectively to the remaining point sources, considering that these smaller point sources would reduce their mercury loadings using appropriate, cost-effective minimization measures. The middle and south Georgia mercury TMDLs issued February 28, 2002, can be found at <http://www.epa.gov/region4/water/tmdl/georgia/index.htm>.

Point sources loadings are not small—For these TMDLs, the reductions in point source loadings, alone or in combination with nonpoint sources, can sufficiently achieve water

quality standards. In this situation, the TMDL should consider reductions in both the point sources and nonpoint sources to achieve the water quality standard. Appendix A provides an example of a TMDL where point source loadings of mercury from mining areas are large.

6.2.3.4 What kind of monitoring provisions have been associated with approved TMDLs?

Monitoring provisions in approved TMDLs have included point source effluent and influent monitoring, as well as water column, fish tissue, sediment, and air deposition monitoring. Examples of mercury TMDLs with post-TMDL monitoring are the middle and south Georgia mercury TMDLs approved in 2002. For facilities with the potential to discharge significant amounts of mercury on the basis of their large flow volume or other factors, the TMDL provides the permitting authority with two options for the wasteload allocation:

- Implement criteria-end-of-pipe.
- Monitor for mercury in their influent and effluent using more sensitive analytical techniques (Method 1631) and implement cost-effective mercury minimization if mercury is present in effluent at concentrations greater than source water concentrations and if the discharge exceeds the water quality target.

For other facilities expected to be discharging below the water quality target, the TMDL expects that they will verify through monitoring whether they are significant dischargers of mercury. Other follow-up activities include further characterization of the air sources and additional ambient monitoring of mercury concentrations in water, sediment, and fish.

The mercury TMDL for the coastal bays and gulf waters of Louisiana (approved July 2005) includes similar monitoring provisions for point source dischargers with flows above a specified discharge volume. The TMDL also indicates that Louisiana will conduct water, fish tissue, and air deposition monitoring and that the state will develop a statewide mercury risk reduction program by the end of 2005, including an assessment of all mercury sources. (See the TMDL and supporting documents at http://oaspub.epa.gov/pls/tmdl/waters_list.tmdl_report?p_tmdl_id=11642.)

TMDLs involving past mining activity have also included follow-up monitoring; examples include two of the TMDLs described in Appendix A (Clear Lake, California and Arivaca Lake, Arizona). The mercury TMDL for Arivaca Lake lists several follow-up actions and monitoring activities, including additional watershed investigations to identify other potential mine-related mercury sources, including sediment sampling; evaluation of livestock BMPs to reduce erosion of soils containing mercury and follow-up monitoring; and fish tissue monitoring to evaluate progress toward the TMDL target (see the TMDL at <http://www.epa.gov/waters/tmdldocs/17.pdf>). The Clear Lake, California mercury TMDL also identifies the need for follow-up monitoring of fish tissue and sediment (see Appendix A, and the TMDL at <http://www.waterboards.ca.gov/centralvalley/programs/tmdl/ClearLake/ClkTMDLfinal.pdf>).

EPA recommends that states and authorized tribes periodically review TMDLs during implementation to ensure that progress is being made toward achieving water quality standards. Such “adaptive implementation” provides the flexibility to refine and improve a TMDL as data is collected on the success of implementation activities. States may refine information on the contributions from sources, such as runoff from abandoned mining sites, sediment loading of mercury-laden sediments, or air deposition as data and modeling tools improve. Thus, states should consider the application of adaptive implementation in determining load allocations for these sources. Post-TMDL monitoring is an important tool for evaluating implementation success and, if necessary, making refinements in the TMDL.

7 NPDES Implementation Procedures

7.1 What are the general considerations in NPDES permitting?

The CWA prohibits the discharge of any pollutant including mercury from a point source into waters of the United States except in compliance with an NPDES or other CWA permit (see CWA sections 301(a) and 402). EPA or states and tribes authorized to administer the NPDES program issue NPDES permits. These permits must contain (1) technology-based effluent limitations, which represent the degree of control that can be achieved by point sources using various levels of pollution control technology (see CWA sections 301, 304, and 306); and (2) more stringent limitations, commonly known as WQBELs, when necessary to ensure that the receiving waters achieve applicable water quality standards (see CWA section 301(b)(1)(C)).²⁰

Most WQBELs are expressed as numerical limits on the amounts of specified pollutants that may be discharged. However, WQBELs may also be expressed in narrative form, such as BMPs or pollutant minimization measures (e.g., practices or procedures that a facility follows that result in a reduction of pollutants to waters of the United States) when it is infeasible to calculate a numeric limit (see 40 CFR 122.44(k)(3)). In addition, BMPs may be imposed in the form of NPDES permit conditions to supplement numeric effluent limitations when the permitting authority determines that such requirements are necessary to carry out the purposes and intent of the Act (see CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4)).

As noted above, NPDES permits must contain WQBELs when necessary to achieve applicable water quality standards. The procedure for determining the need for WQBELs is called a “reasonable potential” determination. Under EPA’s regulations at 40 CFR 122.44(d)(1)(i), effluent limitations must control all pollutants that the permitting authority determines “are or may be discharged at a level [that] will cause, have the reasonable potential to cause, or contribute to an excursion above any [applicable] water quality standard.” Thus, if a pollutant discharge has the reasonable potential to cause or contribute to an exceedence of applicable water quality standards, the discharger’s NPDES permit must contain a WQBEL for that pollutant (See 40 CFR 122.44(d)(1)(iii)-(vi)). The procedure for determining reasonable potential must consider the variability of the pollutant in the effluent, other loading sources, and dilution (when allowed by the water quality standards) (See 40 CFR 122.44(d)(1)(ii)). The procedure, while specifying whether a discharge must have WQBELs, does not specify the actual value of the permit limitation. The *Technical Support Document for Water Quality-based Toxics Control* (TSD) (USEPA 1991) contains EPA’s guidance on determining reasonable potential.

²⁰ When developing WQBELs, the permitting authority must ensure that the level of water quality achieved by such limits is “derived from and complies with water quality standards (see 40 CFR 122.44(d)(1)(vii)(A)).

7.2 How does EPA recommend implementing the fish tissue criterion for NPDES permits?

As discussed in section 3.1, states and authorized tribes that decide to use the recommended criterion as the basis for new or revised methylmercury water quality standards have the option of adopting the criterion as a fish tissue residue concentration into their water quality standards, adopting it as a traditional water column concentration, or adopting both the criterion as a fish tissue residue concentration and a traditional water column translation. If states or authorized tribes choose to use both approaches, they should clearly describe how each will be used for specific applications in their standards and describe applicable implementation procedures.

EPA recommends three different approaches for implementing the fish tissue-based methylmercury water quality criterion in NPDES permits, depending on the form in which the state or authorized tribe expressed the criterion (i.e., as a fish tissue value or as a water column concentration). Additionally, states and authorized tribes that adopt the recommended criterion as a fish tissue residue value may choose to implement it through NPDES permitting as a water column translation of the fish tissue value. Each of these approaches is discussed in more detail below and is summarized in Figure 5.

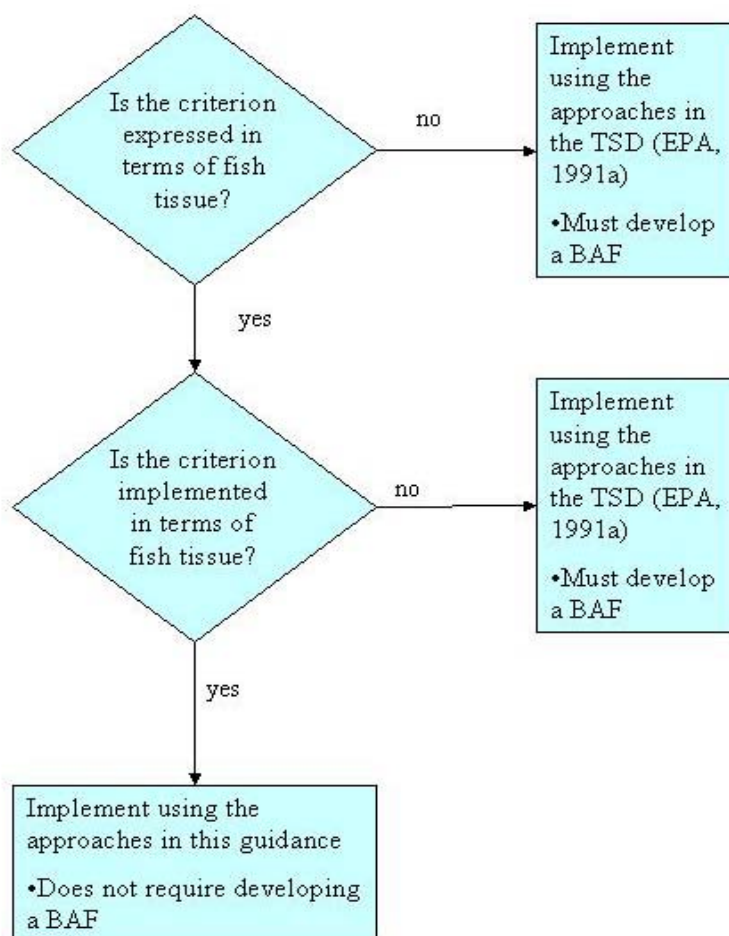


Figure 5. Implementing the fish tissue criterion in NPDES permits

The recommendations below assume that an approved TMDL is not available. If EPA has approved or established a TMDL containing a wasteload allocation for the discharge of mercury, the WQBEL for that mercury discharge must be consistent with the wasteload allocation's assumptions (see 40 CFR 122.44(d)(1)(vii)(B)).

This chapter provides EPA's guidance on how a permitting authority could implement the fish tissue criterion in NPDES permits consistent with the CWA and its implementing regulations. States and authorized tribes retain the discretion to develop and use implementation procedures for determining reasonable potential and establishing effluent limits in NPDES permits that differ from those in the guidance. Such procedures may use other information that is relevant to determining reasonable potential and establishing effluent limits, where appropriate. If a state or authorized tribe develops its own permit implementation procedures, EPA recommends that states and authorized tribes should make the procedures public so that all stakeholders can be aware of the requirements and expectations of the permit program. In addition, the permit's fact sheet or statement of basis should also explain the basis of the permit conditions and effluent limitations and how these are consistent with the state's or authorized tribes' implementation procedures, the CWA, and applicable federal regulations.

7.3 What are the implementation procedures when the criterion is adopted as a water column value?

This approach assumes that a state or authorized tribe decides to adopt a new or revised water quality criterion for methylmercury in the form of a water column concentration value. Expressing a criterion as a water column value is very common, and permitting authorities have considerable historical experience in implementing such criteria in NPDES permits. Under this approach, EPA recommends that the permitting authority make reasonable potential determinations and calculate numeric effluent limitations using procedures consistent with those described in the TSD (USEPA 1991) or equivalent state procedures.

This approach relies upon the measurement of mercury in effluents. Because the level of mercury in many effluents is often very small, the permitting authority should specify that the NPDES regulated discharger use the most sensitive analytical method approved under 40 CFR Part 136 and report the quantitation level associated with that test. Mercury levels in effluents can often be below the quantitation levels of some analytical methods. By specifying the most sensitive method, the permitting authority minimizes the chance that it would not require a WQBEL when one is actually necessary.

7.4 What are the implementation procedures when the criterion is adopted as a fish tissue value and the permitting authority uses a water column translation of a fish tissue value?

This approach assumes that a state or authorized tribe decides to adopt a new or revised water quality criterion for methylmercury in the form of fish tissue, but translates it into a water column value for use in making reasonable potential determinations and developing appropriate numeric WQBEL when necessary. Section 3.1.2.2 of this

guidance discusses the procedures for translating the fish tissue criterion into a water column value for water quality standards purposes. These procedures may also be used to translate a fish tissue criterion into a water column value for reasonable potential determinations and numeric WQBELs. Once the criterion has been translated into a water column value, the TSD (USEPA 1991) or equivalent state procedures can be used to complete a reasonable potential determination and develop numeric WQBELs.

Because the level of mercury in many effluents is often very small, the permitting authority should specify that the NPDES regulated discharger use the most sensitive analytical method approved under 40 CFR Part 136 for total mercury and report the quantitation level associated with that test. Federal regulations at 40 CFR 122.45(c) generally require effluent monitoring for metal using the total form of the metal.

In addition, the permitting authority may also specify effluent monitoring using draft EPA Method 1630 where the permitting authority is concerned about the level of methylmercury (as opposed to total mercury) being discharged. Federal regulations at 122.41(j)(4) generally require that effluent monitoring results must be conducted according to the test procedures approved under Part 136, unless other test procedures have been specified in the permit.

7.5 What are the implementation procedures when the criterion is adopted as a fish tissue value and the permitting authority does not use a water column translation of the fish tissue value?

This approach assumes that a state or authorized tribe decides to adopt a new or revised water quality criterion for methylmercury in the form of fish tissue and directly implements the criterion without translating it into a water column concentration. As a result, the permitting authority will use a different approach than it has used before for determining reasonable potential and expressing effluent limits. EPA recommends the approach described below, which is summarized in Figure 6.

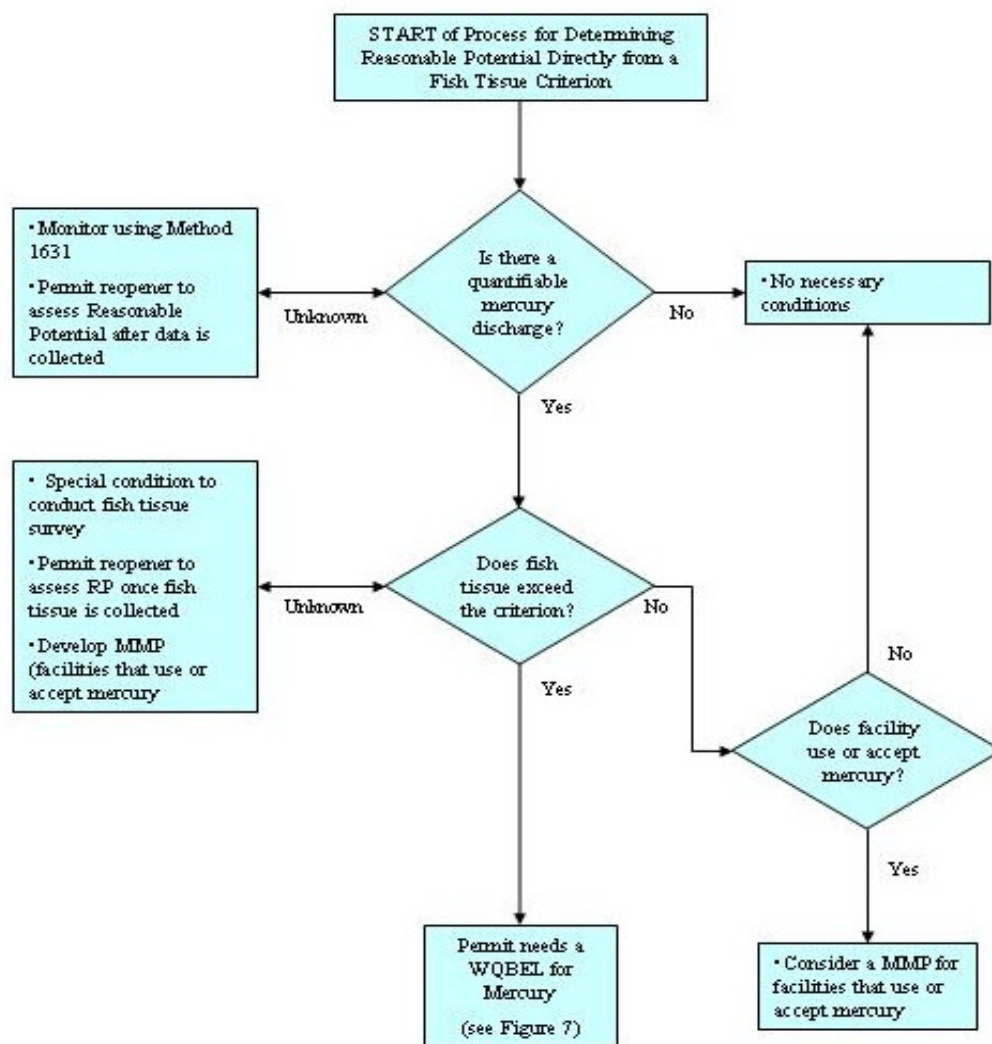


Figure 6. Determining reasonable potential

7.5.1 How to determine the need for permit limits to control mercury (i.e., how to determine reasonable potential)

As discussed in section 3.1.2.1. of this document, EPA recommends that states and authorized tribes adopt new or revised methylmercury water quality criteria in the form of a fish tissue residue concentration. When adopted in standards as a tissue value, states and authorized tribes do not translate from a traditional water column value to a tissue residue value using BAFs, which can vary highly by location and can be expensive. This section provides recommendations for how a permitting authority could determine reasonable potential in the absence of an available translation of the fish tissue value to a water column value.

When determining reasonable potential, the permitting authority must determine whether the discharge “causes, has reasonable potential to cause, or contributes” to an excursion above the applicable water quality criterion (see 40 CFR 122.44(d)(1)(ii)). The NPDES

permit fact sheet should provide the rationale and assumptions used in determining whether WQBELs proposed in the associated draft permit are appropriate. The recommendations in this guidance could be applied on a permit-by-permit basis where appropriate to support the reasonable potential determination that satisfies CWA section 301(b)(1)(C) and 40 CFR 122.44(d)(1)(ii) with respect to a water quality criteria for methylmercury expressed as fish tissue value, in the absence of a water column translation of that value.

EPA believes that, depending on the particular facts, a permitting authority could reasonably conclude that reasonable potential exists if two conditions are present (1) the NPDES permitted discharger has mercury in its effluent at a quantifiable level and (2) fish tissue from the waterbody into which the discharger discharges exceeds the fish tissue water quality criterion. Under these circumstances, the effluent data indicates that the mercury loadings in the effluent contribute to the mercury load to the waterbody, and the fish tissue indicates that the mercury load causes a water quality criterion excursion. This approach is also consistent with federal regulations pertaining to the Great Lakes Basin that contained an approach for determining reasonable potential using fish tissue data (see 40 CFR Part 132, Appendix F, Procedure 5.F.4). EPA recommends that permitting authorities use this approach because it has the advantage of significantly reducing environmental monitoring costs and does not involve developing a site-specific BAF for each waterbody in a state.

EPA recognizes that the mere presence of mercury at a quantifiable level in an effluent is not necessarily an indication that the mercury discharge is the sole cause of the fish contamination or even a substantial contributor of such contamination. However, mercury in an effluent discharge may contribute to the mercury present in fish tissue at levels above the fish tissue criterion, and therefore the discharge may be found, in some circumstances, to exhibit the reasonable potential to cause or contribute to the excursion above applicable water quality standards. EPA notes that the reasonable potential procedures as a whole are intended as conservative screening procedures to determine when a permit should contain a WQBEL to reduce the contribution to existing contamination or to prevent further possible degradation.

EPA notes that, unlike typical water quality criteria that are expressed as water column values, the fish tissue residue water quality criterion integrates spatial and temporal complexity and the cumulative effects of loadings from point and nonpoint sources that occur in aquatic systems that affect methylmercury bioaccumulation, including the effluent variability of point sources. Therefore, EPA believes that comparing the fish tissue residue concentration in receiving water directly to the applicable criterion expressed as a fish tissue value appropriately accounts for the factors specified in 40 CFR 122.44(d)(1)(ii) for a criterion expressed as a fish tissue residual value.

7.5.1.1 How to determine that the NPDES permitted discharger has mercury in its effluent at quantifiable levels

EPA recommends that permitting authorities require some monitoring using the appropriate version of Method 1631 to characterize the discharger's effluent for mercury from all facilities for which the mercury levels are unknown or undetected. Method 1631 is relatively new, and the facility might not have used it to analyze its effluent. As a

result, previous monitoring might show undetectable levels of mercury when use of Method 1631 would show detectable or quantifiable amounts. As a result, EPA recommends monitoring using Method 1631 to help identify all facilities that contribute to mercury water quality impairment. At time of permit issuance, the permitting authority should have at least one data point using Method 1631 as part as the permit application submitted by the facility.

One of three outcomes will be reached in answering the first condition of the above described reasonable potential analysis:

- It is unknown whether the discharge includes quantifiable amounts of mercury.
- The discharge does not include quantifiable amounts of mercury.
- The discharge includes quantifiable amounts.

The recommended reasonable potential determination and recommended permit conditions for each of the outcomes is described in detail below.

7.5.1.1.1 *What are the recommended permit conditions when it is unknown whether the discharge includes quantifiable amounts of mercury because there are limited or no effluent data to characterize the discharge of mercury using Method 1631?*

In this situation, EPA recommends the permitting authority include permit conditions comprised of:

- Effluent monitoring using the appropriate version of Method 1631 to characterize the discharger's effluent for mercury
- A reopener clause to identify the actions that the permitting authority may take should the monitoring information indicate that a mercury effluent limit is necessary

EPA recommends that permitting authorities require some monitoring, using the appropriate version of Method 1631, by all facilities for which the mercury levels are unknown or previously undetected to characterize the discharger's effluent for mercury, unless prior testing was done using Method 1631. Method 1631 is relatively new, and the facility might not have used it to analyze its effluent. As a result, the previous monitoring might show undetectable levels of mercury when using Method 1631 would show detectable or quantifiable amounts. As a result, EPA recommends this additional monitoring to help identify all facilities that contribute to mercury water quality impairment. The permitting authority could obtain this monitoring data either as part of the permit application, by requiring periodic (e.g., quarterly to annually) monitoring as part of the permit, or the permitting authority could invoke its authority under CWA section 308 to require NPDES facilities to collect information necessary for the development of NPDES permit limits. The permit should include a reopener clause such that, as soon as there is complete information and an indication that a more stringent limit is required, the permitting authority can establish the necessary requirements. The permitting authority may also decide to no longer require the monitoring if the information shows that the facility is not discharging mercury at quantifiable levels.

EPA recommends that when selecting the monitoring frequency, permitting authorities consider the factors in section 5.7.5 of the *Technical Support Document for Water Quality-based Toxics Control* (USEPA 1991). This section acknowledges that EPA has not recommended a specific monitoring frequency, but recognizes that the choice of a monitoring frequency is a site-specific decision and provides the permitting authority a number of factors to consider when making these decisions.

Until the permitting authority has sufficient data to determine whether there is reasonable potential, and depending on the particular facts, these permit conditions might be considered as being as stringent as necessary to meet water quality standards, as required by CWA section 301(b)(1)(C).

7.5.1.1.2 What are the recommended permit conditions when the discharge is analyzed using Method 1631 and does not include quantifiable amounts of mercury?

In this situation, EPA recommends the permitting authority first review the monitoring data to determine if it is representative of the effluent. If the permitting authority believes the monitoring data are representative and all data are below the level of quantification, no further permit conditions may be necessary. If the discharge is below the level of quantification, EPA does not consider the discharge to have reasonable potential to cause or contribute to an excursion of the applicable fish tissue water quality criterion. In contrast, if the permitting authority believes the data are not representative, the authority should consider requiring additional monitoring, as described in section 7.5.1.1.1 above.

7.5.1.1.3 What are the recommended actions for discharges that include quantifiable amounts of mercury?

In this case, the permitting authority should evaluate data on the concentrations of mercury in the fish tissue from the waterbody into which the discharger discharges and determine appropriate permit conditions (see section 7.5.1.2 below).

7.5.1.2 How to determine appropriate permit conditions for facilities discharging quantifiable amounts of mercury

When applying EPA's recommended fish tissue reasonable potential procedure, once the permitting authority has concluded that the first condition of the two-part reasonable potential analysis has been satisfied (i.e., that the NPDES permitted discharger has mercury in its effluent at a quantifiable level), the permitting authority should then address the second condition. That is, does the fish tissue from the waterbody into which the discharger discharges exceed the fish tissue water quality criterion?

One of three outcomes will be reached in answering this question:

- The fish tissue concentration of mercury is unknown.
- The fish tissue concentration of mercury does not exceed the criterion.
- The fish tissue concentration of mercury exceeds the criterion.

For discharges with quantifiable levels of mercury, the recommended reasonable potential determination and recommended permit conditions for each of the outcomes is described in detail below.

EPA recognizes that when evaluating reasonable potential, the permitting authority should exercise discretion and careful judgment in determining whether fish tissue data are representative of current ambient conditions. EPA guidance for sampling strategies for fish tissue monitoring is provided in section 4.2 of this guidance.

7.5.1.2.1 *What are the recommended permit conditions for facilities discharging quantifiable amounts of mercury but the concentrations of mercury in tissue of fish in the receiving waterbody are unknown?*

In waterbodies for which there are no fish tissue data, a permitting authority cannot determine whether there is reasonable potential using a fish tissue approach. Therefore, EPA recommends the permitting authority include permit conditions comprised of:

- A permit special condition to conduct a mercury fish tissue survey for the receiving water
- A reopener clause to identify the actions that the permitting authority may take should the monitoring information indicate that a mercury effluent limit is necessary
- A permit special condition under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4) to develop a mercury minimization plan for facilities that use mercury in any aspect of their operations or accept wastewaters that may contain mercury

In this instance, the permitting authority should start a process for collecting fish tissue data in the vicinity of the facility. One approach for collecting this information is for the permitting authority to invoke its authority under CWA section 308 (state permitting authorities would use comparable state authorities) to require NPDES facilities to collect information necessary for the development of NPDES permit limits. In this case, the permitting authority could issue a section 308 letter or include special conditions in the permit to require the permittee to conduct a methylmercury fish tissue monitoring study. EPA recommends that the permitting authority require that the study design be consistent with the recommendations on conducting ambient monitoring in section 4.2 of this guidance.

EPA recommends that the permitting authority require only one study per waterbody. The authority could do this by contacting all facilities that discharge into the waterbody and encourage them to jointly work to conduct the study. Additionally, in waterbodies where the permitting authority expects to find high water column values or believes it will need a site-specific BAF to complete issuing the permits, the authority should consider requiring the facility to measure water column concentrations of mercury as part of the study.

EPA further recommends that the permit should include a reopener clause such that, as soon as there is complete information and an indication that a more stringent limit is required, the permitting authority can establish the necessary requirements.

Additionally, in this situation EPA recommends that the permit should also include a pollutant minimization plan for the reasons as described in section 7.5.1.2.2 below.

7.5.1.2.2 *What are the recommended permit conditions for facilities discharging quantifiable amounts of mercury but the concentrations of mercury in tissue of fish in the receiving waterbody do not exceed the criterion?*

If the concentration of mercury in tissue of fish in the receiving water does not exceed the criterion, depending on the particular facts, the permitting authority might reasonably conclude that the discharge does not have reasonable potential to cause or contribute to an excursion of the applicable fish tissue water quality criterion.

In such situations, EPA recommends the permitting authority consider including permit conditions comprised of a permit special condition under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4) to develop a mercury minimization plan for facilities that use mercury in any aspect of their operations or accept wastewaters that may contain mercury.

A mercury minimization plan helps ensure that the discharge continues to have no reasonable potential to cause or contribute to an exceedence of water quality standards. The recommendation to consider including in the permit a requirement to develop a mercury minimization plan is also based on the extent of potential mercury impairment across the country and the scientific complexities of and uncertainties when assessing mercury loadings and evaluating these effects. Given these uncertainties, a permit requirement that a permittee at least develop a plan to minimize the discharge of mercury would ensure that if the monitoring data demonstrates that a discharge does have reasonable potential, the permittee and the permit writer are prepared to establish a limit as stringent as necessary. Furthermore, EPA believes that a requirement simply to develop a mercury minimization plan may provide dischargers of mercury with sufficient information to voluntarily and economically reduce the discharge of mercury into our nation's waters.

EPA recommends that facilities, when developing mercury minimization plans, start with their existing best management plans and spill prevention and containment control plans. Many of the activities covered by these plans can also serve to reduce mercury sources to wastewater. In addition, for facilities that do not use mercury in any aspect of their operations or accept wastewaters that may contain mercury, EPA does not believe these facilities have pollution prevention opportunities and, thus, should not be required to develop a mercury minimization plan.

The facility should determine the content of a mercury minimization plan on a case-by-case basis. After reviewing many PMPs, EPA recommends that a plan include at least the following elements:

- The identification and evaluation of current and potential mercury sources
- For POTWs, the identification of both large industrial sources and other commercial or residential sources that could contribute large mercury loads to the POTW
- Monitoring to confirm current or potential sources of mercury

- The identification of potential methods for reducing or eliminating mercury, including requiring BMPs or assigning limits to all potential sources of mercury to a collection system, material substitution, materials recovery, spill control and collection, waste recycling, process modifications, housekeeping and laboratory use and disposal practices, and public education
- Implementation of appropriate minimization measures identified in the plan
- Monitoring to verify the results of pollution minimization efforts

7.5.1.2.3 *What are the recommended permit conditions for facilities discharging quantifiable amounts of mercury and the concentrations of mercury in tissue of fish in the receiving waterbody exceed the criterion?*

EPA believes that, depending on the particular facts, a permitting authority might reasonably conclude that reasonable potential exists if two conditions are present (1) the NPDES permitted discharger has mercury in its effluent at quantifiable levels, and (2) the concentrations of mercury in tissue of fish from the waterbody into which the discharger discharges exceed the fish tissue water quality criterion. When reasonable potential exists, it is necessary to establish an appropriately protective WQBEL in the permit. For guidance on how to develop appropriate WQBELs, see the following section.

7.5.2 *Where reasonable potential exists, how can WQBELs be derived from a tissue value?*

As discussed in section 3.1.2.1 of this document, EPA recommends that states and authorized tribes adopt new or revised methylmercury water quality criteria in the form of a fish tissue residue concentration. When adopted in standards as a tissue value, states and authorized tribes do not translate from a tissue residue value to a traditional water column value using BAFs, which can vary highly by location and can entail extensive costs to develop. When developing WQBELs, the permitting authority must ensure that the level of water quality to be achieved by such limits is “derived from and complies with water quality standards” (see 40 CFR 122.44(d)(1)(vii)). This section provides recommendations for how a permitting authority could derive appropriate WQBELs in the absence of an available translation of the fish tissue value to a water column value. The process described in this section is shown in Figure 7.

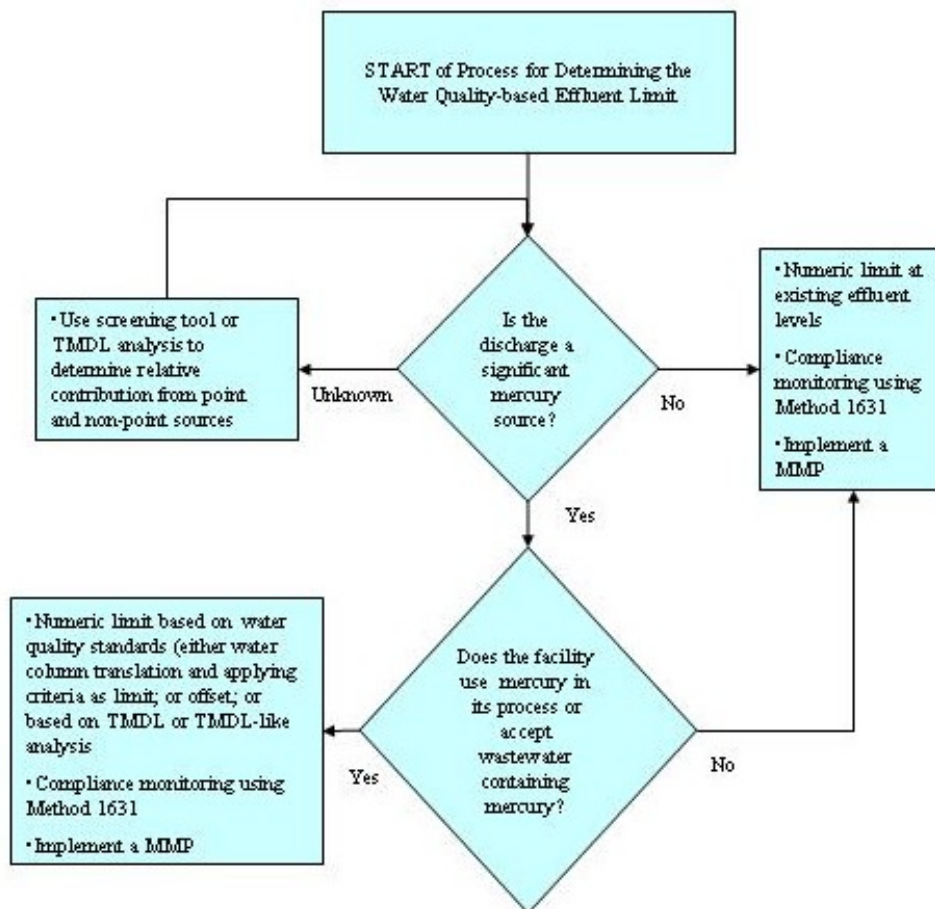


Figure 7. Process for determining the WQBEL

EPA recommends that the permitting authority, when establishing appropriate WQBELs, first determine whether the discharge is a significant source of mercury. EPA recommends different WQBELs depending on whether the discharge is considered to be significant or not significant, as described in 7.5.2.3 and 7.5.2.2, respectively. EPA's guidance on how to determine whether a discharge is significant is described in section 7.5.2.1 below. Additionally, EPA recommends that the permitting authority, when establishing appropriate WQBELs for a significant discharger, consider whether the facility uses or accepts mercury in its process.

The NPDES permit fact sheet must provide an explanation that how the WQBELs proposed in the associated draft permit are appropriate. The recommendations in this guidance could be applied on a permit-by-permit basis where appropriate to support effluent limitations and other conditions that satisfy CWA section 301(b)(1)(C) and 40 CFR 122.44(d)(1) with respect to mercury.

7.5.2.1 How to determine if the discharge is a "significant" source of mercury

When determining the sufficiency of a WQBEL to attain and maintain water quality standards, the permitting authority may consider the effluent controls in conjunction with the other point and nonpoint source controls (including expected mercury reductions

from airborne deposition as a result of existing or expected controls on air emissions) and their cumulative effect on water quality standards attainment. Because air deposition and other nonpoint sources are expected to play a significant role in the mercury loading to many waters, EPA recommends that permitting authorities take into account these loadings—and their potential change—when determining what WQBELs are appropriate. One way of doing this is to use a screening level approach, such as that used in Mercury Maps²¹ (USEPA 2001d). The Mercury Maps report identified watersheds where EPA believed mercury air deposition likely contributed greater than 95 percent of mercury concentrations in fish tissue. For example, mercury mines, large-producer gold mines, and mercury-cell chlor-alkali facilities were considered significant sources on the basis of simple presence in the watershed. Municipal wastewater treatment plants and pulp and paper mills were considered significant when their estimated cumulative load contributed greater than 5 percent of the estimated waterbody-delivered air deposition load. Another option for determining the relative significance of point source discharges is to do a TMDL, or TMDL-like analysis, as part of the permit. Depending on the facts in each case, permitting authorities should determine what sources are potentially large sources of mercury other than air deposition.

For a discharge not to be considered “significant,” under existing loading conditions, EPA recommends that the loading of the point source (or cumulative loading of all point sources) to the receiving water are expected to account for a small or negligible component of the current total mercury loadings and that, upon implementation of the permit’s mercury minimization program requirements, any further reductions from the point source(s) would result in no discernable improvement in water quality. This is not a situation where a wasteload allocation to a point source is increased because of an assumption that loads from nonpoint sources will be reduced. To the contrary, this is a situation where mercury minimization activities will maintain or reduce current point source loadings of mercury to levels at which there are no discernable impacts to water quality.

If permitted discharges are regulated consistent with the recommendations described in this guidance, EPA believes that the discharge is likely to have no discernible effect on water quality. EPA believes that discharger mercury loadings that remain following implementation of the minimization program requirements would have no discernible impact to water quality because, due to the large contribution of mercury from nonpermitted sources, even entirely eliminating the point source discharges of mercury would cause no discernible improvement to water quality. Therefore, EPA believes, depending on the particular facts, limits on these point sources consistent with this guidance are likely to be as stringent as necessary to implement water quality standards.

EPA notes that point source discharges of bioaccumulative chemicals like mercury might have particular local significance apart from their contribution to the cumulative load. Point source discharges by their nature could create hot spots where observed elevated concentrations have potential impact on human health if fish stay in the immediate area. Consequently, comparing contributions from the air and water sources at long distances downstream from the point source could conceal the real impact of mercury from point

21 For more information about Mercury Maps see section 4.2.2.

source discharges. Instead, permitting authorities should evaluate the relative contributions of point sources to the total load at the point of discharge. In some cases, elevated receiving water concentrations may be dictated caused solely by the mercury concentration in the effluent as opposed to the mercury delivered from air deposition.

7.5.2.2 What are EPA's recommended permit conditions for discharges that are not significant sources of mercury?

Here, a permitting authority is addressing the situation where there are data showing that there is reasonable potential and thus a WQBEL is necessary. However, if one's mercury discharge is determined to be insignificant, EPA believes that an appropriate WQBEL could be comprised of both of the following:

- A numeric effluent limit for the mass loading of mercury established at the existing effluent level (or any existing numeric limit, whichever is more stringent) including compliance monitoring using the appropriate version of Method 1631
- A permit condition to implement appropriate mercury minimization measures identified in a mercury minimization plan

EPA believes these minimum permit conditions may be appropriate because they help to ensure the discharge does not cause or contribute to an exceedence of water quality standards, to protect against possible localized impacts, and to minimize the discharge of mercury. EPA also believes that, depending on the particular facts, when the discharge is not a significant source of mercury, permit numeric effluent limits established at the existing effluent quality (or any existing numeric limit, whichever is more stringent) and implementation of a mercury minimization plan are likely to be as stringent as necessary to meet water quality standards.

EPA believes that mercury reductions achieved through implementation of mercury minimization programs could potentially result in important reductions in mercury loadings. EPA bases this belief on its study of pollutant minimization programs and their success in reducing loadings of mercury to the environment. See the *Mercury Report to Congress* (USEPA 1997b) and draft *Overview of P2 Approaches at POTWs* (USEPA 1999). These reports show that POTWs and industrial dischargers have implemented source controls, product substitution, process modification, and public education programs with great success. These minimization practices focus on sources and wastes that originate with and are under the reasonable control of a facility, and not pollutants in rainwater or source water.

As an example, POTWs can educate the public to prevent pollution by avoiding household products that contain high levels of mercury or substituting those products for ones that are mercury-free or more environmentally friendly. The most cost-effective approach for POTWs to substantially reduce mercury discharges appears to be pollution prevention and waste minimization programs that focus on high concentration, high volume discharges to the collection system, with considerable effort also directed at high concentration, low volume discharges such as medical and dental facilities.

Using pollutant minimization or prevention programs can also reduce the transfer from wastewater to other media via disposal of mercury-containing sludge that may reenter the

environment. For example, mercury removed at a POTW through treatment is likely to reenter the environment through POTW sludges that are then either incinerated or applied to land (although some is captured by air emission controls on incineration). EPA believes that a better approach for reducing mercury releases to the environment is to prevent mercury from entering the wastewater collection system at the source through product substitution, waste minimization or process modification, or remove and recycle mercury at the source (i.e., source controls) using state-of-the-art technology. These measures aimed at reducing influent loads to POTWs also reduce the use of mercury in the community, which could also reduce the amount of mercury entering the environment through other media or sources (e.g., products that contain low levels of mercury may be disposed of as a nonhazardous solid waste and incinerated, releasing mercury to the air). Where pollution prevention approaches have been implemented, substantial reductions in mercury concentrations in POTW influents, sludges, and effluents have been achieved. For a discussion of this, see the draft *Overview of P2 Approaches at POTWs* (USEPA 1999). For an example of guidance on how to develop a mercury minimization plan, see the EPA Region 5 final document *Mercury Minimization Program Guidance* dated November 2004 (http://www.epa.gov/region5/water/npdestek/mercury_pmp_nov_04_guidance.pdf). Many of the recommendations contained in the document are drawn from existing guidance and practice of the state permitting authorities in Region 5.

Finally, mercury is a bioaccumulative, persistent pollutant that has been linked to adverse health effects. For example, children who are exposed to low concentrations of methylmercury prenatally might be at risk of poor performance on neurobehavioral tests, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory. In this scenario, EPA believes, as a matter of policy, that point sources that can cost effectively reduce their mercury discharges should do so. Because air sources or historical contamination are likely dominant causes of impairment this does not mean that point sources should not implement cost-effective, feasible pollution prevention measures to reduce their contribution of mercury, however small, to the environment. In short, EPA believes it is reasonable to expect that NPDES permittees implement cost-effective, feasible, and achievable measures to reduce the amount of mercury they discharge into the environment and that, depending on the particular facts, permit limits that require such implementation are likely to derive from and comply with water quality standards as required by EPA regulations at 40 CFR 122.44(d)(vii)(A).

7.5.2.3 What are EPA's recommended permit conditions for discharges that are significant sources of mercury?

If a facility is a significant source of mercury, the permitting authority should first consider whether or not the facility uses mercury in its process or accepts wastewater containing mercury when deciding on appropriate WQBELs.

7.5.2.3.1 What are appropriate WQBELs for significant dischargers that do not use mercury and do not accept wastewater containing mercury in their processes?

For significant dischargers that do not use mercury in their processes and do not accept wastewater containing mercury, EPA believes that the permitting authority may express the WQBEL that is comprised of the following:

- A numeric effluent limit for the mass loading of mercury established at the existing effluent level of mercury (or any existing numeric limit, whichever is more stringent) including compliance monitoring using the appropriate version of Method 1631
- A permit condition to implement appropriate mercury minimization measures identified in a mercury minimization plan

If such a discharge has the reasonable potential to cause or contribute to an exceedence of water quality standards and the discharge is significant, EPA believes that during the first term of the permit and depending on the particular facts, permit terms that limit the discharge of mercury to existing effluent quality (or any existing numeric limit, whichever is more stringent), require the facility to develop and implement a mercury minimization plan, and require monitoring are likely to be as stringent as necessary to meet water quality standards. Given the extent of mercury impairment across the United States mostly due to nonpoint sources such as air deposition or previous contamination, and that assuming these dischargers do not use or accept mercury in their processes but rather receive it from diffuse sources, EPA believes that, depending on the particular facts, permit conditions that prohibit an increase of mass loadings of mercury and mandate a reduction of loadings when consistent with a mercury minimization plan are likely to be as stringent as necessary to meet standards as required by CWA section 301(b)(1)(C). EPA generally believes these minimum permit conditions are appropriate and sufficient to ensure the discharge does not cause or contribute to an exceedence of water quality standards, protect against possible localized impacts, and minimize the discharge of mercury. EPA believes these permit terms are appropriate in cases where the facility itself does not use mercury in its processes. EPA expects that the implementation of a mercury minimization plan will reduce the discharge of mercury. However, if at the end of the first permit term, data and information indicate that a more stringent limit is necessary to ensure that the discharge does not cause or contribute to an exceedence of water quality standards, including localized effects, the permit should be revised at renewal.

7.5.2.3.2 What are appropriate WQBELs for significant dischargers that use mercury in their processes or accept wastewater containing mercury?

For significant dischargers that use mercury in their processes or accept wastewater containing mercury, EPA believes that the permitting authority may express the WQBEL that is comprised of the following:

- A numeric WQBEL for the mass loading of mercury. Such a limit could be based on a TMDL, a TMDL-like analysis, an offset, or established using the criteria as the effluent limit (through development of a site-specific BAF) including compliance monitoring using the appropriate version of EPA Method 1631

- A permit condition to implement appropriate mercury minimization measures identified in a mercury minimization plan

Because there are significant direct water inputs of mercury from these facilities, states and authorized tribes should carefully consider making these watersheds a priority for TMDL development so that the TMDL can provide the basis for the appropriate permit limits. Cumulative loads from point sources and localized nonpoint sources such as abandoned mines, contaminated sediments, and naturally occurring sources can potentially combine to cause localized impairment due to mercury. These situations are more complicated because the specific location and magnitude of each source could be significant as to its effect on fish tissue concentrations. For these situations, a TMDL provides the best basis for developing the appropriate permit limits, and thus, these situations should receive a higher priority for completion.

Once EPA has approved or established a TMDL containing a wasteload allocation for the discharge of mercury, the permitting authority develops a WQBEL for a point source discharge that is consistent with the requirements and assumptions of the wasteload allocation in the TMDL (See 40 CFR 122.44(d)(1)(vii)(B)). Besides developing a WQBEL, the permitting authority also specifies monitoring requirements for the WQBEL (See 40 CFR 122.44(i) and 122.48). EPA recommends that permitting authorities require the permittee to use the version of Method 1631 then in effect to assure that even trace levels of mercury are quantified.

In addition, EPA recommends that the permit require the dischargers to implement appropriate mercury minimization measures identified through the mercury minimization plan if the monitoring data shows that mercury is present in the final effluent. In many instances, the mercury minimization plan may be a recommended part of the wasteload allocation. Where it is not, EPA believes that implementing the plan should help the facility achieve the WQBEL.

In the absence of a final TMDL, a permitting authority could develop an analysis similar to what would be provided in a TMDL. Such a TMDL-like analysis that applied similar factors used in a TMDL could be included in the fact sheet of the draft permit as a justification for the effluent limit being as stringent as necessary to attain the water quality standard.

It is also possible for the permitting authority to issue a discharger a permit prior to TMDL development where it is demonstrated that other pollutant source reductions (such as nonpoint source reductions implemented by the discharger or other sources) will offset the discharge in a manner consistent with water quality standards. The ultimate result of this type of “offset” may be a net decrease in the loadings of the pollutant of concern in the CWA section 303(d) listed water, and therefore, the point source being permitted might be considered as not causing or contributing to a violation of water quality standards.

Establishing the proper WQBEL in a specific permit is a fact-based determination. There are a number of ways to develop a permit that ensure that a discharge does not cause or contribute to an exceedence of water quality standards. Historically, EPA has not considered a discharge with effluent limitations at or below either the numeric water

quality criteria or a quantification of a narrative water quality criterion to “cause or contribute to a violation of water quality standards.”

For these significant dischargers, a state or authorized tribe may decide to translate the fish tissue criterion into a water column value for use in making reasonable potential determinations and developing appropriate numeric WQBELs. Section 3.1.2.2 of this guidance discusses the procedures for translating the fish tissue criterion into a water column value for water quality standards purposes. These procedures may also be used to translate a fish tissue criterion into a water column value for reasonable potential determinations and numeric WQBELs. Once the criterion has been translated into a water column value that accounts for the effects of bioaccumulation, the TSD (USEPA 1991) or equivalent state procedures can be used to complete a reasonable potential determination and develop numeric WQBELs. Once such a water column criteria concentration value is developed, a WQBEL established at the criterion concentration would be appropriate for receiving waters that exceed the fish tissue criterion.

7.5.2.4 What are EPA’s recommendations for indirect dischargers to POTWs that are significant sources of mercury?

POTWs are required to prohibit discharges from Industrial Users in amounts that result in or cause a violation of any requirement of the POTW’s NPDES permit. (See 40 CFR 403.2(a) and (b), 403.3(i) and 403.3(n)). POTWs that accept mercury in their collections systems may need to ensure that their pretreatment program protects the POTW’s effluent from contributing to excursions of the fish tissue criterion. The General Pretreatment Regulations (40 CFR 403) require that each POTW required to develop an approved pretreatment program must protect against pass through and interference which may be caused by industrial discharges to the treatment facilities by developing local limits for mercury and other pollutants or demonstrating that limits are not necessary for these pollutants. POTWs are also required to prohibit discharges from Industrial Users in amounts that result in or cause a violation of any requirement of the POTW’s NPDES permit. (See 403.2(a) and (b), 403.3(i) and 403.3(n)).

Federal categorical pretreatment standards, which are applicable to certain classes of industries, establish technology-based minimum pretreatment standards. However, the categorical standards do not address POTW-specific problems which may arise from discharges by categorically regulated industries. In addition, many types of industries that discharge significant quantities of pollutants are not regulated by the categorical standards. Hence, there is a need for many POTWs to establish site-specific discharge limits in order to protect the treatment facilities, receiving water quality, and worker health and safety, and to allow for beneficial use of sludge.

As described above, this guidance typically recommends that permit limits for POTWs consist of a numeric effluent limit and a requirement to develop and implement appropriate mercury minimization measures. EPA expects that a POTW’s numeric limit for mercury would be the basis for the development of local limits in the pretreatment program consistent with guidance on the development of local limits. The mercury minimization program requirements could also be the basis for establishing pollutant minimization program requirements for dischargers to the collection system.

7.6 What are the recommended analyses for new sources or new dischargers discharging quantifiable amounts of mercury?

Additional permitting requirements apply to new sources or new dischargers that will be discharging new or increasing concentrations of pollutants. The NPDES regulations at 40 C.F.R. §122.4(i) currently prohibit the issuance of a permit to a new source or new discharger whose discharge will cause or contribute to a violation of water quality standards.

In addition, such increased discharges of mercury must be consistent with the applicable antidegradation policy. Federal regulations at 40 CFR 131.6 specify that tribal or state water quality standards must include an antidegradation policy. Federal Regulations at 40 CFR 131.12 identify the elements of an acceptable antidegradation policy. The Federal antidegradation policy is composed of three levels of protection commonly referred to as tiers. The first element identified at 40 CFR 131.12(a)(1) protects the minimum level of water quality necessary to support existing uses and applies to all waters. This element prohibits lowering water quality to the point where existing uses are impaired. The second element is found at 40 CFR 131.12(a)(2), and protects water quality where water quality is better than that needed to support designated uses in and on the water. Where these conditions exist, the water body is considered not impaired and water quality must be maintained and protected unless it is demonstrated that lowering water quality is necessary to support important social and economic development and that existing uses will be fully protected. The third element at 40 CFR 131.12(a)(3) involves the protection of water quality in water bodies that are of exceptional ecological, aesthetic or recreational significance. Water quality in such water bodies, identified and specifically designated by States as Outstanding National Resource Waters must be maintained and protected.

One potential means of satisfying antidegradation (and 40 CFR 122.4(i) for new sources or new dischargers to water quality limited segments) may be a demonstration that other mercury source reductions (such as nonpoint source reductions implemented by the discharger) will offset the new or increased discharge. The ultimate result of this type of “offset” might be a net decrease in the loadings of mercury to the receiving water, and therefore, depending on the particular facts, the discharge might not be considered an increased loading. EPA’s recommendations for addressing mercury in new sources and new discharges are summarized in Figure 8.

7.6.1 *What are the recommendations for permitting authorities when considering issuing permits for new sources or new dischargers where the fish tissue concentrations in the receiving waterbody are unknown?*

In waterbodies for which there are no fish tissue data, a permitting authority cannot determine the applicable antidegradation requirements. In these instances, the permitting authority should start a process for collecting such data in the vicinity of the facility. One approach for collecting this information is for the permitting authority to invoke its authority under CWA section 308 to require point sources to collect information necessary for the development of NPDES permit limits. In this case, the permitting authority could issue a section 308 letter to require the permittee to conduct a methylmercury fish tissue monitoring study prior to issuance of a permit. EPA

recommends that the permitting authority require that the study design be consistent with the recommendations on conducting ambient monitoring in section 4.2 of this guidance.

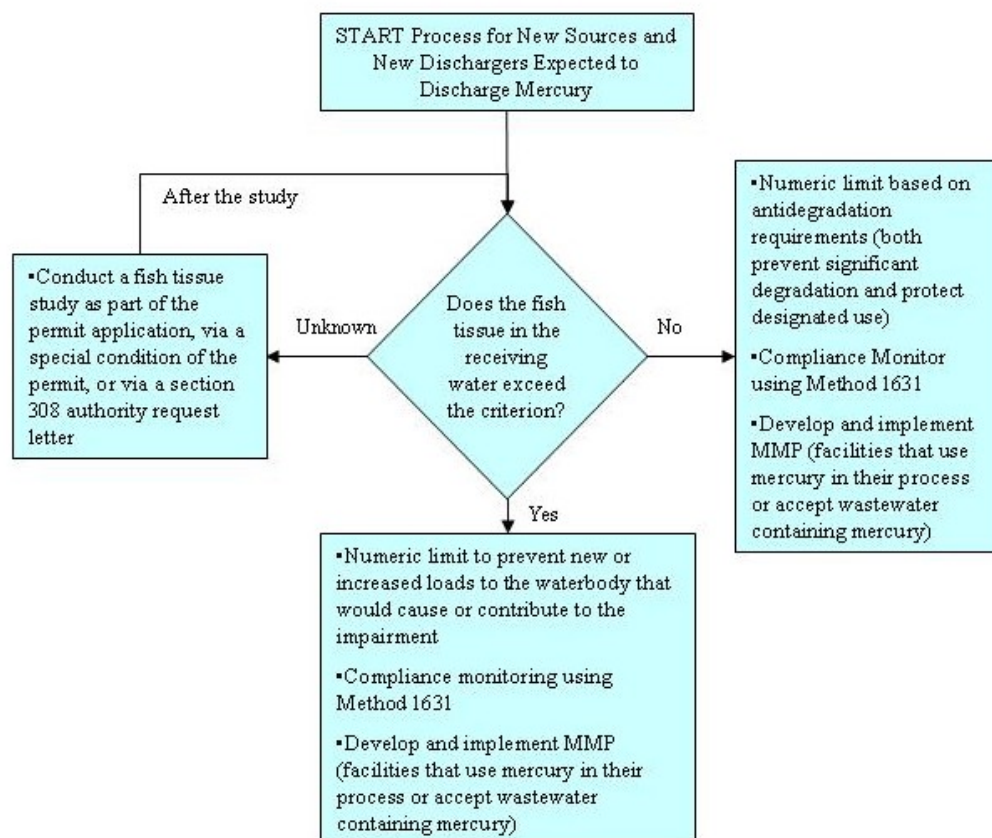


Figure 8. Procedures for addressing new sources and new discharges

Once the permitting authority has determined the appropriate antidegradation requirements on the basis of the fish tissue concentrations in the receiving water, the permitting authority can then determine the appropriate permit requirements for new sources or new dischargers, as described below.

7.6.2 What are the recommended permit conditions for new sources or new dischargers where the fish tissue in the receiving water does not exceed the criterion?

In this situation, EPA believes that the permitting authority may establish permit conditions that are comprised of the following:

- A numeric effluent limitation, the level to which the discharger is ultimately allowed to lower water quality (on the basis of the applicable antidegradation requirements) including compliance monitoring using the appropriate version of Method 1631

- A permit condition to implement appropriate mercury minimization measures identified through the mercury minimization plan if the facility uses mercury in its process or accepts wastewater containing mercury

In this case, the receiving water does not currently exceed the fish tissue criterion. EPA believes that new sources or new dischargers that increase the discharge of mercury should be required to implement mercury minimization plans and should be allowed to discharge at levels as determined by the antidegradation analysis.

Permits for proposed new sources or new dischargers of mercury that would lower water quality in a high-quality water must be consistent with the applicable antidegradation provisions of a state's or authorized tribe's water quality standards. Under EPA's antidegradation regulations for water quality standards, the quality of waters better than levels necessary to protect human health can be lowered only if the state or authorized tribe determines that allowing lower water quality is necessary to accommodate important economic or social development in the area in which the waters are located (see 40 CFR 131.12(a)(2)). EPA encourages states and authorized tribes to regard *any* increase in mercury used in a discharger's process or in wastewater accepted by a discharger as a significant lowering of water quality for the purposes of triggering a tier 2 antidegradation review. If the state's or authorized tribe's antidegradation analysis determines that the proposed lowering of water quality should not be allowable, the permitting authority would not authorize or allow any such new or increased discharge. Where the state's or authorized tribe's antidegradation analysis determines that a lowering of water quality is allowable, the level to which the discharger is ultimately allowed to lower water quality (on the basis of the applicable antidegradation requirements) would then be subject to a reasonable potential analysis. Also, EPA's antidegradation regulations for water quality standards protect the minimum level of water quality necessary to support existing uses by prohibiting lowering water quality to the point where existing uses are impaired (see 40 CFR 131.12(a)(1)).²²

EPA recognizes that an increase in the discharge of mercury may be due to the presence in stormwater or input process water that does not originate with and is not under the reasonable control of a facility. While an mercury minimization plan, to the extent that there are available BMPs to minimize mercury discharges, may still be appropriate in such circumstances, EPA would not generally expect that such dischargers would trigger the need for an antidegradation review or numeric WQBELs, unless they were causing or contributing to a significant lowering of water quality.

In addition, EPA recommends that the permit require the dischargers to implement appropriate mercury minimization measures identified through the mercury minimization plan if the facility uses mercury in its process or accepts wastewater containing mercury.

²² This part of the antidegradation analysis is similar to the reasonable potential determination and WQBEL development process that a permitting authority conducts for an existing discharger. See sections 7.5.1.2.2 and 7.5.2 for more details.

7.6.3 What are recommended permit conditions for new sources or new dischargers where the fish tissue in the receiving water exceeds the criterion?

In this situation, EPA believes that the WQBEL may be comprised of the following:

- A numeric WQBEL for the mass loading of mercury established at levels consistent with 40 CFR 122.4(i) and 122.44(d)(1)(vii). Such a limit could be based on a TMDL, a TMDL like analysis, or via an offset, including compliance monitoring using the appropriate version of Method 1631
- A permit condition to implement appropriate mercury minimization measures identified through the mercury minimization plan if the facility uses mercury in its process or accepts wastewater containing mercury

Existing EPA regulations do not establish an absolute prohibition on new or increasing discharges for point sources on water quality limited segments. Instead, the NPDES regulations at 40 CFR 122.4(i) prohibit the issuance of a permit to a new source or new discharger whose discharge will cause or contribute to a violation of water quality standards, including the applicable antidegradation policy. A permit may be issued if the discharge would not cause or contribute to the exceedence of the water quality standards. For example, it is possible for a discharger to be issued a permit, under appropriate circumstances, where it is demonstrated that other pollutant source reductions will offset the discharge in a manner consistent with water quality standards. The ultimate result of this type of offset may be a net decrease in the loadings of the pollutant of concern in the impaired water and, therefore, be considered not to “cause or contribute to a violation of water quality standards.” This regulation applies only to “new sources” and “new dischargers” as defined in sections 122.2 and 122.29 of the NPDES regulations. Existing dischargers and increases in existing discharges are not subject to this regulation.

Existing dischargers, as well as new sources and new dischargers, are subject to the regulation at 40 CFR 122.44(d)(1)(vii) (A). That regulation provides that when developing water quality-based permit effluent limitations, the permitting authority is to set the limitations to ensure that the level of water quality to be achieved “is derived from, and complies with all applicable water quality standards.” This would necessarily be a permit-by-permit determination. After a TMDL has been established, the regulation provides that the effluent limitations must be consistent with the assumptions and requirements of any approved wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)).

Where a facility has a currently effective effluent limit for mercury and seeks a less stringent limit, the permitting authority must also comply with anti-backsliding requirements (see CWA section 402(o) and 40 CFR 122.44(l); see also CWA section 303(d)(4)). These requirements are described in EPA’s *NPDES Permit Writers Manual* (USEPA 1996a).

7.7 What are the special conditions for mercury in a facility's intake?

7.7.1 *How to consider mercury intakes with a reasonable potential approach*

For some dischargers, the only source of mercury in a facility's discharge might be the intake water from the same body of water as where the facility discharges. An example of this is a discharge of cooling water where the source of the cooling water is upstream of the discharge. In these situations, where there are no known sources or additional contributions of mercury at the facility, the permitting authority could decide that there is no reasonable potential for the discharge to exceed water quality standards. Furthermore, any slight increase in concentration after discharge (due to evaporation or other water loss) should not have an effect on the bioaccumulation of methylmercury in the fish unless the fish are known to frequently inhabit the water immediately in the area of the discharge. In making this decision, the permitting authority should conduct monitoring of both the intake and discharge to verify that there are no known sources of additional contributions of mercury at the facility. Also, EPA recommends that permitting authorities consider requiring an evaluation of whether the methylmercury concentration significantly increases for facilities with anaerobic conditions in the discharge. This approach is also consistent with federal regulations pertaining to the Great Lakes Basin that contained an approach for determining reasonable potential using fish tissue data (see 40 CFR Part 132, Appendix F, Procedure 5.D).

7.7.2 *How to consider mercury in intakes in WQBELs*

For facilities that take in water from the same body of water that they discharge into, a no net increase limit may be appropriate. This type of effluent limit allows a facility to discharge into a waterbody no more mercury than it takes out of the waterbody when the concentration of mercury in the waterbody above the facility already exceeds the water quality criterion. EPA recommends that permits for these type of facilities contain:

- Effluent limits that constrain the mass discharges to not exceed the mass intake of mercury from the waterbody, or if proper operation and maintenance of a facility's treatment system results in removal of a pollutant, effluent limits that reflect these reductions from the influent loading
- Monitoring of the influent and effluent using the current version of EPA Method 1631 to quantify the amount of mercury entering and exiting the facility
- A requirement to develop a mercury minimization plan

This approach is also consistent with federal regulations pertaining to the Great Lakes Basin that contained an approach for determining reasonable potential using fish tissue data (see 40 CFR Part 132, Appendix F, Procedure 5.E).

8 Related Programs

8.1 How does pollution prevention play a role in the methylmercury criterion?

Under the national pretreatment program, POTWs routinely control the volume and concentration of pollutants contributed by significant industrial users (SIUs)²³ to their collection system and wastewater treatment plant. However, as water quality criteria, sludge standards, and air emissions become more restrictive, even low levels of pollutants such as mercury might cause noncompliance with these standards. As such, POTWs must either expand pollutant control efforts or install treatment technologies to remove the problem pollutants.

In many cases, large-scale treatment technology is either not yet available or not economically feasible for controlling mercury at POTWs. Instead, POTWs are choosing to develop and implement pollution prevention (P2) strategies to reduce the amount of mercury received by the wastewater treatment plant. Although SIUs can contribute a significant mercury load to the treatment plant, non-SIU sources can also be identified as causing or contributing to the problem. For example, the Western Lake Superior Sanitary District (WLSSD) determined that one SIU and many small non-SIUs (dental facilities) contribute a major portion of the mercury in their wastewater. Sectors historically more difficult to control (e.g., residential) or beyond the POTW's direct control (e.g., pollutants in contaminated inflow/rainfall) can also contribute substantial loadings.

Effective mercury source reduction relies on the POTW effectively communicating to sector entities that minimal individual efforts can collectively reduce the mercury loading to the environment. Forming partnerships and working with sector representatives to investigate mercury sources, explore alternatives, and assist in implementation of selected options is integral to a successful reduction strategy. Permitting authorities developing a P2 plan should consider a POTW's role in compliance assistance. The sections below provide summary level guidance for developing a POTW P2 plan.

Through the pretreatment program, POTWs should maintain close contact with local sewer dischargers and have a good understanding of specific industrial process operations. Thus, they can uniquely promote P2 to numerous facilities and provide public awareness and education. In general, success of a POTW P2 effort depends upon a behavioral change on the part of the POTW and the community. As noted by the City of Palo Alto, "Experience shows that people are more likely to change their behaviors if they fully understand environmental problems and the range of possible solutions if they have participated in the process leading to a policy decision and if they believe regulators are dealing with them in good faith...." (City of Palo Alto 1996). By undertaking the

²³ EPA defines an SIU as (1) any Industrial User (IU) subject to a categorical pretreatment standard (national effluent guidelines); (2) any user that discharges an average of 25,000 gallons per day or more of process wastewater or that contributes a process waste stream making up 5 percent or more of the average dry weather hydraulic or organic capacity of the POTW treatment plant; or (3) any other user designated by the Control Authority (POTW) to be a SIU on the basis that it has a reasonable potential for adversely affecting the POTW's operation or for violating a pretreatment standard or requirement (40 CFR 403.3(t)).

following activities prior to developing its plan, the POTW might minimize community resistance and apathy:

- Conduct a preliminary investigation of the problem and potential sources. Verify that the problem is not a wastewater treatment plant operational issue. Further, identify internal sources and any area government facilities in addition to industrial, commercial, and uncontrollable sources that could be contributing to or causing the problem.
- Meet with upper management (e.g., utility director, mayor, council) and discuss the problem, preliminary findings, and potential ramifications. Upper management support will be essential for obtaining necessary resources, funding, equipment, and authority for implementing a P2 plan. Their support will also be necessary for resolving any wastewater treatment plant and government facility issues. Upper management may also advise development of a POTW mission statement that declares goals and the chosen approach. Exhibit 1 provides an example of the WLSSD mission statement (WLSSD 1997).
- Establish a workgroup composed of representatives from government, industry, community, and environmental organizations, preferably those that are either familiar with P2 strategies or familiar with the pollutant of concern. The workgroup likely will develop or help develop the plan, guide plan implementation, and measure plan success. Therefore, findings from the preliminary investigation will guide the POTW to select appropriate committee members and experts. Bear in mind that the workgroup size should ensure representation of most interests but not grow so large as to be counterproductive. This group could also prove valuable in disseminating information.

Exhibit 1. Example Mission Statement

The WLSSD Commitment to Zero Discharge

The WLSSD as a discharger to Lake Superior is committed to the goal of zero discharge of persistent toxic substances and will establish programs to make continuous progress toward that goal. The District recognizes step-wise progress is only possible when pollution prevention strategies are adopted and rigorously pursued. These approaches will focus upon our discharge as well as indirect sources.

WLSSD will work with its users to implement programs, practices, and policies which will support the goal. We will call upon the resources and assistance of the State and federal governments for support, including financial support of the programs to ensure that our users are not penalized unfairly.

WLSSD recognizes that airborne and other indirect sources beyond District control must be addressed in order for significant reductions to occur.

With the support and expertise needed, the POTW and workgroup can draft a plan by doing the following:

- *State the problem* to provide background information about the POTW, problems caused by mercury, and why the POTW is taking action (described in terms the most people can understand).

- *Identify the goals* to determine if the POTW intends to help minimize mercury introduced to all environmental media (air, water, solid waste), known as “front-end” P2, or merely minimize the amount of mercury discharged to the wastewater treatment plant. The latter option ignores mercury transfers to other media (e.g., air, solid waste) and is the less environmentally sound option. It may be essential for the POTW to implement a front-end P2 approach and establish waste collection programs for the proper recycling/disposal of mercury-bearing wastes (e.g., thermometers, fluorescent light bulbs).
- *Define an approach* that outlines the sectors selected for P2 efforts, the criteria for targeting efforts (e.g., size of the source loading, authority available to control the source or sector, time necessary to produce desired results), where efforts will be voluntary or mandatory, who will execute the various program efforts, and how the POTW will proceed where mercury introduction is beyond its control (e.g., contaminated stormwater).
- *Identify assessment techniques* that identify how the POTW will monitor influent, effluent, sludge, and sources to assess success and that identify possible follow-up activities to ensure P2 measures continue to be implemented.
- *Create contingency plans* that describe actions to be taken if planned efforts do not succeed, such as obtaining authority to mandate and enforce P2 or other source control requirements or installing wastewater treatment plant technology.

Plans might develop in response to a specific problem (e.g., elevated wastewater treatment plant effluent mercury levels) or proactively to minimize potential problems. Plans will vary in complexity and in resources necessary to achieve goals. Plan updates should detail successful and failed efforts such as in the form of lessons learned.

8.2 What regulations has EPA issued pursuant to the CAA to address air emissions of mercury?

As rules and standards pursuant to the CAA have been developed, proposed, and promulgated since 1990, compliance by emitting sources and actions taken voluntarily have already begun to reduce emissions of mercury to the air across the country. EPA expects a combination of ongoing activities will continue to reduce mercury emissions to the air over the next decade.

EPA has made substantial progress in addressing mercury air emissions under the CAA. In particular, EPA has issued regulations addressing the major contributors of mercury to the air, including, for example, municipal waste combustors, medical waste incinerators, chlor-alkali plants, industrial boilers, and hazardous waste combustors. EPA issued regulations for these source categories under different sections of the CAA, including sections 111, 112, and 129. Indeed, as the result of EPA’s regulatory efforts, the United States achieved a 45 percent reduction in domestic mercury air emissions between 1990 and 1999 (see Figure 4 and <http://www.epa.gov/ttn/chief/trends/index.html>). Most recently, EPA issued a regulation under CAA section 111 that directly regulates mercury emissions from coal-fired power plants (see 70 FR. 28,606 (May 18, 2005) (codified at 40 CFR Parts 60, 72, and 75) (standards for power plants)).

The relevant regulations that EPA has issued to date under the CAA are described briefly below.

8.2.1 Municipal Waste Combustors

In 1995, EPA promulgated final regulations that apply to all new and existing waste-to-energy plants and incinerators with the capacity to burn more than 250 tons of municipal solid waste, including garbage, per day (see 60 FR 65,415 (Dec. 19, 1995), codified at 40 CFR Part 60). These regulations cover approximately 130 existing waste-to-energy plants and incinerators, and any new plants and incinerators built in the future. The regulations have reduced emissions of a number of HAPs, including mercury, by approximately 145,000 tons per year. The regulations have resulted in about a 90 percent reduction in mercury emissions from domestic municipal waste combustors from 1990 emissions levels (see Figure 4 (56.7 tons per year of mercury emitted from domestic municipal waste combustors in 1990 versus 4.9 tons per year in 1999)).

8.2.2 Medical Waste Incinerators

Medical waste incinerators (MWIs) are used by hospitals, health care facilities, and commercial waste disposal companies to dispose of hospital waste and medical or infectious waste. EPA adopted regulations controlling mercury emissions from MWIs on September 15, 1997 (62 FR 48,348, codified at 40 CFR Part 60, subpart Ce). EPA estimated that the regulations would reduce mercury emissions from these facilities by about 90 percent, with all existing MWIs required to comply with the regulations by September 15, 2002 (see Figure 4 (49.7 tons per year of mercury emitted from domestic municipal waste incinerators in 1990 versus 1.6 tons per year in 1999)). At the time the regulations were issued, EPA expected that 50 percent to 80 percent of the 2,400 then-existing MWIs would close in response to the rule. In fact, EPA's rule resulted in a significant change in medical waste disposal practices in the United States. Because of the increased cost of on-site incineration under the final rule, few health care facilities are likely to install new MWIs and many health care facilities have discontinued use of their existing MWIs. Instead they have switched to other methods of waste disposal such as off-site commercial waste disposal. EPA expected the standards to apply to between 10 and 70 new MWIs, most of which would employ mercury control technology by the compliance deadline.

8.2.3 Chlor-alkali Plants

On December 19, 2003, EPA issued final regulations to reduce mercury emissions from chlorine production plants that rely on mercury cells (see 68 FR 70,904, codified at 40 CFR Part 63 subpart IIIB). The regulations impose requirements for more stringent work practice limits, representing the best practices from the industry, than were required by a preexisting regulation that covered this source category. Today, there are 9 such plants in the United States, as compared to 20 when work on the rule began. The regulations, which require a combination of controls for point sources, such as vents and management practices to address fugitive air emissions, will reduce mercury air emissions from existing chlor-alkali plants by about 50 percent by the compliance date of December 19, 2006. In

addition, EPA is initiating a study of fugitive mercury emissions at existing chlor-alkali plants, which could result in the proposal of further regulatory changes in the future.

8.2.4 Industrial Boilers

In September 2004, EPA issued a final rule to limit emissions of HAP, including mercury, from new and existing industrial, commercial, and institutional boilers and process heaters (ICI boiler and process heaters) at major stationary sources (see 69 FR 55,218 (Sept. 13, 2004), codified at 40 CFR Part 63, Subpart DDDDD). ICI boilers and process heaters burn coal and other substances such as wood to produce steam to generate electricity or mechanical energy and to provide heat. ICI boilers and process heaters are used at facilities such as refineries, chemical and manufacturing plants, and paper mills. In addition, boilers can stand alone to provide heat for shopping malls and university heating systems. EPA promulgated emissions limitations for mercury for all new solid fuel boilers and process heaters and for large existing solid fuel units. EPA expects that this rule will reduce total emissions of HAP from regulated sources by 50,000 to 58,000 tons per year (see 69 FR 55,218, 55,244). The largest segment of emissions and projected emissions reductions from these sources involve hydrogen chloride. However, EPA expects that the standards will reduce mercury emissions from new and existing facilities by about 2 tons per year.

8.2.5 Hazardous Waste Combustors

In 1999, EPA established standards for HAPs, including mercury, for incinerators, cement kilns, and lightweight aggregate kilns that burn hazardous waste under CAA section 112 (64 FR 52,828, 53,011 (September 30, 1999)). The 1999 standards were challenged and subsequently vacated by the United States Court of Appeals for the District of Columbia Circuit. In 2002, EPA issued interim emission standards, which are found at 40 CFR 63.1203 (a)(2) and (b)(2) (mercury standards for existing and new hazardous waste burning incinerators), section 63.1204 (a)(2) and (b)(2) (mercury standards for existing and new hazardous waste-burning cement kilns), and section 63.1205 (a)(2) and (b)(2) (mercury standards for existing and new hazardous waste-burning lightweight aggregate kilns). Recently, EPA issued a rule that supersedes the interim standards issued in 2002 (see 70 FR 59,402 (Oct. 12, 2005) (final standards for hazardous air pollutants from hazardous waste combustors: Phase 1 Final Replacement Standards and Phase II)). The October 2005 rule sets mercury standards under CAA section 112 for specific types of sources, including some sources that were not covered by the interim standards (e.g., liquid fuel fired boilers and solid fuel fired boilers).

8.2.6 Coal-fired Power Plants

On March 15, 2005, EPA issued the first-ever federal rule to permanently cap and reduce mercury emissions from coal-fired power plants (see 70 FR 28606 (May 18, 2005) (CAMR)). This rule makes the United States the first country in the world to regulate mercury emissions from coal-fired power plants. The CAMR, which builds on EPA's CAIR (70 FR 25,162 (May 12, 2005)), will significantly reduce mercury emissions from coal-fired power plants. When fully implemented, CAIR and CAMR will reduce coal-fired utility emissions of mercury from 48 tons a year to 15 tons, a reduction of nearly 70

percent. EPA expects that air deposition from these utilities will also decrease by nearly 70 percent (see Figure 9).

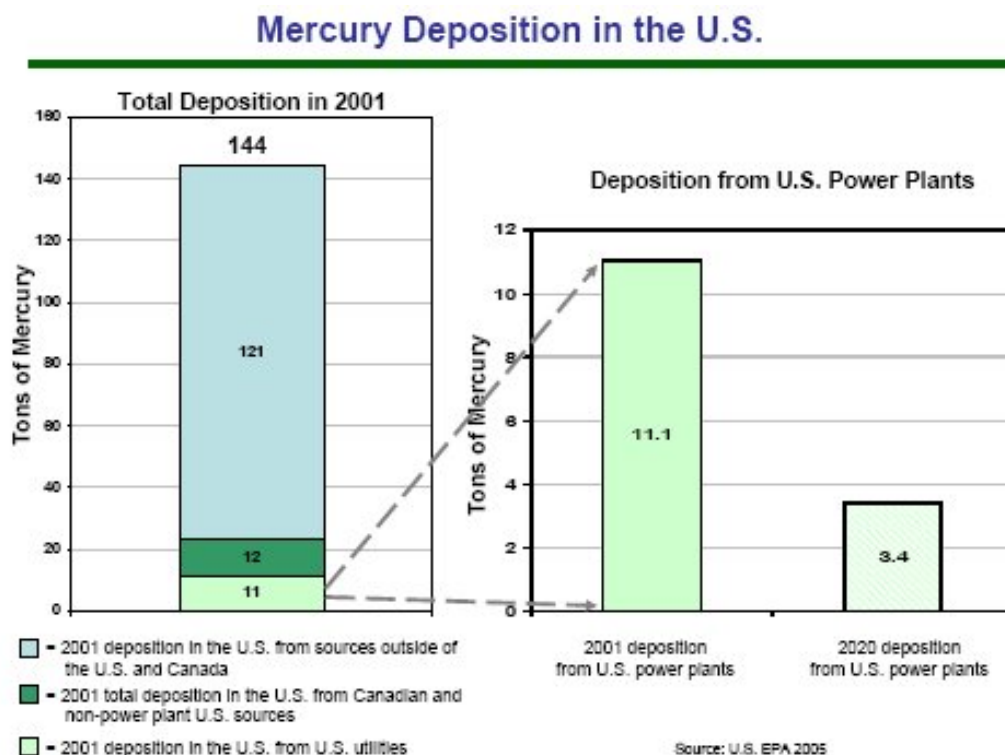


Figure 9. Mercury deposition in the United States following CAMR and CAIR

The CAMR establishes “standards of performance” limiting mercury emissions from new and existing coal-fired power plants and creates a market-based cap-and-trade program that will reduce nationwide utility emissions of mercury in two distinct phases. The first phase cap is 38 tons, and emissions will be reduced by taking advantage of “co-benefit” reductions—that is, mercury reductions achieved by reducing sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions under CAIR. In the second phase, due in 2018, coal-fired power plants will be subject to a second cap, which will reduce emissions to 15 tons upon full implementation.

EPA’s modeling shows that the first phase of CAMR will significantly reduce the majority of coal-fired power plant mercury emissions that deposit in the United States, and those reductions will occur in areas where mercury deposition is currently the highest. The CAMR is expected to make additional reductions in emissions that are transported regionally and deposited domestically, and it will reduce emissions that contribute to atmospheric mercury worldwide. Mercury emitted from coal-fired power plants comes from mercury in coal, which is released when the coal is burned. While coal-fired power plants are currently the largest remaining source of human-generated mercury emissions in the United States, they contribute very little to the global mercury pool. Recent estimates of annual total global mercury emissions from all sources—both natural and human-generated—range from roughly 4,400 to 7,500 tons per year. Human-caused U.S. mercury emissions are estimated to account for roughly 3 percent of the

global total, and U.S. coal-fired power plants are estimated to account for only about 1 percent.

In addition to EPA's regulatory efforts under the CAA, in 1996, the United States eliminated the use of mercury in most batteries under the Mercury Containing and Rechargeable Battery Management Act. This action reduces the mercury content of the waste stream, which further reduces mercury emissions from waste combustion. In addition, voluntary measures to reduce use of mercury containing products, such as the voluntary measures committed to by the American Hospital Association, will contribute to reduced emissions from waste combustion.

For more information about CAMR and other CAA actions to control mercury, see http://www.epa.gov/mercury/control_emissions/decision.htm.

9 References

- Ambrose, R.B., Jr., T.A. Wool, J.P. Connolly, and R.W. Schanz. 1988. *WASP4, A hydrodynamic and water quality model—Model theory, User's Manual and Programmer's Guide*. EPA-600-3-87-039. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.
- Atkeson, T., D. Axelrad, C. Pollman, and G. Keeler. 2002. *Integrating Mercury Deposition and Aquatic Cycling in the Florida Everglades*. Florida Department of Environmental Protection, Tallahassee, FL.
<<ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf>>
- AMSA (Association of Metropolitan Sewerage Agencies). 2000. *Evaluation of Domestic Sources of Mercury*. Association of Metropolitan Sewerage Agencies, Washington, DC. <<http://www.amsa-cleanwater.org/pubs/mercury/mercury.cfm>>
- AZDEQ (Arizona Department of Environmental Quality). 1999. *Total Maximum Daily Load and Implementation Plan for Mercury, Arivaca Lake, Arizona*. Arizona Department of Environmental Quality, EPA Region 9, and Tetra Tech, Inc.
- Baeyens, W., C. Meuleman, B. Muhaya, M. Leermakers. 1998. Behaviour and speciation of mercury in the Scheldt Estuary (water, sediments and benthic organisms). *Hydrobiologia*, 366:63-79.
- Balogh, S.J., M.L. Meyer, and D.K. Johnson. 1998. Transport of Mercury in Three Contrasting River Basins. *Environ. Sci. Technol.* 32:456-462.
- Barber, M.C. 2002. *Bioaccumulation and Aquatic System Simulator (BASS) User's Manual Beta Test Version 2.1*. EPA-600-R-01-035. U.S. Environmental Protection Agency, Office of Research and Development, Ecosystems Research Division, Athens, GA.
- Barkay, T., S.M. Miller, and A.O. Summers. 2003. Bacterial mercury resistance from atoms to ecosystems. *FEMS Microbiology Reviews*, 27:355-384.
- Becker, D.S., and G.N. Bigham. 1995. Distribution of mercury in the aquatic food web of Onondaga Lake, New York. *Water Air Soil Poll.*, 80:563-571.
- Benoit, J.M., C.C. Gilmour, R.P. Mason, G.S. Riedel, and G.F. Riedel. 1998. Behavior of mercury in the Patuxent River estuary. *Biogeochemistry*, 40:249-265.
- Benoit, J.M., C.C. Gilmour, A. Heyes, R.P. Mason, and C. Miller. 2003. Geochemical and Biological Controls over Methylmercury Production and Degradation in Aquatic Systems, *Biogeochemistry of Environmentally Important Trace Metals*. ACS Symposium Series 835.
- Bigham, G.N., and G.M. Vandal. 1994. *A drainage basin perspective of mercury transport and bioaccumulation: Onondaga Lake, New York*. Twelfth International Neurotoxicology Conference, Hot Springs, Arkansas.

- Bloom, N.S. 1989. Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection. *Can. J. Fish. Aquat. Sci.* 46:1131-1140.
- Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49:1010-1017.
- Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* 14:49-59.
- Bloom, N.S., and W.F. Fitzgerald. 1988. Determination of Volatile Mercury Species at the Picogram Level by Low Temperature Gas Chromatography with Cold Vapor Atomic Fluorescence Detection. *Anal. Chim. Acta.* 208:151-161.
- Brumbaugh, W.G., D.P. Krabbenhoft, D.R. Helsel, J.G. Wiener, and K.R. Echols. 2001. *A National Pilot Study of Mercury Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish*. Biological Science Report: USGS/BRD/BSR-2001-0009. U.S. Geological Survey, Columbia Environmental Research Center, Columbia, MO.
- Bullock, O., and K. Brehme. 2002. Atmospheric Mercury Simulation Using the CMAQ Model: Formulation Description and Analysis of Wet Deposition Results. *Atmosph. Environ.*, 36:2135-2146.
- Burkhard, L.P. 2003. Factors influencing the design of BAF and BSAF field studies. *Environ. Toxicol. Chem.* 22:351-360.
- Burkhard, L.P., D.E. Endicott, P.M. Cook, K.G. Sappington, and E.L. Winchester. 2003. Evaluation of Two Methods for Prediction of Bioaccumulation Factors. *Environ. Sci. Technol.* 37(20):4626-4634.
- Burrows, W.C., and P.A. Krenkel. 1973. Studies on Uptake and Loss of Methylmercury-203 by Bluegills (*Lepomis macrochirus* Raf.). *Environ. Sci. Technol.* 7(13):1127-1130.
- Byun, D.W., and J.K.S. Ching, Eds, 1999. *Science algorithms of EPA Models-3 Community Multiscale Air Quality (CMAQ) modeling system*. EPA/600/R-99/030. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.
- Byun, D.W., and K.L. Schere. 2006. Review of the Governing Equations, Computational Algorithms, and Other Components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. *J. Applied Mechanics Reviews*, 59(2):51-77.
- Cambell, K.R., C.J. Ford, and D.A. Levine. 1998. Mercury Distribution in Poplar Creek, Oak Ridge, Tennessee, USA. *Environ. Chem.* 17:1191-1198.
- Carpi, A., and S.E. Lindberg. 1997. Sunlight-mediated emission of elemental mercury from soil amended with municipal sewage sludge. *Environ. Sci. Technol.* , 31(7):2085-2091.

- CDC (Centers for Disease Control and Prevention). 2001. Blood and Hair Mercury Levels in Young Children and Women of Childbearing Age—United States, 1999. *Morbidity and Mortality Weekly Report*. 50(08):140-143.
- CDC (Centers for Disease Control and Prevention). 2005. *Third National Report on Human Exposure to Environmental Chemicals*. Atlanta, GA. NCEH Pub#: 05-0725. <<http://www.cdc.gov/exposurereport>>
- Central Valley Water Board. 2005. Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Mercury in Cache Creek, Bear Creek, Sulphur Creek, and Harley Gulch. Final Report. California Regional Water Quality Control Board, Central Valley Region. Rancho Cordova, CA. Available at: <http://www.waterboards.ca.gov/centralvalley/programs/tmdl/Cache-SulphurCreek/index.html>
- City of Palo Alto. 1996. Public Participation/Community Education. Palo Alto Regional Water Quality Control Plant, Palo Alto, CA.
- Cizdziel, J.V., T.A. Hinnners, J.E. Pollard, E.M. Heithmar, and C.L. Cross. 2002. Mercury concentrations in fish from Lake Mead, USA, related to fish size, condition, trophic level, location, and consumption risk. *Arch. Environ. Contam. Toxicol.* 43:309-317.
- Cizdziel, J.V., T.A. Hinnners, C.L. Cross, and J.E. Pollard. 2003. Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. 2003. *J. Environ. Monit.* 5:802-807.
- Cleckner, L.B., E.S. Esseks, P.G. Meier, and G.J. Keeler. 1995. Mercury Concentrations in Two Great Waters. *Water, Air, Soil Poll.*, 80:581-584, 1995.
- Dennis, R.L., D.W. Byun, J.H. Novak, K.J. Galluppi, C.J. Coats, and M.A. Vouk. 1996. The next generation of integrated air quality modeling: EPA's Models-3, *Atmos. Environ.* 30:1925-1938.
- DeWild, J.F., M.L. Olson, and S.D. Olund. 2002. Determination of methyl mercury by aqueous phase ethylation, followed by gas chromatographic separation with cold vapor atomic fluorescence detection. U.S. Geological Survey Open-File Report 01-445, Washington, DC.
- Doyon, J.F., R. Schentagne, and R. Verdon. 1998. Different mercury bioaccumulation rates between sympatric populations of dwarf and normal lake whitefish (*Coregonus clupeaformis*) in the La Grande complex watershed, James Bay, Quebec. *Biogeochemistry* 40:203-216.
- EPRI (Edison Power Research Institute). 1999. *Dynamic mercury cycling model for Win95/NT. A model for mercury cycling in Lakes*. D-MCM Version 1.0. Users guide and Technical Reference. Edison Power Research Institute, Lafayette, CA.
- EPRI (Edison Power Research Institute). 2002. *Dynamic mercury cycling model (D-MCM) for Windows 98/NT 4.0/2000/XP. A model for mercury cycling in lakes*. D-MCM Version 2.0. Edison Power Research Institute, Lafayette, CA.

- Frescholtz, T., and M.S. Gustin. 2004. Soil and foliar mercury emission as a function of soil concentration. *Water Air Soil Poll.* 155:223-237.
- FTN Associates, Ltd. 2002. TMDLs for Segments Listed for Mercury in Fish Tissue for the Ouachita River Basin, and Bayou Bartholomew, Arkansas and Louisiana to Columbia. Little Rock, AR.
<[http://www.epa.gov/region6/water/ecopro/latmdl/ouarmercury\(f\).pdf](http://www.epa.gov/region6/water/ecopro/latmdl/ouarmercury(f).pdf)>
- Gbundgo-Tugbawa, S., and C.T. Driscoll. 1998. Application of the regional mercury cycling model (RMCM) to predict the fate and remediation of mercury in Onondaga Lake, New York. *Water Air Soil Poll.* 105:417-426.
- Gilbert, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring VanNostrand Reinhold Company. New York, NY.
- Giblin, F.J., and E.J. Massaro. 1973. Pharmacodynamics of methylmercury in the rainbow trout (*Salmo gairdneri*): Tissue uptake, distribution and excretion. *Toxicol. Appl. Pharm.* 24(1):81-91.
- Gilmour, C.C., and E.A. Henry. 1991. Mercury Methylation in Aquatic Systems Affected by Acid Deposition. *Environ. Pollut.* 71:131-149.
- Gilmour, C.C., G.S. Reidel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordall. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40:327-345.
- Glass, G.E., J.A. Sorensen, and G.R. Rapp, Jr. 2001. Methylmercury Bioaccumulation Dependence on N. Pike Age and Size in Twenty Minnesota Lakes. ACS Sym Ser. 772, Persistent, Bioaccumulative, and Toxic Chemicals I, Ch. 11, pp 150-163.
- Greenfield, B.K., T.R. Hrabik, C.J. Harvey, and S.R. Carpenter. 2001. Predicting mercury levels in yellow perch: use of water chemistry, trophic ecology, and spatial traits. *Can. J. Fish. Aquat. Sci.* 58:1419-1429.
- Greenfield, J., T. Dai, and H. Manguerra. 2002. Watershed Modeling Extensions of the Watershed Characterization System, Ft. Lauderdale, FL, February 2002.
- Grell, G., J. Dudhia, and D. Stauffer. 1994. *A Description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5)*. NCAIR/TN-398+STR., 138 pp, National Center for Atmospheric Research, Boulder CO.
- Grieb, T. M., C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie, and D.B. Porcella. 1990. Factors affecting mercury accumulation in fish in the Upper Michigan Peninsula. *Environ. Toxicol. Chem.* 9:919-930.
- Gustin, M.S., J.A. Ericksen, D.E. Schorran, D.W. Johnson, S.E. Lindberg, and J.S. Coleman. 2004. Application of controlled mesocosms for understanding mercury air-soil-plant exchange. *Environ. Sci. Technol.* 38: 6044-6050.

- Hammerschmidt, C.R., J.G. Wiener, B.E. Frazier, and R.G. Rada. 1999. Methylmercury content of eggs in yellow perch related to maternal exposure in four Wisconsin lakes. *Environ. Sci. Technol.* 33:999-1003.
- Hinners, T.A. 2004. Possible ramifications of higher mercury concentrations in fillet tissue of skinnier fish. 2004 National Forum on Contaminants in Fish, San Diego, California, January 25-28.
- Horvat, M., L. Liang, and N.S. Bloom. 1993. Comparison of Distillation with Other Current Isolation Methods for the Determination of Methylmercury Compounds in Low Level Environmental Samples. *Anal. Chim. Acta* 282:153-168.
- Hrabik, T.R., and C.J. Watras. 2002. Recent Declines in Mercury Concentration in a Freshwater Fishery: Isolating the Effects of De-acidification and Decreased Atmospheric Mercury Deposition in Little Rock Lake. *Sci. Total Environ.* 297:229-237.
- Huckabee, J.W., J.W. Elwood, and S.G. Hildebrand. 1979. Accumulation of mercury in freshwater biota. Nriagu (ed.) *The Biogeochemistry of Mercury in the Environment*. Elsevier/North-Holland Biomedical Press.
- Hurley, J. P., M.M. Shafer, S.E. Cowell, J.T. Overdier, P.E. Hughes, and D.E. Armstrong, D.E.. 1996. Trace metal assessment of Lake Michigan tributaries using low level techniques. *Environ. Sci. Technol.* 30:2093-2098.
- Hurley, J.P., S.E. Cowell, M.M. Shafer, P.E. Hughes. 1998. Partitioning and Transport of Total and Methyl Mercury in the Lower Fox River, Wisconsin. *Environ. Sci. Technol.* 32:1424-1432.
- Jackson, T.A. 1991. Biological and environmental control of mercury accumulation by fish in lakes and reservoirs of northern Manitoba, Canada. *Can. J. Fish. Aquat. Sci.* 48:2449-2470.
- Jackson, T.A. 1998. Mercury in aquatic ecosystems. In: *Metal Metabolism in Aquatic Environments*, W.J. Langston and M.J. Bebianno (eds) pp. 77-158. Chapman & Hall, London.
- Kamman, N., C.T. Driscoll, B. Estabrook, D.C. Evers, and E.K. Miller. 2004. Biogeochemistry of Mercury in Vermont and New Hampshire Lakes: An Assessment of Mercury in Water, Sediment and Biota of Vermont and New Hampshire Lakes. Comprehensive Final Project Report. Vermont Department of Environmental Conservation. Waterbury, VT.
- Kehrig, H.A., O. Malm, and I. Moreira. 1998. Mercury in a widely consumed fish *Micropogonias furnieri* (Demarest, 1823) from four main Brazilian estuaries. *Sci. Total Environ.* 213:263-271.
- Kidd, K., R. Hesslein, R. Fudge, and K. Hallard. 1995. The influence of trophic level as measured by delta-N-15 on mercury concentrations in fresh-water organisms. *Water Air Soil Poll.* 80(1-4):1011-1015.

- Landis, M.S., M. Lynam, and R.K. Stevens. 2004. The Monitoring and Modeling of Mercury Species in Support of Local Regional and Global Modeling. In: N. Pirrone and K.R. Mahaffey (eds), *Dynamics of Mercury Pollution on Regional and Global Scales*. Kluwer Academic Publishers, New York, NY.
- Lasorsa, B., S. Allen-Gil. 1995. The methylmercury to total mercury ratio in selected marine, freshwater, and terrestrial organisms. *Water Air Soil Poll.* 80:905-913.
- Lin, C.J., and S.O. Pehkonen. 1999. The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33:2067-2079.
- Lindberg, S.E., and J.E. Stratton. 1998. Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* 32(1):49-57.
- Mahaffey, K.R., R.P. Clickner, C.C. Bodurow. 2004. Blood organic mercury and dietary mercury intake: national health and nutrition examination survey, 1999 and 2000. *Environ. Health Persp.* 112:562-570.
- Mason, R.P., and W.F. Fitzgerald. 1990. Alkylmercury Species in the Equatorial Pacific. *Nature*. 347:457-459.
- Mason, R.P., F.M.M. Morel, and H.F. Hemond. 1995. The role of microorganisms in elemental mercury formation in natural waters. *Water Air Soil Poll.* 80:775-787.
- Mason, R.P., and K.A. Sullivan. 1997. Mercury in Lake Michigan. *Environ. Sci. Technol.* 31:942-947.
- Mason, R.P., and K.A. Sullivan. 1998. Mercury and Methylmercury Transport through an Urban Watershed. *Water Res.* 32:321-330.
- Mason, R.P., and A.L. Lawrence. 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* 18(11):2438-2447.
- McGeer, J.C., K.V. Brix, J.M. Skeaff, D.K. DeForest, S.I. Brigham, W.J. Adams, and A. Green. 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: implications for hazard assessment of metals in the aquatic environment. *Environ. Toxicol. Chem.* 22(5):1017-1037.
- McKim, J.M., G.F. Olson, G.W. Holcombe, and E.P. Hunt. 1976. Long-term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): toxicity, accumulation, distribution, and elimination. *J. Fish. Res. Board Can.* 33:2726-2739.
- McNally, D. 2003. Annual Application of MM5 for Calendar Year 2001, Topical report submitted to EPA, March 2003.
- Mierle, G., and R. Ingram. 1991. The role of humic substance in the mobilization of mercury from watersheds. *Water Air Soil Poll.* 56:349-357.

- Morel, F., A.M.L. Kraepiel, and M. Amyot. 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29:543-566.
- Monson, B.A., P.L. Brezonik. 1998. Seasonal Patterns of Mercury Species in Water and Plankton from Softwater Lakes in Northeastern Minnesota. *Biogeochemistry*. 40:147-162.
- Neter, J., M.H. Kutner, C.J. Nachtsheim, and W. Wasserman. 1996. *Applied Linear Statistical Models*. 4th Ed. Irwin. Chicago, IL.
- Niessen, S., N. Mikac, and J.C. Fischer. 1999. Microwave-assisted determination of total mercury and methylmercury in sediment and porewater. *Analysis*. 27:871-875.
- NRC (National Research Council). 2000. Toxicological effects of methylmercury. Committee on the Toxicological Effects of Methylmercury. National Academy Press. Washington, DC.
- Park, J.G., and L.R. Curtis. 1997. Mercury Distribution in Sediments and Bioaccumulation by Fish in Two Oregon Reservoirs: Point-Source and Nonpoint-Source Impacted Systems. *Arch. Environ. Contam. Toxicol.* 33:423-429.
- Phillips, P.T. 1980. *Quantitative Aquatic Biological Indicators. Pollution Monitoring Series*. Applied Science Publishers Ltd, London, England.
- QEA. (Quantitative Environmental Analysts, LLC). 2000. *Bioaccumulation model QUAFDCHN*. Version 1.0. Montvale, NJ.
- Rae, D. 1997. *Impacts of Mercury Reductions in Minnesota*. Prepared for MN Pollution Control Agency, September 30, 1997.
- Rasmussen, P.E. 1994. Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* 28(13):2233-2241.
- Rodgers, D.W., and F.W.H. Beamish. 1982. Dynamics of Dietary Methylmercury in Rainbow Trout, *Salmo Gairdneri*. *Aquat. Toxicol.* 2:271-290.
- Scholtz, M.T., B.J.V. Heyst, and W.H. Schroeder. 2003. Modelling of mercury emissions from background soils. *Sci. Total Environ.* 304:185-207.
- Schroeder, W.H., J. Munthe, J. and O. Lindqvist. 1989. Cycling of mercury between water air and soil compartments of the environment. *Water Air Soil Poll.* 48:337-347.
- Sellers, P., C.A. Kelly, J.W.M. Rudd, and A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. *Nature*. 380:694.
- Simoneau, M., M. Lucotte, S. Garceau, D. Laliberte. 2004. Fish growth rates modulate mercury concentrations in walleye (*Sander vitreus*) from eastern Canadian lakes. *Environ. Res.* 98:73-82.

- Slotton, D. G., J. E. Reuter, et al. 1995. Mercury Uptake Patterns of Biota in a Seasonally Anoxic Northern California Reservoir. *Water, Air, and Soil Pollution* 80(1-4): 841-850.
- Slotton, D.G., S.M. Ayers, T.H. Suchanek, R.D. Weyland, A.M. Liston. 2004. Mercury Bioaccumulation and Trophic Transfer in the Cache Creek Watershed, California, in Relation to Diverse Aqueous Mercury Exposure Conditions. Subtask 5B. Final Report., University of California, Davis, Dept. of Env. Science and Policy and Dept. Wildlife, Fish and Conservation Biology. Prepared for the CALFED Bay-Delta Program, Directed Action #99-B06. Available at: <http://loer.tamug.tamu.edu/calfed/FinalReports.htm>.
- Soneston, L. 2003. Fish mercury levels in lakes—adjusting for Hg and fish-size covariation. *Environ. Pollut.* 125:255-265.
- Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rapp, Jr. 1990. Airborne Mercury Deposition and Watershed Characteristics in Relation to Mercury Concentrations in Water, Sediments, Plankton, and Fish of Eighty Northern Minnesota Lakes. *Environ. Sci. Technol.* 24(11):1716-1727.
- St. Louis, V., J.W.M. Rudd, C.A. Kelly, B.D. Hall, K.R. Rolffus, K.J. Scott, S.E. Lindberg, and W. Dong. 2001. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* 35:3089-3098.
- Szefer, P., M. Domaga-a-Wieloszewska, J. Warzocha, A. Garbacik-Weso-owska, and T. Ciesielski. 2003. Distribution and relationships of mercury, lead, cadmium, copper and zinc in perch (*Perca fluviatilis*) from the Pomeranian Bay and Szczecin Lagoon, southern Baltic. *Food Chem.* 81(1):73-83.
- Tetra Tech, Inc. 2001. Total Maximum Daily Load for Mercury in McPhee and Narraguinnep Reservoirs, Colorado. Prepared for EPA Region 8 by Tetra Tech, Inc.
- Ullrich, S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: a review of factors affecting methylation. *Crit. Rev. Env. Sci. Tec.* 31:241-293.
- USEPA (U.S. Environmental Protection Agency). 1983. *Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses*. U.S. Environmental Protection Agency, Office of Water, Washington, DC. <<http://www.epa.gov/waterscience/library/wqstandards/uaavol123.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1991. *Technical Support Document for Water Quality-based Toxics Control*. EPA 505/2-90-001. U.S. Environmental Protection Agency, Office of Water Enforcement and Permits and Office of Water Regulations and Standards. <<http://www.epa.gov/npdes/pubs/owm0264.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1994. *Water quality standards handbook*. EPA-823-B-94-005a&b. U.S. Environmental Protection Agency, Office of Water. Washington, DC <<http://www.epa.gov/waterscience/standards/handbook>>

- USEPA (U.S. Environmental Protection Agency). 1995a. *Final water quality guidance for the Great Lakes System*. U.S. Environmental Protection Agency, Washington, DC. 60FR15366.
- USEPA (U.S. Environmental Protection Agency). 1995b. *Interim economic guidance for water quality standards: workbook*. EPA 823/B-95-002. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
<<http://www.epa.gov/waterscience/standards/econworkbook>>
- USEPA (U.S. Environmental Protection Agency). 1995c. *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors*. EPA 820/B-95-005. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 1996a. *NPDES Permit Writers Manual*. EPA-833-B-96-003. U.S. Environmental Protection Agency, Office of Wastewater Management, Washington, DC.
<<http://www.epa.gov/npdes/pubs/owm0243.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1996b. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. EPA-821-R-96-011. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 1997a. *Mercury Study Report to Congress*. Volume I: Executive Summary. EPA-452/R-97-003. U.S. Environmental Protection Agency, Washington, DC.
<<http://www.epa.gov/ttn/oarpg/t3/reports/volume1.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1997b. *Mercury Study Report to Congress*. Volume III: Fate and Transport of Mercury in the Environment. EPA-452/R-97-005. U.S. Environmental Protection Agency, Washington, DC.
<<http://www.epa.gov/ttn/oarpg/t3/reports/volume3.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1997c. *Mercury Study Report to Congress*. Volume VII: Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States. EPA-452/R-97-009. U.S. Environmental Protection Agency, Washington, DC.
<<http://www.epa.gov/ttn/oarpg/t3/reports/volume7.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1997d. *New Policies for Establishing and Implementing Total Maximum Daily Loads (TMDL)*. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/owow/tmdl/ratepace.html>>
- USEPA (U.S. Environmental Protection Agency). 1997e. *Exposure Factors Handbook*. EPA/600/P-95/002Fa-c. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

- USEPA (U.S. Environmental Protection Agency). 1998a. *Guidance for conducting fish and wildlife consumption surveys*. EPA 823-B-98-007. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/waterscience/fish/fishguid.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1998b. *Results of the EPA Method 1631 Validation Study, February, 1998*. U.S. Environmental Protection Agency, Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 1998c. *Ambient Water Quality Criteria Derivation Methodology Human Health Technical Support Document*. EPA/822/B-98/005. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/waterscience/criteria/humanhealth/awqc-tsd.pdf>>
- USEPA (U.S. Environmental Protection Agency). 1999. *Overview of P2 Approaches at POTWs*. Draft. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 2000a. *AQUATOX*. EPA Release 1. File Version 1.69. EPA-823-B-00-007. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/waterscience/models/aquatox/technical/techdoc.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2000b. Draft Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study: Application of the Everglades Mercury Cycling Model (E-MCM) to Site WCA 3A-15. Prepared for the United States Environmental Protection Agency and Florida Department of Environmental Protection by Tetra Tech, Inc. Lafayette, CA.
- USEPA (U.S. Environmental Protection Agency). 2000c. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. Volume 1: Fish Sampling and Analysis. Third Edition. EPA/823/B-00/007. U.S. Environmental Protection Agency, Office of Water. Washington, DC
<<http://www.epa.gov/ost/fishadvice/volume1/index.html>>
- USEPA (U.S. Environmental Protection Agency). 2000d. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. Volume 2: Risk Assessment and Fish Consumption Limits. Third Edition. EPA/823/B-00/008. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/ost/fishadvice/volume2/index.html>>
- USEPA (U.S. Environmental Protection Agency). 2000e. *Methodology for deriving ambient water quality criteria for the protection of human health*. EPA-822-B-00-004. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://epa.gov/waterscience/criteria/humanhealth/method/method.html>>
- USEPA (U.S. Environmental Protection Agency). 2000f. *Deposition of Air Pollutants to the Great Waters: Third Report to Congress*. EPA-453/R-00-005. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. <<http://www.epa.gov/oar/oaqps/gr8water/3drprt>>

- USEPA (U.S. Environmental Protection Agency). 2000g. *Use of Fish and Shellfish Advisories and Classifications in 303(d) and 305(b) Listing Decisions*. U.S. Environmental Protection Agency, Office of Science and Technology and Office of Wetlands, Oceans, and Watersheds, Washington, DC.
<<http://www.epa.gov/waterscience/library/wqstandards/shellfish.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2000h. *Guidance for the Data Quality Objectives Process*. EPA/600/R-96/055. U.S. Environmental Protection Agency, Office of Environmental Information. Washington, DC.
<<http://www.epa.gov/quality/qs-docs/g4-final.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2000i. *Estimated Per Capita Fish Consumption in the United States: Based on Data Collected by the United States Department of Agriculture's 1994–1996 Continuing Survey of Food Intakes by Individuals*. U.S. Environmental Protection Agency, Office of Science and Technology. Office of Water, Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 2000j. *Quality Assurance Project Plan for Analytical Control and Assessment Activities in the National Study of Chemical Residues in Lake Fish Tissue*. EPA-823-R-02-006. U.S. Environmental Protection Agency, Office of Water. Washington, DC.
<<http://www.epa.gov/waterscience/fishstudy/qapp.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2001a. *Mercury TMDLs for Subsegments within Mermentau and Vermillion-Teche River Basins*. EPA, Region 6 Watershed Management Section, Water Quality Protection Division with cooperation from Louisiana Department of Environmental Quality, Office of Environmental Assessment, Environmental Technology Division.
<<http://www.epa.gov/region6/water/tmdl.htm>>
- USEPA (U.S. Environmental Protection Agency). 2001b. *Water quality criteria: Notice of Availability of water quality criterion for the protection of human health: Methylmercury*. U.S. Environmental Protection Agency, Office of Water, Washington, DC. Fed. Regist., 66:1344.
<<http://www.epa.gov/fedrgstr/EPA-WATER/2001/January/Day-08/w217.htm>>
- USEPA (U.S. Environmental Protection Agency). 2001c. *Water quality criterion for the protection of human health: Methylmercury*. EPA-823-R-01-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
<<http://www.epa.gov/waterscience/criteria/methylmercury/document.html>>
- USEPA (U.S. Environmental Protection Agency). 2001d. *Mercury Maps: A quantitative spatial link between air deposition and fish tissue*. Peer reviewed final report. EPA-823-R-01-009. U.S. Environmental Protection Agency, Office of Water. Washington, DC. <<http://www.epa.gov/waterscience/maps/report.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2001e. *Total Maximum Daily Load for Total Mercury in the Middle/Lower Savannah River, GA*. U.S. Environmental Protection Agency, Region 4, Atlanta, GA.
<<http://www.epa.gov/owow/tmdl/examples/mercury.html>>

- USEPA (U.S. Environmental Protection Agency). 2001f. Draft. *Results of Lake Michigan Mass Balance Study: Mercury Data Report*. EPA 905-R-01-012. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL.
- USEPA (U.S. Environmental Protection Agency). 2001g. Draft. Survey of Chemical Contaminants in Fish, Invertebrates and Plants Collected in the Vicinity of Tyonek, Seldovia, Port Graham and Nanwalek—Cook Inlet, Alaska. EPA 910-R-01-003. U.S. Environmental Protection Agency, Region 10, Seattle, WA.
- USEPA (U.S. Environmental Protection Agency). 2001h. *Mercury TMDLs for Subsegments Within Mermentau and Vermillion-Teche River Basins*. U.S. Environmental Protection Agency, Region 6. Dallas, TX.
<http://www.epa.gov/region6/water/ecopro/latmdl/mercurytmdls_f.pdf>
- USEPA (U.S. Environmental Protection Agency). 2001i. *Robust Estimation of Mean and Variance Using Environmental Data Sets with Below Detection Limit Observations*. U.S. Environmental Protection Agency, Office of Research and Development, Las Vegas, NV. <<http://www.epa.gov/esd/cmb/research/papers/jn103.pdf>>
- USEPA (U.S. Environmental Protection Agency). 2002a. Total Maximum Daily Load (TMDL) Development for Total Mercury in the Ochlockonee Watershed Including Listed Segments of the Ochlockonee River. U.S. Environmental Protection Agency, Region 4, Atlanta, GA.
- USEPA (U.S. Environmental Protection Agency). 2002b. *Consolidated Assessment and Listing Methodology, Toward a Compendium of Best Practices*. First Edition. U.S. Environmental Protection Agency, Office of Wetlands, Oceans and Watersheds, Washington, DC. <<http://www.epa.gov/owow/monitoring/calm.html>>
- USEPA (U.S. Environmental Protection Agency). 2002c. *National Sediment Quality Survey Database, 1980–1999*. U.S. Environmental Protection Agency, Office of Water, Washington, DC. <<http://www.epa.gov/waterscience/cs/nsidbase.html>>
- USEPA (U.S. Environmental Protection Agency). 2002d. *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-02-019. U.S. Environmental Protection Agency, Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 2002e. *Integrated Risk Information System (IRIS). Methylmercury*. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment. Oral RfD and inhalation RfC assessments last revised 7/27/2001. Carcinogenicity assessment last revised 5/1/1995. <<http://www.epa.gov/iris/subst/0073.htm>>
- USEPA (U.S. Environmental Protection Agency). 2002f. *Estimated Per Capital Fish Consumption in the United States*. EPA-821-C-02-003. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
<http://www.epa.gov/waterscience/fish/consumption_report.pdf>
- USEPA (U.S. Environmental Protection Agency). 2003a. *Office of Water Water Quality Trading Policy*. U.S. Environmental Protection Agency, Office of Water,

Washington, DC.

<<http://www.epa.gov/owow/watershed/trading/tradingpolicy.html>>

USEPA (U.S. Environmental Protection Agency). 2003b. *Methodology for deriving ambient water quality criteria for the protection of human health* (2000). Technical Support Document Volume 2. Development of National Bioaccumulation Factors. EPA-822-R-03-030. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

<<http://www.epa.gov/waterscience/humanhealth/method/tsdvol2.pdf>>

USEPA (U.S. Environmental Protection Agency). 2004a. Proposed National Emission Standards for Hazardous Air Pollutants; and, in the Alternative, Proposed Standards for Performance for New and Existing Stationary Sources, Electric Utility Steam Generating Units: Notice of Data Availability. U.S. Environmental Protection Agency, Office of Air and Radiation, Washington, DC. *Fed. Regist.*, December 1, 2004, 69:69864. <<http://a257.g.akamaitech.net/7/257/2422/06jun20041800/edocket.access.gpo.gov/2004/pdf/04-26579.pdf>>

USEPA (U.S. Environmental Protection Agency). 2004b. *Mercury Pollutant Minimization Program Guidance*. U.S. Environmental Protection Agency, Region 5, NPDES Programs Branch.

<http://www.epa.gov/region5/water/npdestek/mercury_pmp_nov_04_guidance.pdf>

USEPA (U.S. Environmental Protection Agency). 2005a. *2004 National Listing of Fish Advisories*. EPA-823-F-05-004. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

<<http://www.epa.gov/waterscience/fish/advisories/factsheet.pdf>>

USEPA (U.S. Environmental Protection Agency). 2005b. *Regulatory Impact Analysis of the Clean Air Mercury Rule*. Final Report. EPA-452/R-05-003. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Quality Strategies and Standards Division, Research Triangle Park, NC.

<http://www.epa.gov/ttn/atw/utility/ria_final.pdf>

USEPA (U.S. Environmental Protection Agency). 2005c. Technical Support Document. Revision of December 2000 Regulatory Finding on the Emissions of Hazardous Air Pollutants From Electric Utility Steam Generating Units and the Removal of Coal and Oil-Fired Electric Utility Steam Generating Units from the section 112(c) List: Reconsideration. U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2005d. *Technical Support Document for the Final Clean Air Mercury Rule: Air Quality Modeling*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. <http://www.epa.gov/ttn/atw/utility/aqm_oar-2002-0056-6130.pdf>

USEPA (U.S. Environmental Protection Agency). 2005e. Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units. U.S. Environmental Protection Agency. *Fed. Regist.*, May 18, 2005, 70:28606.

- Voiland, M.P., K.L. Gall, D.J. Lisk, and D.B. MacNeill. 1991. Effectiveness of recommended fat-trimming procedures on the reduction of PCB and Mirex levels in Brown trout (*Salmo trutta*) from Lake Ontario. *J. Great Lakes Res.* 17(4):454-460.
- Wagemann, R., E. Trebacz, R. Hunt, R., and G. Boila. 1997. Percent methylmercury and organic mercury in tissues of marine mammals and fish using different experimental and calculation methods. *Environ. Toxicol. Chem.* 16(9):1859-1866.
- Watras, C.J., and N.S. Bloom. 1992. Mercury and methylmercury in individual zooplankton: implications for bioaccumulation. *Limnol. Oceanogr.* 37:1313-1318.
- Watras, C.J., K.A. Morrison, J.S. Host, and N.S. Bloom. 1995. Concentration of Mercury Species in Relationship to Other Site-Specific Factors in the Surface Waters of Northern Wisconsin Lakes. *Limnol. Oceanogr.* 40:556-565.
- Watras, C.J., R.C. Back, S. Halvorsen, R.J.M. Hudson, K.A. Morrison, and S.P. Wentz. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219(2-3):183-208.
- WLSSD (Western Lake Superior Sanitary District). 1997. *The WLSSD Commitment to Zero Discharge*. Western Lake Superior Sanitary District, Duluth, MN.
<http://www.wlssd.com/ENVPROG_files/committm.htm>
- Wentz, S. P. 2003. A Spatially and Temporally Variable Model of Mercury Concentrations in Aquatic Communities with Applications to Public Health Protection and Water Quality Assessment, Ph.D. Thesis, Purdue University.
- Wentz, S.P. 2004. A Statistical Model and National Data Set for Partitioning Fish-Tissue Mercury Concentration Variation Between Spatiotemporal and Sample Characteristic Effects. Scientific Investigation Report 2004-5199. U.S. Geological Survey, Reston, VA.
- Wren, C.D., and H.R. MacCrimmon. 1986. Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. *Water Res.* 6:763-769.
- Yantosca, B. 2004. *GEOS-CHEMv7-01-02 User's Guide*. Atmospheric Chemistry Modeling Group, Harvard University, Cambridge, MA.

Appendix A. Synopsized Mercury TMDLs Developed or Approved by EPA

- I. Ochlockonee Watershed, Georgia**
- II. Arivaca Lake, Arizona**
- III. McPhee and Narraguinep Reservoirs, Colorado**
- VI. Clear Lake, California**

I. Ochlockonee Watershed, Georgia

Description of the Applicable Water Quality Standards

TMDLs are established to attain and maintain the applicable narrative and numerical water quality standards. The state of Georgia's Rules and Regulations for Water Quality Control do not include a numeric criterion for the protection of human health from methylmercury, but they do provide a narrative "free from toxics" water quality standard. Because mercury can cause toxicity in humans, a numeric "interpretation" of the narrative water quality standard was used to assure that a TMDL will protect human health. The state of Georgia has made a numeric interpretation of their narrative water quality standard for toxic substances at a numeric concentration of no more than 0.3 mg/kg methylmercury in fish tissue. This numeric interpretation protects the "general population," which is the population that consumes 17.5 grams per day or less of freshwater fish.

This approach is consistent with EPA's recently adopted guidance value for the protection of human health from methylmercury described in the document titled, *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001c). The methodology uses a "weighted consumption" approach. When only trophic level 3 and 4 fish have been collected, the methodology assumes that 8 grams per day (58.4 percent) of the total fish consumption is trophic level 3 fish (e.g., catfish and sunfish) and 5.7 grams per day (41.6 percent) are trophic level 4 fish (e.g., largemouth bass). EPA collected site-specific data from the Ochlockonee River on ambient mercury in fish tissue and in the water column in the summer of 2000 and in March and April 2001 at two locations. Using a weighted consumption approach, site-specific fish tissue concentration data collected in the Ochlockonee River yields a weighted fish tissue concentration of 0.6 mg/kg, which is greater than the state's current applicable water quality criterion of 0.3 mg/kg. This was calculated as

$$\text{Weighted Fish Tissue Concentration} = (\text{Avg Trophic 4 Conc.} \times .416) + (\text{Avg Trophic 3 Conc.} \times .584)$$

where:

Avg. Trophic Level 3 Concentration = 0.2 mg/kg

Avg. Trophic Level 4 Concentration = 1.0 mg/kg

Weighted Fish Tissue Concentration = 0.6 mg/kg

To establish the TMDL, EPA determined the maximum allowable concentration of mercury in the ambient water that will prevent accumulation of methylmercury in fish tissue above the applicable water quality standard of 0.3 mg/kg level. To determine this EPA used the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000e). EPA also used the recommended national values from the Human Health Methodology, including the reference dose of 0.0001 mg/kg/day methylmercury; a standard average adult body weight of 70 kg; and the consumption rate for the general population of 17.5 grams per day. For the other factors in the calculation, bioaccumulation and fraction of methylmercury, EPA used site-

specific data from the Ochlockonee River collected in summer of 2000 and March and April of 2001. From this site-specific data, EPA determined a representative weighted BAF. This BAF was calculated by taking the average calculated BAF from each of the two trophic levels to determine a “weighted” BAF on the basis of the different consumption rates for trophic levels and a median measured fraction methylmercury of 0.17. Using this approach, an allowable concentration of mercury in the ambient water of Ochlockonee River for the protection of human health is 1.6 ng/L. This was calculated as

$$WQS = \frac{((Reference\ Dose - RSC) \times Body\ Weight \times Units\ Conversion)}{(Consumption\ Rate \times Weighted\ BAF \times Fraction\ MeHg)}$$

Where:

WQS = water quality standard = 1.6 ng/L

Reference Dose = 0.0001 mg/kg/day MeHg

RSC = relative source contribution from other fish species =
0.000027 mg/kg/day MeHg

Body Weight = 70 kg

Units Conversion = 1,000,000 mg/kg

Consumption Rate = 0.0175 kg/day Fish

Weighted Bioaccumulation Factor = 1,063,270 l/kg

Fraction of the Mercury as Methylmercury = 0.17 as measured

Source Assessment

A TMDL evaluation must examine all known potential sources of the pollutant in the watershed including point sources, nonpoint sources, and background levels. The source assessment was used as the basis of development of a model and the analysis of TMDL allocation options. This TMDL analysis includes contributions from point sources, nonpoint sources, and background levels. There are 16 water point sources in the Ochlockonee River watershed that could potentially have mercury in their discharge.

According to a review of the *Mercury Study Report to Congress* (USEPA 1997a), significant potential air emission sources include coal-fired power plants, waste incinerators, cement and limekilns, smelters, pulp and paper mills, and chlor-alkali factories. In the report, a national airshed model (RELMAP) was applied to the continental United States. This model provides a distribution of both wet and dry deposition of mercury as a function of air emissions and global sources and was used to calculate dry and wet deposition rates for south Georgia as derived by RELMAP.

The MDN includes a national database of weekly concentrations of mercury in precipitation and the seasonal and annual flux of mercury in wet deposition. EPA reviewed the MDN data for a sampling station near south Georgia. This data was compared with the RELMAP deposition predictions and was found to be substantially higher. Using the MDN data, the average annual wet deposition rate was determined to be 12.75 µg/square meter. The dry deposition rate was determined to be 6.375 µg/square meter on the basis of the RELMAP results.

Loading Capacity—Linking Water Quality and Pollutant Sources

The link between the fish tissue endpoint and the identified sources of mercury was the basis for the development of the TMDL. This helped estimate total assimilative capacity of the river and any needed load reductions. In this TMDL, models of watershed loading of mercury were combined with a model of mercury cycling and bioaccumulation in the water. This enabled a translation between the endpoint for the TMDL (expressed as a fish tissue concentration of mercury) and the mercury loads to the water. The loading capacity was then determined by the linkage analysis as a mercury loading rate that was consistent with meeting the endpoint fish tissue concentration.

Watershed-scale loading of water and sediment was simulated using the WCS. The complexity of this loading function model falls between that of a detailed simulation model, which attempts a mechanistic, time-dependent representation of pollutant load generation and transport, and simple export coefficient models, which do not represent temporal variability. The WCS provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet is intended to be applicable without calibration. Solids load, runoff, and ground water can then be used to estimate pollutant delivery to the receiving waterbody from the watershed. This estimate is based on pollutant concentrations in wet and dry deposition and processed by soils in the watershed and ultimately delivered to the receiving waterbody by runoff, erosion, and direct deposition. The WCS calculated loads for each subbasin are shown in Table A1.

Table A1. Annual average mercury load from each subbasin

Watershed name	Total Hg load (mg)	Areal load (mg/ha)	Impervious area (mg/yr)	Sediment (mg/yr)	Runoff (mg/yr)	Deposition on water (mg/yr)
Barnett Creek	786098.4	25.6	116614.69	422879.88	177553.9	68850
Middle/Lower Ochlockonee	307965.8	21.24	125771.73	89440.3	54786.29	37867.5
Tired Creek	827172.8	22.03	252386.89	317969.16	194751.7	61965
Lower Ochlockonee	359317.5	15.62	100125.11	130407.68	97802.16	30982.5
Little Ochlockonee	873773.4	19.89	140023.69	433136.75	219614.2	80898.75
Bridge Creek	454417.5	23.11	53496.45	261042.44	98468.66	41310
Upper/Middle Ochlockonee	627746.1	20.67	152881.42	254746.48	182250.7	37867.5
Upper Ochlockonee	766396.8	20.1	164465.44	320337	186825.6	94668.75

WASP5 (Ambrose, et al. 1988) was chosen to simulate mercury fate in the Ochlockonee River. WASP5 is a general, dynamic mass balance framework for modeling contaminant fate and transport in surface waters. Environmental properties and chemical concentrations are modeled as spatially constant within segments. Each variable is advected and dispersed among water segments and exchanged with surficial benthic segments by diffusive mixing. Sorbed or particulate fractions can settle through water column segments and deposit to or erode from surficial benthic segments. Within the bed, dissolved variables can migrate downward or upward through percolation and pore water diffusion. Sorbed variables can migrate downward or upward through net sedimentation or erosion.

The toxics WASP model, TOXI5, combines a kinetic structure adapted from EXAMS2 with the WASP5 transport structure and simple sediment balance algorithms to predict dissolved and sorbed chemical concentrations in the bed and overlying waters. TOXI5 simulates the transport and transformation of chemicals as a neutral compound and up to four ionic species, also for particulate material. Local equilibrium is assumed so that the distribution of the chemical between each of the species and phases is defined by distribution or partition coefficients. The predicted mercury concentrations are shown in Table A2.

Table A2. Predicted mercury for annual average load and flow

Calculated concentrations	River reach					
	1	2	3	4	5	6
Total Hg: Water column (ng/L)	6.33	5.84	5.55	5.76	5.65	5.17
Total Hg: Sediment (ng/g)	7.05	9.07	9.81	8.17	7.63	6.97
Methyl Hg: Water column (ng/L)	0.90	0.82	0.77	0.79	0.77	0.71

Allocations

To determine the total maximum load that can come into the Ochlockonee River, the current loading conditions are evaluated and the instream concentration is determined using the modeling approach described above. This allows the development of a relationship between load and instream mercury concentrations. Using this developed relationship, the total maximum load could be determined. Because the water column mercury concentration response is linear with respect to changes in load, a proportion could be developed to calculate the total maximum mercury load from the watershed that would achieve the derived water quality target of 1.6 ng/L. The TMDL was calculated as the ratio of the water quality target to the highest segment concentration (1.6 ng/L divided by 6.3 ng/L) applied to the current annual average load of 5.00 kg/yr. This gives a TMDL load of 1.22 kg/yr mercury. This represents a 76 percent reduction from the current annual average load.

In a TMDL assessment, the total allowable load is divided and allocated to the various pollutant sources. The calculated allowable load of mercury that can come into the Ochlockonee River without exceeding the applicable water quality target of 1.6 ng/L is 1.22 kilograms/year. Because EPA's assessment indicates that over 99 percent of the current loading of mercury is from atmospheric sources, all the load reduction is being assigned to the load allocation and no reduction is required of the wasteload allocation. Therefore, the load allocation and the wasteload allocation for the Ochlockonee River are:

Load allocation (atmospheric sources) = 1.16 kilograms/year

Wasteload allocation (NPDES sources) = 0.06 kilograms/year

EPA estimates that atmospheric deposition contributes over 99 percent of current mercury loadings to the river; therefore, significant reductions in atmospheric deposition will be necessary if the applicable water quality standard is to be attained. On the basis of

the total allowable load of 1.22 kilograms per year, a 76 percent reduction of mercury loading is needed to achieve the applicable water quality standard. EPA believes that an estimated 31 percent to 41 percent reduction in mercury deposition to the Ochlockonee River watershed can be achieved by 2010 through full implementation of existing CAA requirements. In addition, there are a number of activities planned or underway to address remaining sources of mercury, and EPA expects that further reductions in mercury loadings will occur over time as a result of these activities. EPA is not able to estimate the reductions in mercury deposition to the Ochlockonee River watershed that will be achieved from future activities. However, as contemplated by CWA section 303(d)(1)(C), this TMDL quantifies the water quality problem facing the Ochlockonee River watershed and identifies the needed reductions in loadings from atmospheric deposition—by CAA initiatives or under other authorities—for the watershed to achieve applicable standards for mercury. In addition, as EPA collects additional data and information for the Ochlockonee River watershed and as new legal requirements are imposed under the CAA, EPA will continue to evaluate the effectiveness of regulatory and nonregulatory air programs in achieving the TMDL's water quality target.

The analysis of NPDES point sources in the watershed indicates that the cumulative loading of mercury from these facilities is less than 1 percent of the total estimated current loading. Even if this TMDL allocated none of the calculated allowable load to NPDES point sources (i.e., a wasteload allocation of zero), the waterbody would not attain the applicable water quality standards for mercury because of the very high mercury loadings from atmospheric deposition. At the same time, however, EPA recognizes that mercury is an environmentally persistent bioaccumulative toxic with detrimental effects to human fetuses even at minute quantities, and should be eliminated from discharges to the extent practicable. Taking these two considerations into account, this TMDL provides a wasteload allocation applicable to all Georgia NPDES facilities in the watershed in the amount of 0.06 kg/year. The TMDL was written so that all NPDES permitted facilities will achieve this wasteload allocation either through the discharge of mercury at concentrations below the applicable water quality standard of 1.6 ng/L or through the implementation of a pollutant minimization plan.

In the context of this TMDL, EPA believes it can reasonably offer the choice of the two approaches to the permitting authority for the following reasons. First, on the basis of EPA's analysis, the Agency expects either wasteload allocation option, in the aggregate, to result in point source mercury loadings less than the wasteload allocation. Second, EPA believes this flexibility is the best way of ensuring that the necessary load reductions are achieved without causing significant social and economic disruption. EPA recognizes that NPDES point sources contribute a small share of the mercury contributions to the Ochlockonee River. However, EPA also recognizes that mercury is a highly persistent toxic pollutant that can bioaccumulate in fish tissue at levels harmful to human health. Therefore, EPA has determined, as a matter of policy, that NPDES point sources known to discharge mercury at levels above the amount present in their source water should reduce their loadings of mercury using appropriate, cost-effective mercury minimization measures to ensure that the total point source discharges are at a level equal to or less than the wasteload allocation specified in this TMDL. The point sources' WLA will be applied to the increment of mercury in their discharge that is above the amount of

mercury in their source water. EPA recommends that the permitting authority make this choice between the two options in consultation with the affected discharger because EPA is not able to make the case-by-case judgments in this TMDL that EPA believes are appropriate.

II. Arivaca Lake, Arizona

Description of the Applicable Water Quality Standards

Authorities develop TMDLs to meet applicable water quality standards. These may include numeric water quality standards, narrative standards describing designated uses, and other associated indicators supporting designated uses (beneficial uses apply only to California). A numeric target identifies the specific goals or endpoints for the TMDL that equate to attainment of the water quality standard. The numeric target may be equivalent to a numeric water quality standard (where one exists) or it may represent a quantitative interpretation of a narrative standard.

The applicable numeric targets for the Arivaca TMDL are the Arizona water quality standard of 0.2 µg/L mercury in the water column and the Arizona Fish Consumption Guideline criterion of 1 mg/kg mercury concentration in fish tissue. Arizona has adopted water quality standards for mercury that apply to a number of the designated uses specified for Arivaca Lake, including protection of aquatic life and wildlife and protection of human and agricultural uses. Of these numeric criteria, the most stringent is the chronic aquatic life criterion of 0.01 µg/L dissolved mercury (see Table 7 on page 15 in the TMDL). Arizona has also issued a fish consumption advisory for this lake because mercury concentrations in fish tissue exceed 1 mg/kg mercury.

Mercury bioaccumulates in the food chain. Within a lake fish community, top predators usually have higher mercury concentrations than forage fish, and tissue concentrations generally increase with age class. Top predators (such as largemouth bass) are often target species for sport fishermen. Arizona bases its Fish Consumption Guideline on average concentrations in a sample of sport fish. Therefore, the criterion should not apply to the extreme case of the most-contaminated age class of fish within a target species; instead, the criterion is most applicable to an average-age top predator. Within Arivaca Lake, the top predator sport fish is the largemouth bass. The selected target for the TMDL analysis is an average tissue concentration in 5-year-old largemouth bass of 1.0 mg/kg.

Source Assessment

A TMDL evaluation must examine all known potential sources of the pollutant in the watershed, including point sources, nonpoint sources, and background levels. The source assessment is used as the basis of development of a model and the analysis of TMDL allocation options. There are no permitted point source discharges and no known sources of mercury-containing effluent in the Arivaca watershed. External sources of mercury load to the lake include natural background load from the watershed, atmospheric deposition, and possible nonpoint loading from past mining activities.

Watershed background load: The watershed background load of mercury was derived from mercury in the parent rock and from the net effects of atmospheric deposition of mercury on the watershed. Some mercury also exists within the parent rock formations of the Arivaca watershed, although no concentrated ore deposits are known. The net contributions of both atmospheric deposition and weathering of native rock were assessed by measuring concentrations in sediment of tributaries to Arivaca Lake. EPA collected 25 sediment and rock samples from dry tributaries in the Arivaca watershed and analyzed them for mercury. From these data, most of the sediment samples from the Arivaca watershed were considered at or near background mercury levels.

Nonpoint loadings from mining: No known mining for mercury itself has occurred in the watershed. However, mining activities for minerals other than mercury, especially historical mining practices for gold, might contribute to mercury loading in the watershed. Gold and silver mining commonly occurred in the area surrounding Arivaca Lake but apparently not within the watershed itself. The U.S. Bureau of Mines identified only one exploratory prospect, for manganese and uranium, within the Arivaca watershed itself.

Ruby Dump: Ruby Dump is in the southern portion of Arivaca watershed at the very upstream end of Cedar Canyon Wash. The dump apparently served the town of Ruby and the Montana Mine. The waste is characterized by numerous mining artifacts (e.g., crucibles) but also includes many common household items such as bottles and plates. Samples were taken at three different locations of the Ruby Dump: top of the hill (just below the fire pit), the middle of the hill, and the base of the dump. The mercury results for these samples, from the top of the hill to the bottom, were 1,467 ppb, 1,244 ppb (blind duplicate was 495 ppb), and 486 ppb. The average of these four samples is 918 ppb, which is the number used in the watershed modeling to represent mercury concentration in sediment eroding from this site.

Near-field atmospheric deposition: Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. After a review of *Mercury Study Report to Congress* (USEPA 1997a) and a search of EPA's AIRS database of permitted point sources, there are no significant U.S. sources of airborne mercury within or near the Arivaca watershed. Also, the most nearby parts of Mexico immediately to the southwest (prevailing wind direction) of the watershed are sparsely populated. Because of the lack of major nearby sources, especially sources along the axis of the prevailing wind, EPA does not believe that near-field atmospheric deposition of mercury attributable to individual emitters is a major component of mercury loading to the Arivaca watershed. Because no significant near-field sources of mercury deposition were identified, mercury from atmospheric deposition onto the watershed is treated as part of a general watershed background load in this analysis.

Far-field atmospheric deposition: In May 1997, the MDN began collecting deposition data at a new station in Caballo, in the southwestern quadrant of New Mexico. This station is the closest MDN station to the Arivaca Lake and was used to estimate loads to Arivaca Lake. Because the climate at Arivaca is wetter than at Caballo, the distribution of wet and dry deposition is likely to be different. Monthly wet deposition rates at Arivaca were estimated as the product of the volume-weighted mean concentration for wet

deposition at Caballo times the rainfall depth at Arivaca. This approach was used because volume-weighted mean concentrations are usually much more stable between sites than wet deposition rates, which are sensitive to rainfall amount. Dry deposition at Arivaca was then calculated as the difference between the total deposition rate at Caballo and the estimated Arivaca wet deposition rate. The estimates derived for Arivaca were 5.3 $\mu\text{g}/\text{m}^2/\text{yr}$ by wet deposition and 7.1 $\mu\text{g}/\text{m}^2/\text{yr}$ by dry deposition. In sum, mercury deposition at Arivaca is assumed to be equivalent to that estimated for Caballo, New Mexico, but Arivaca is estimated to receive greater wet deposition and less dry deposition than Caballo because more of the particulate mercury and reactive gaseous mercury that contribute to dry deposition will be scavenged at a site with higher rainfall.

Loading Capacity—Linking Water Quality and Pollutant Sources

The linkage analysis defines the connection between numeric targets and identified sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, associated numeric targets, and the identified sources. This provided the basis for estimating total assimilative capacity and any needed load reductions. Specifically, models of watershed loading of mercury were combined with a model of mercury cycling and bioaccumulation in the lake. This enabled a translation between the numeric target (expressed as a fish tissue concentration of mercury) and mercury loading rates. The loading capacity was then determined via the linkage analysis as the mercury loading rate that is consistent with meeting the target fish tissue concentration.

Watershed model: Watershed-scale loading of water and sediment was simulated using the Generalized Watershed Loading Function (GWLF) model. The complexity of this loading function model falls between that of detailed simulation models, which attempt a mechanistic, time-dependent representation of pollutant load generation and transport, and simple export coefficient models, which do not represent temporal variability. GWLF provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery yet is intended to be applicable without calibration. Solids load, runoff, and ground water seepage can then be used to estimate particulate and dissolved-phase pollutant delivery to a stream, on the basis of pollutant concentrations in soil, runoff, and ground water. Applying the GWLF model to the period from October 1985 through September 1998 yielded an average of 11.0 cm/year runoff and 2,520,000 kg sediment yield by sheet and rill erosion. The sediment yield estimate is likely to be less than the actual yield rate from the watershed because mass wasting loads were not accounted for; however, mass wasting loads are thought to be of minor significance for loading of bioavailable mercury to the lake.

Estimates of watershed mercury loading were based on the sediment loading estimates generated by GWLF by applying a sediment potency factor. These estimates are shown in Table A3. A background loading estimate was first calculated, then combined with estimates of loads from individual hot spots. The majority of the EPA sediment samples showed no clear spatial patterns, with the exception of the hot spot area identified at Ruby Dump. Therefore, background loading was calculated using the central tendency of sediment concentrations from all samples excluding Ruby Dump. The background sediment mercury concentrations were assumed to be distributed lognormally, as is typical for environmental concentration samples, and an estimate of the arithmetic mean

of 70.9 ppb was calculated from the observed geometric mean and coefficient of variation. Applying this assumption to the GWLF estimates of sediment transport yields an estimated rate of mercury loading from watershed background of 178.9 g/yr.

Loading from the Ruby Dump was calculated separately, but was also based on the GWLF estimate of sediment load generated per hectare of “rangeland” (the land use surrounding the hot spots), as reduced by the sediment delivery ratio for the watershed. The extent of the hot spot was observed to be 200 feet by 50 feet. The mercury concentration assigned to surface sediments at the dump was the arithmetic average of the four EPA samples taken in October 1997, or 918 ppb. From these assumptions, less than 1 percent of the watershed mercury load to Arivaca Lake appears to originate from Ruby Dump, which is the only identified hot spot in the watershed.

Table A3. Annual total mercury load to Arivaca Lake

Watershed year	Mercury loading to lake (grams per year)			
	From watershed	From Ruby Dump	From direct atmospheric deposition to lake	Total
1986	170.16	0.65	4.208	175.018
1987	184.34	0.7	4.208	189.248
1988	205.61	0.79	4.208	210.608
1989	70.9	0.27	4.208	75.378
1990	198.52	0.76	4.208	203.488
1991	99.26	0.38	4.208	103.848
1992	163.07	0.62	4.208	167.898
1993	233.97	0.89	4.208	239.068
1994	141.8	0.54	4.208	146.548
1995	219.79	0.84	4.208	224.838
1996	170.16	0.65	4.208	175.018
1997	191.43	0.73	4.208	196.368
1998	276.51	1.06	4.208	281.778
Grand Total	2,325.52	8.88	54.704	2,389.10
Annual Average	178.89	0.68	4.21	183.78

The direct deposition of mercury from the atmosphere onto the Arivaca Lake surface was calculated by multiplying the estimated atmospheric deposition rates times the lake surface area, resulting in a load of 4.2 g/yr.

Lake hydrology model: The water level in Arivaca Lake is not actively managed, and releases occur only when storage capacity is exceeded. Therefore, lake hydrology was represented by a simple monthly water balance. Applying the water balance model requires pan evaporation data as an input in addition to the watershed meteorological data. Because no evaporation data were available at the local Cooperative Summary of the Day meteorological station, pan evaporation data for Tucson were used. Pan evaporation for 1980 through 1995 was obtained from the BASINS 2.0 Region 9 data files. Later pan evaporation data were not available for Tucson, so monthly averages were used for the 1996 through 1998 water balance. The water balance model was run for

the period 1985 through 1998. This water balance approach provides a rough approximation of the seasonal cycle of changes in volume and surface area of Arivaca Lake and of the amount of water released downstream over the spillway. It cannot capture daily or event scale movement of water in and out of the lake.

Mercury cycling and bioaccumulation model: Cycling and bioaccumulation of mercury within the lake were simulated using the D-MCM (EPRI 1999). D-MCM predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. It can be used to develop and test hypotheses, scope field studies, improve understanding of cause/effect relationships, predict responses to changes in loading, and help design and evaluate mitigation options.

Because strong anoxia in the hypolimnion is a prominent feature during summer stratification for the Arizona lakes simulated in this study, D-MCM was modified to explicitly allow significant methylation to occur in the hypolimnion. In previous applications of D-MCM, the occurrence of methylation was restricted to primarily within surficial sediments. That the locus of methylation likely includes or is even largely within the hypolimnion is supported by (1) the detection of significant very high methylmercury concentrations in the hypolimnia of Arivaca Lake and (2) almost complete losses of sulfate in Arivaca Lake in the hypolimnion resulting from sulfate reduction. An input was added to the model to specify the rate constant for hypolimnetic methylation, distinct from sediment methylation.

Results of the model calibration are shown in Table A4. The model calculations are the predicted annual ranges after the model has reached steady state. The observed concentrations are from July 1997.

Table A4. Predicted and observed mercury for annual average load and flow

	Predicted	Observed
Methyl Hg: Water column (ng/L)	0.00–12.07	14.3
Hg II: Water column (ng/L)	0.00–6.28	1.46–8.3
Methyl Hg: 5-year-old largemouth bass (mg/kg)	1.18	1.18

Allocations

A TMDL represents the sum of all individual allocations of portions of the waterbody's loading capacity. Allocations may be made to point sources (wasteload allocations) or nonpoint sources (load allocations). The TMDL (sum of allocations) must be less than or equal to the loading capacity; it is equal to the loading capacity only if the entire loading capacity is allocated. In many cases, it is appropriate to hold in reserve a portion of the loading capacity to provide a margin of safety (MOS), as provided for in the TMDL regulation. The allocations and MOS are shown in Table A5. These allocations, from the best currently available information, predict attainment of acceptable fish tissue concentrations within a time horizon of approximately 10 years. A delay in achieving

standards is unavoidable because time will be required for mercury to cycle through the lake and food chain after load reductions occur.

Table A5. Summary of TMDL allocations and needed load reductions (in g-Hg/yr)

Source	Allocation	Existing load	Needed reduction
Wasteload allocations	0.0	0.0	0.0
<i>Load allocations</i>			
Atmospheric deposition	4.2	4.2	0
Ruby dump	0.7	0.7	0
Watershed background	111.2	178.9	67.7
Total	116.1	183.8	67.7
Unallocated reserve	38.7		
Loading capacity	154.8		

The model was used to evaluate the load reductions necessary to meet the numeric target. The response of concentrations of mercury in 5-year-old largemouth bass to changes in external mercury loads is nearly linear. This is because the sediment burial rates are high and sediment recycling is low, with the majority of the methylmercury that enters the food chain being created in the anoxic portion of the water column. The model calculates that the numeric target of 1 mg/kg in 5-year-old largemouth bass is predicted to be met with a 16 percent reduction in total watershed loads to Arivaca Lake, which results in a loading capacity of 154.8 grams mercury per year.

There are uncertainties associated with mercury sources and the linkage between mercury sources and fish tissue concentrations in Arivaca Lake. As a result, the TMDL reserves 38.7 g-Hg/yr (25 percent of the loading capacity) for the MOS and allots the remaining load of 116.1 g-Hg/yr for sources. Because no permitted point source discharges occur within the Arivaca watershed, the wasteload allocation is zero and the load allocation is 116.1 g-Hg/yr.

The load allocation provides loads for three general sources: direct atmospheric deposition onto the lake surface, hot spot loading from Ruby Dump, and generalized background watershed loading, including mercury derived from parent rock and soil material, small amounts of residual mercury from past mining operations, and the net contribution of atmospheric deposition onto the watershed. Direct deposition to the lake surface is a small part of the total load and is believed to derive from long-range transport of global sources which are not readily controllable. The load from Ruby Dump is also small. As a result, the TMDL does not require reductions from these sources, and their load allocations are their existing loads.

Background watershed loading appears to be the major source of mercury to Arivaca Lake. The intensive watershed survey conducted for this TMDL did not identify any significant terrestrial sources of mercury. Regarding air deposition to the watershed land surface, insufficient data were available to calculate reliable estimates of the proportion of mercury deposited from the air that actually reaches Arivaca Lake. Therefore, a load allocation of 111.2 g-Hg/yr was established for overall background watershed loading.

This requires a 38 percent reduction from existing estimated loads from this source. This reduction is believed feasible for several reasons.

Potential for erosion control: Reduction of mercury loading from the watershed to Arivaca Lake depends on reduction in sediment erosion rates. Improved livestock management practices could obtain significant reductions in erosion rates. As a side benefit, implementation of livestock BMPs could result in significant reductions in loadings of DOC and nutrients to the lake. The availability of high levels of DOC and nutrients in the lake appears to affect the methylation process. Reduction of DOC and nutrient levels should reduce the efficiency of the methylation process at Arivaca Lake, effectively increasing the lake's mercury loading capacity.

Reductions in atmospheric deposition of mercury: Although reliable estimates are unavailable, new mercury air emissions to the environment appear to be declining. U.S. mercury emissions have declined significantly since 1990 and are expected to decline further upon implementation of new emission limits on incinerators as required by recent EPA regulations. Reductions in air deposition in Arivaca Lake watershed would eventually result in decreases in mercury loading to the lake itself.

Potential location and remediation of undiscovered mercury sources: Although investigation of the watershed did not reveal any significant localized sources of mercury in the watershed (with the possible exception of Ruby Dump), additional site investigation is warranted to ensure that no significant sources were missed. From past experience with mine site remediation in similar circumstances in Arizona, newly discovered sites could be effectively eliminated as ongoing mercury sources.

Alternative management strategies: Any alterations in rates of methylation or in rates of mercury loss to deep sediments will change the relationship between external mercury load and fish tissue concentration and would thus result in a change in the loading capacity for external mercury loads. The loading capacity could be increased by management intervention methods that decrease rates of bacterial methylmercury production within the lake or increase rates of burial and sequestration of mercury in lake sediment. Selection of such an approach would require further research and feasibility studies. Some alternative strategies that may be suitable for further investigation include the following:

- Hypolimnion aeration or mixing
- Sulfur chemistry modification
- Alum treatment
- Reduce DOC and nutrient levels
- Dredge lake sediments

III. McPhee and Narraguinnep Reservoirs, Colorado

Description of the Applicable Water Quality Standards

The TMDL for McPhee and Narraguinnep Reservoirs in southwestern Colorado was based on the Fish Consumption Advisory action level of 0.5 mg/kg mercury concentration in fish tissue. Colorado Department of Public Health and the Environment listings are based on the risk analysis presented in the May 6, 1991 Disease Control and Epidemiology Division Position Paper for *Draft Colorado Health Advisory for Consumption of Fish Contaminated with Methylmercury*. This paper, using a toxicity value RfD of 0.3 µg/kg/day, establishes a fish tissue concentration of 0.5 mg/kg as the approximate center of the range at which the safe consumption level is 4 meals per month for nonpregnant adults and 1 meal per month for women who are pregnant, nursing, or planning to become pregnant and children 9 years of age or younger. The criterion is applied to an average-age top predator. Within McPhee Reservoir, the top predator among sport fish regularly taken is the smallmouth bass (19 percent of the total catch in 1993). The top predator sport fish in Narraguinnep Reservoir is the walleye. The lake water quality model D-MCM (EPRI 1999) is capable of predicting mercury concentrations in fish tissue for each age class at each trophic level. Average mercury concentrations in fish tissue of target species are assumed to be approximated by the average concentration in 15-inch smallmouth bass in McPhee and the 18-inch walleye in Narraguinnep. Therefore, the selected target for the TMDL analysis in McPhee Reservoir is an average tissue concentration in 15-inch smallmouth bass of 0.5 mg/kg or less. The selected target in Narraguinnep Reservoir is the 18-inch walleye of 0.5 mg/kg or less.

Source Assessment

McPhee and Narraguinnep Reservoirs have several sources of mercury. The sources external to the reservoirs separate into direct atmospheric deposition onto the lakes (from both near- and far-field sources) and transport into the lakes from the watershed. The watershed loading occurs in both dissolved and sediment-sorbed forms. Ultimate sources in the watershed include mercury in parent rock, mercury residue from mine tailings and mine seeps, point source discharges, and atmospheric deposition on to the watershed, including deposition and storage in snowpack.

Table A6. Summary of mercury load estimates for McPhee Reservoir

Reservoir	Watershed runoff (g/yr)	Watershed sediment (g/yr)	Interbasin transfer (g/yr)	Atmos. deposition (g/yr)	Total (g/yr)	Load per volume (mg/ac-ft)	Load per surface area (mg/m ²)
McPhee	2,576	222		251	3,049	4.66	0.098
Narraguinnep	2.7	22.7	15.9	36.8	78.1	4.59	0.035

Past mining activities likely provide an important source of mercury load to the McPhee and Narraguinnep watershed. Three large mining districts exist in the Dolores River watershed, the LaPlata, the Rico, and the area around Dunton on the West Dolores River. The quantity of mercury loading from mining operations has been estimated through a

combination of observed data in the water column and sediment coupled with the watershed linkage analysis.

Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. Two large coal-fired power plants are in the Four Corners area within about 50 miles of the McPhee and Narraguinnep Reservoirs. The plants in the Four Corners area (2,040 megawatt (MW) capacity) and the Navajo plant (1,500 MW capacity) are upwind of McPhee and Narraguinnep Reservoirs. It is likely that the mercury emitted from these plants contributes to the mercury loading of McPhee and Narraguinnep Reservoirs. No direct measurements of atmospheric deposition of mercury are available, therefore EPA cannot assess the significance of this loading and must await further investigation, including the establishment of a mercury deposition monitoring site in the area.

Loading Capacity—Linking Water Quality and Pollutant Sources

Models of watershed loading of mercury are combined with a model of mercury cycling and bioaccumulation in the lake to translate the numeric target, expressed as a fish tissue concentration of mercury, to mercury loading rates. The coupled models estimate mercury loading to the reservoirs and predict mercury cycling and speciation within the reservoir. An estimated load reduction of 52 percent is needed for long-term average mercury concentrations in a standardized 15-inch smallmouth bass to drop to 0.5 mg/kg wet muscle.

Allocations

The loading capacity for McPhee Reservoir was estimated to be 2.59 kilograms mercury per year. Narraguinnep Reservoir loading capacity was estimated at 39.1 grams of mercury per year. This is the maximum rate of loading consistent with meeting the numeric target of 0.5 mg/kg in fish tissue. Due to the uncertainties regarding the linkage between mercury sources and fish tissue concentrations in McPhee and Narraguinnep Reservoirs, an allocation of 70 percent of the loading capacity was used for this TMDL. The TMDL calculated for McPhee Reservoir is equivalent to a total annual mercury loading rate of 1,814 g/yr (70 percent of the loading capacity of 2,592 kg/yr), while Narraguinnep Reservoir is equivalent to a total annual mercury loading rate of 27.3 g-Hg/yr (70 percent of 39.1 g-Hg/yr).

Table A7. Summary of TMDL allocations and needed load reductions for McPhee Reservoir

Source	Allocation	Existing load	Needed reduction
Atmospheric deposition	63	251	188
Rico/Silver Creek mining area	507	1030	523
Dunton mining area	348	708	360
La Plata mining area	69	141	72
Watershed background	827	919	92
Total	1,814	3,049	1,235
Unallocated reserve	778		
Loading capacity	2,590		

Measurements in g-Hg/yr

Table A8. Summary of TMDL allocations and needed load reductions for Narraguinnep Reservoir

Source	Allocation	Existing load	Needed reduction
Atmospheric Deposition	9.2	36.8	27.6
Interbasin Transfer from McPhee Reservoir	9.5	15.9	6.4
Watershed Background	8.6	25.4	16.8
Total	27.3	78.1	50.8
Unallocated Reserve	11.8		
Loading Capacity	39.1		

Measurements in g-Hg/yr

IV. Clear Lake, California

Description of the Applicable Water Quality Standards

The EPA promulgated the CTR in May 2000 (65 FR 31682). The CTR contains a water quality criterion of 50 ng/L total recoverable mercury for water and organism consumption and is intended to protect humans from exposure to mercury in drinking water and fish and shellfish consumption. This criterion is enforceable in California for all waters with a municipal or domestic water supply designated use and is applicable to Clear Lake. However, the state of California does not consider this criterion to be sufficiently protective of the consumers of fish from Clear Lake.

The water quality management plan or Basin Plan for the Central Valley Regional Water Quality Control Board adopted new water quality standards for mercury for Clear Lake at the same time it adopted mercury TMDLs for Clear Lake. The state's water quality criteria are for fish tissue and are intended to protect designated uses for fishing and wildlife habitat. The applicable criteria are: 0.09 mg/kg and 0.19 mg/kg of mercury in fish tissue for trophic levels 3 and 4 fish, respectively. These levels were recommended by the U.S. Fish and Wildlife Service to protect wildlife, including osprey and bald eagles, at Clear Lake; these levels allow adults to safely consume about 3.5 fish meals per month (26 grams/day) if eating mainly trophic level 4 fish such as catfish and bass. The 26 grams/day assumes a diet comprised of 70 percent trophic level 4 fish and 30 percent

trophic level 3 fish. The 90th percentile consumption rate of a small group of residents of Clear Lake, primarily members of the Elem Pomo Indian Tribe, is 30 grams/day of Clear Lake fish, as reported in 1997.

Source Assessment

Clear Lake is in Lake County in northern California. It is a shallow, eutrophic waterbody that is comprised of three basins, the Upper, Lower, and Oaks Arms. It is the largest natural lake entirely within California's boundaries. Tourism and sport fishing are important sectors of the local economy. Five Native American Indian Tribes use resources of the lake and its watershed.

The Clear Lake watershed lies within a region naturally enriched in mercury. The Sulphur Bank Mercury Mine (SBMM) site, on the shores of Oak Arm, was a highly productive source of mercury between 1872 and 1957. Similar smaller mines were in the Clear Lake watershed, all of which are now inactive. Levels of mercury in Clear Lake sediments rose significantly after 1927, when open pit operations became the dominant mining method at SBMM. EPA declared the SBMM a federal Superfund site in 1991, and since then, several remediation projects have been completed, including regrading and vegetation of mine waste piles along the shoreline and construction of a diversion system for surface water runoff. EPA is conducting a remedial investigation to fully characterize the SBMM site to propose final remedies.

Inorganic mercury loads entering Clear Lake come from: ground water and surface water from the SBMM site; tributaries and other surface water that flows directly into the lake; and atmospheric deposition, including atmospheric flux from SBMM. Some mercury deposited historically in the lake due to mining operations or erosion at SBMM might also contribute to mercury concentrations in fish today.

Ground water and surface water from the SBMM site: SBMM covers approximately 1 square mile on the east shore of the Oaks Arm of Clear Lake. The site contains approximately 120 acres of exposed mine overburden and tailings (referred to as waste rock). Two small unprocessed ore piles are also on the site. Mercury in samples of mine materials ranged from 50 to 4,000 mg/kg. All piles of mine materials exhibit the potential to generate acid rock drainage. The abandoned mine pit, the Herman Impoundment, is filled with 90 feet of acidic water (pH = 3), and has a surface area of about 20 acres. The average concentrations in the Herman Impoundment of water and sediment are around 800 ng/L and 26 mg/kg, respectively. A geothermal vent located at the bottom of the impoundment continues to discharge gases, minerals (including mercury), and fluids into the pit.

A large pile of waste rock, known as the waste rock dam (WRD) stretches about 2,000 feet along the shore of the western side of the SBMM site. The WRD lies between Herman Impoundment and Clear Lake. The surface water in the impoundment is 10–14 feet above the surface of Clear Lake, which creates a gradient of ground water flow toward the lake. Surface runoff from the northern side of the site is bounded by a wetland that drains to Clear Lake. Surface runoff from the northern waste rock piles is directed through culverts into the northern wetland. In 1990, rock and geofabric barriers were installed at the culverts to reduce transport of suspended solids. The northern wetland is

used for cattle grazing and as a source of fish, tules, and other resources used by the members of the Elem Pomo Tribe. Waste rock piles extend into the wetlands.

Inputs of mercury from SBMM are estimated to be between 1 and 568 kg/year. EPA Superfund Program's estimate of mercury transported in ground water from the WRD is used as the lower bound input. Regional Board staff estimate that 568 kg/year is the maximum upper bound estimate of all inputs from SBMM, including past and continuing contributions to the active sediment layer. This is approximately 96.5 percent of total sources.

Ground water from SBMM appears to contribute mercury that is readily methylated, relative to mercury from other inputs. Ground water flow from the mine site has been detected entering Clear Lake by subsurface flow through lake sediments. Mercury in ground water from the WRD is solubilized and likely in chemical forms that are easily taken up by methylating bacteria. Acidic drainage from the mine site also contains high sulfate concentrations that enhance the rates of methylation by sulfate-reducing bacteria. This assertion is supported by data showing that methylation rates near the mine site are significantly higher than in other parts of the Clear Lake. In contrast to mercury in SBMM ground water, mercury in lakebed and tributary sediments originates primarily as cinnabar, which has low solubility in water.

Tributaries and other surface water flowing directly into the lake: Mercury entering Clear Lake from its tributaries originates in runoff from naturally mercury-enriched soils, sites of historical mining activities, and mercury deposited in the watershed from the atmosphere. Geothermal springs might contribute to tributary loads, especially in the Schindler Creek tributary to Oaks Arm. Tributary and watershed runoff loads of mercury range from 1 to 60 kg/year, depending upon flow rates. Loads in average water years are 18 kg/year. This is approximately 3 percent of total sources.

Geothermal springs and lava tubes that directly discharge to Clear Lake do not appear to be significant sources of mercury. Mercury concentrations in surficial sediment samples collected near lakebed geothermal springs were not elevated, relative to levels in sediment away from geothermal springs.

Atmospheric deposition including flux from the SBMM site: Small amounts of mercury deposit directly on the surface of Clear Lake from the global atmospheric pool and potentially from local, mercury-enriched sources. Atmospheric loads to the lake surface from the global pool were estimated using data from MDN monitoring stations in Mendocino County and San Jose. Estimates ranged from 0.6 to 2.0 kg/year. This is approximately 0.3 percent of total sources.

Loading Capacity–Linking Water Quality and Pollutant Sources

The Regional Board staff assumes that there is a directly proportional relationship between methylmercury in fish and mercury in the surficial sediment. This is a simplification of a highly complex process. Many factors affect methylation or concentrations of methylmercury, including sulfide and sulfate concentrations, temperature, organic carbon, and so on. Factors that affect accumulation of methylmercury in fish include species, growth rate, prey availability, and the like. To

reduce levels of methylmercury in fish, loads of mercury to the lake must be reduced. Section 5.3.1 of the Staff Report provides examples of remediation projects that demonstrate removal of inorganic mercury from a range of aquatic environments has been effective in reducing concentrations of mercury in fish.

A set of first order relationships, each controlled by a single variable of concentration of mercury or methylmercury provide basis for the assumption of a directly proportional relationship between mercury in fish and in surficial sediment in Clear Lake. Concentrations of methylmercury in water and methylmercury in biota are related by BAFs. Relationships between methylmercury in the water column and in sediment can be described as a flux rate of methylmercury from sediment. Concentrations of methylmercury and mercury in sediment are related through calculation of a methylation efficiency index (ratio of methylmercury to mercury in surficial sediment).

In each of these steps in the linkage analysis, one variable is related to another by a simple ratio or linear equation. For example, BAFs are calculated by dividing the concentration of methylmercury in fish by the concentration of methylmercury in the water. Data are available to determine BAF and methylation indices that are specific for Clear Lake. With the current understanding of the transport, methylation, and uptake processes in Clear Lake, staff is unable to refine these relationships to incorporate effects of other factors. The end result was that methylmercury in biota was related linearly to mercury in surficial sediment.

Meeting the recommended water quality standards would require reduction of existing fish tissue concentrations by 60 percent. Using the linear relationship, the linkage analysis indicates that overall mercury loads to Clear Lake sediment must be reduced by 60 percent in order to reduce methylmercury concentrations in fish tissue by the proportional amount. The Regional Board is establishing the assimilative capacity of inorganic mercury in Clear Lake sediments as 70 percent of existing levels to include a margin of safety of 10 percent to account for the uncertainties in the linkage analysis.

Allocations

The strategy for meeting the fish tissue criteria is to reduce the inputs of mercury to the lake from tributaries and the SBMM site, combined with active and passive remediation of contaminated lake sediments. The load allocations for Clear Lake will result in a reduction in the overall mercury sediment concentration by 70 percent of existing concentrations. The load allocations are assigned to the active sediment layer of the lakebed, the SBMM terrestrial site, the tributary creeks and surface water runoff to Clear Lake, and atmospheric deposition. Table A9 summarizes the load allocations. The load allocation to the active sediment layer is expressed as reducing concentrations of mercury in the active sediment layer to 30 percent of current concentrations. The load allocation to the SBMM terrestrial site is 5 percent of the ongoing loads from the terrestrial mine site. The load allocation for the mine also includes reducing mercury concentrations in surficial sediment to achieve the sediment compliance goals for Oaks Arm shown in Table A10. The load allocation to tributary and surface water runoff is 80 percent of existing loads. These load allocations account for seasonal variation in mercury loads, which vary with water flow and rainfall. The analysis includes an implicit margin of

safety in the reference doses for methylmercury that were used to develop the fish tissue objectives. It also includes an explicit margin of safety of 10 percent to account for uncertainty in the relationship between fish tissue concentrations and loads of mercury. The reductions in loads of mercury from all sources are expected to result in attainment of water quality objectives.

Table A9. Summary of mercury load allocations

Source	Existing load (kg/year)	Needed reduction
Clear Lake sediment	695	70% of existing concentration
Sulphur Bank Mine		95% of existing load
Tributaries	18	20% of existing load
Atmosphere	2	no change

Table A10. Sediment goals for mercury in Clear Lake

Site designation	Location	Sediment mercury goal (mg/kg dry weight) ^a
Upper Arm UA-03	Center of Upper Arm on transect from Lakeport to Lucerne	0.8
Lower Arm LA-03	Center of Lower Arm, north and west of Monitor Point	1.0
Oaks Arm OA-01 ^c	0.3 km from SBMM 0.3 km from SBMM 0.8 km from SBMM 1.8 km from SBMM 3.0 km from SBMM 7.7 km from SBMM	16 ^b
OA-02 ^c		16 ^b
OA-03 ^c		16
OA-04 ^c		10
Narrows O1		3

a. Sediment goals are 30 percent of existing concentrations. Existing concentrations are taken as the average mercury concentrations in samples collected in 1996–2000 (Clear Lake Basin Plan Amendment Staff Report).

b. Due to the exceptionally high concentrations existing at the eastern end of Oaks Arm, sediment goals at OA-01 and OA-02 are not 70 percent of existing concentrations. These goals are equal to the sediment goal established for OA-03.

c. Sediment goal is part of the load allocation for SBMM.

Clear Lake sediment: Reducing mercury concentrations in surficial sediment by 70 percent is an overall goal for the entire lake. To achieve water quality objectives, extremely high levels of mercury in the eastern end of Oaks Arm near SBMM must be reduced by more than 70 percent. To evaluate progress in lowering sediment concentrations, the following sediment compliance goals are established at sites that have been sampled previously.

Sulphur Bank Mercury Mine: Current and past releases from the SBMM are a significant source of mercury loading to Clear Lake. Ongoing annual loads from the terrestrial mine site to the lakebed sediments occur through ground water, surface water, and atmospheric routes. Loads from ongoing releases from the terrestrial mine site should be reduced to 5 percent of existing inputs. Because of its high potential for methylation relative to mercury in lakebed sediments, mercury entering the lake through ground water from the mine site should be reduced to 0.5 kg/year.

Past releases from the mine site are a current source of exposure through remobilization of mercury that exists in the lakebed sediments as a result of past releases to the lake from the terrestrial mine site. Past active mining operations, erosion, and other mercury transport processes at SBMM have contaminated sediment in Oaks Arm. The load allocation assigned to SBMM includes reducing surficial sediment concentrations in Oaks Arm by 70 percent (more at sites nearest the mine site) to meet the sediment compliance goals in Table A10.

EPA anticipates implementing additional actions to address the ongoing surface and ground water releases from the SBMM over the next several years. These actions are expected to lead to significant reductions in the ongoing releases from the mine pit, the mine waste piles, and other ongoing sources of mercury releases from the terrestrial mine site. EPA also plans to investigate what steps are appropriate under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to address the existing contamination in the lakebed sediments from past releases from the SBMM. The Regional Board will continue to work closely with EPA on these important activities. In addition, the Regional Board will coordinate monitoring activities to investigate other sources of mercury loads to Clear Lake. These investigations by EPA and the Regional Board should reduce the uncertainty that currently exists regarding the annual load of mercury to the lake, the contribution of each source to that load, and the degree to which those sources lead to methylmercury exposure to and mercury uptake by fish in the lake. This information should lead to more refined decisions about what additional steps are appropriate and feasible to achieve the applicable water quality criteria.

Tributaries and surface water runoff: Past and current loads of mercury from the tributaries and direct surface water runoff are also a source of mercury loading to the lake and to the active sediment layer in the lakebed. This section excludes loads from surface water runoff associated with the SBMM, which are addressed separately above. The loads of mercury from the tributaries and surface water runoff to Clear Lake should be reduced by 20 percent of existing levels. In an average water year, existing loads are estimated to be 18 kg/year. Loads range from 1 to 60 kg/year depending upon water flow rates and other factors. The load allocation applies to tributary inputs as a whole, instead of to individual tributaries. Efforts should be focused on identifying and controlling inputs from hot spots. The U.S. Bureau of Land Management, U.S. Forest Service, other land management agencies in the Clear Lake Basin, and Lake County will submit plans for monitoring and implementation to achieve the necessary load reductions. The Regional Board will coordinate with those agencies and other interested parties to develop the monitoring and implementation plans. The purpose of the monitoring is to refine load estimates and identify potential hot spots of mercury loading from tributaries or direct surface runoff into Clear Lake. Hot spots can include erosion of soils with concentrations of mercury above the average for the rest of the tributary. If significant sources are identified, the Regional Board will coordinate with the agencies to develop and implement load reductions. The implementation plans will include a summation of existing erosion control efforts and a discussion of feasibility and proposed actions to control loads from identified hot spots. The agencies will provide monitoring and implementation plans within 5 years after the effective date of this amendment and

implement load reduction plans within 5 years thereafter. The goal is to complete the load reductions within 10 years of implementation plan approval.

The Regional Board will work with the Native American Tribes in the Clear Lake watershed on mercury reduction programs for the tributaries and surface water runoff. They will solicit the tribes' participation in the development of monitoring and implementation plans.

Wetlands: The Regional Board is concerned about the potential for wetland areas to be significant sources of methylmercury. Loads and fate of methylmercury from wetlands that drain to Clear Lake are not fully understood. The potential for production of methylmercury should be assessed during the planning of any wetlands or floodplain restoration projects within the Clear Lake watershed. The Regional Board established a goal of no significant increases of methylmercury to Clear Lake resulting from such activities. As factors contributing to mercury methylation are better understood, the Regional Board should examine the possible control of existing methylmercury production within tributary watersheds.

Atmospheric deposition: Atmospheric loads of mercury originating outside of the Clear Lake watershed and depositing locally are minimal. Global and regional atmospheric inputs of mercury are not under the jurisdiction of the Regional Water Board. Loads of mercury from outside of the Clear Lake watershed and depositing from air onto the lake surface are established at the existing input rate, which is estimated to be 1 to 2 kg/year.

Appendix B. Tables from Methylmercury Criteria Document

This appendix contains several tables taken directly from the 2001 methylmercury criteria document. These are repeated here to help the reader understand the development of the 2001 criterion.

Table 5-1. Exposure parameters used in derivation of the water quality criterion. (References cited in this table can be found in the 2001 methylmercury criteria document.)

Parameter	Population			Source
	Children (0-14 years)	Women of Childbearing Age (15-44 years)	Adults in the General Population	
Body Weight, kg	30	67	70	U.S. EPA (2000a)
Drinking Water Intake, L/day	1.0	2.0	2.0	U.S. EPA (2000a)
Freshwater/Estuarine Fish Intake, g/day	156.3 ^b	165.5 ^b	17.5 ^{c24}	U.S. EPA (2000a)
Inhalation, m ³ /day	10.4	11	20	U.S. EPA (1994, 1997h) ^d
Soil Ingestion, g/day	0.0001, 0.01 ^a	0.00005	0.00005	U.S. EPA (1997h)
Mean Marine Fish Intake, g/day	74.9 ^b	91.04 ^b	12.46 ^c	U.S. EPA (2000b)
Median Marine Fish intake, g/day	59.71 ^b	75.48 ^b	0 ^c	U.S. EPA (2000b)
90 th Percentile Marine Fish Intake, g/day	152.29 ^b	188.35 ^b	49.16 ^c	U.S. EPA (2000b)

^aPica child soil ingestion

^bFor children and women of childbearing age, intake rates are estimates of “consumers only” data (as described in U.S. EPA, 2000b)

^cFor adults in the general population, intake rates are estimates of all survey respondents to derive an estimate of long-term consumption (U.S. EPA).

^dInhalation rates for children and women of childbearing age from U.S. EPA, 1997h. Inhalation rates for adults in the general population from U.S. EPA (1994).

²⁴ This is the 90th percentile freshwater and estuarine fish consumption value.

Table 5-14. Average Mercury Concentrations in Marine Fish and Shellfish²⁵
 (References cited in this table can be found in the 2001 methylmercury criteria document)

Species	Concentration ^a (µg Hg/g Wet Wt.)	Species	Concentration (µg Hg/g Wet Wt.)
Finfish			
Anchovy	0.047	Pompano [*]	0.104
Barracuda, Pacific	0.177	Porgy [*]	0.522 ^b
Cod [*]	0.121	Ray	0.176
Croaker, Atlantic	0.125	Salmon [*]	0.035
Eel, American	0.213	Sardines [*]	0.1
Flounder ^{*,c}	0.092	Sea Bass [*]	0.135
Haddock [*]	0.089	Shark [*]	1.327
Hake	0.145	Skate	0.176
Halibut [*]	0.25	Smelt, Rainbot [*]	0.1
Herring	0.013	Snapper [*]	0.25
Kingfish	0.10	Sturgeon	0.235
Mackerel [*]	0.081	Swordfish [*]	0.95 ^c
Mullet	0.009	Tuna [*]	0.206
Ocean Perch [*]	0.116	Whiting (silver hake) [*]	0.041
Pollock [*]	0.15	Whitefish [*]	0.054 ^d
Shellfish			
Abalone	0.016	Oysters	0.023
Clam [*]	0.023	Scallop [*]	0.042
Crab [*]	0.117	Shrimp	0.047
Lobster	0.232	Other shellfish [*]	0.012 ^b
Molluscan Cephalopods			
Octopus [*]	0.029	Squid [*]	0.026

^{*}Denotes species used in calculation of methylmercury intake from marine fish for one or more populations of concern, based on existence of data for consumption in the CSFII (U.S. EPA, 2000b).

^a Mercury concentrations are from NMFS (1978) as reported in U.S. EPA (1997d) unless otherwise noted, measured as µg of mercury per gram wet weight of fish tissue.

^b Mercury concentration data are from Stern et al. (1996) as cited in U.S. EPA (1997c).

^c Mercury concentration data are from U.S. FDA Compliance Testing as cited in U.S. EPA (1997c).

^d Mercury concentration data are from U.S. FDA (1978) as cited in U.S. EPA (1997c).

^e Mercury data for flounder were used to estimate mercury concentration in marine flatfish for intake calculations.

²⁵ More current information on commercial fish and shellfish is provided by the Food and Drug Administration at <http://www.cfsan.fda.gov/%7Efrf/sea-mehg.html>

Table 5-30. Exposure estimates for methylmercury and percent of total exposure based on adults in the general population

Exposure Source	Exposure Estimate (mg/kg-day)	Percent of Total Exposure	Percent of RfD
Ambient water intake	4.3×10^{-9}	0.0047	0.004
Drinking water intake ^a	5.6×10^{-8}	0.0605	0.006
Nonfish dietary intake	0	0	0
Marine fish intake	2.7×10^{-5}	29.33	27
Air intake	4.6×10^{-9}	0.005	0.005
Soil intake	1.3×10^{-9}	0.0014	0.001

^a This represents the high-end of the range of estimates. Because the contribution of ambient water or drinking water intake to total exposure is so negligible in comparison to the sum of intake from other sources, there is not difference in the total exposure estimated using either of these two alternatives.

Appendix C. Analytical Methods

Table C1. Analytical methods for determining mercury and methylmercury in tissue

Method	Form/species and applicable matrices	Sensitivity	Technique	Known studies or literature references using the techniques in this method
Draft Method 1630, with modifications for tissue	Methylmercury in tissue	Methylmercury in tissue	Tissue modification: digest tissue with acid solution, neutralize with acetate buffer, and analyze as per Method 1630 (i.e., distillation with heat and N ₂ flow to separate methylHg from sample, ethylation with sodium tetraethyl borate, N ₂ purging of methylethylHg onto graphite carbon (Carbotrap) column, thermal desorption of methylethylHg and reduction to Hg ⁰ , followed by CVAFS detection.	- EPA Cook Inlet Contaminant Study - Lake Michigan fish and invertebrates, Mason and Sullivan 1997 - NE Minnesota lake plankton, Monson and Brezonik 1998²⁶ - Method performance testing in freshwater and marine fish, Bloom 1989
Method 1631, Draft Appendix A	Total mercury in tissue, sludge, and sediment	Total mercury in tissue, sludge, and sediment	Digest tissue with HNO ₃ /H ₂ SO ₄ . Dilute digestate with BrCl solution to destroy remaining organic material. Analyze digestate per Method 1631 (i.e., add BrCl to oxidize all Hg compounds to Hg(II). Sequentially pre-reduced with hydroxylamine hydrochloride to destroy the free halogens and reduced with SnCl ₂ to convert Hg(II) to Hg(0). Hg(0) is purged from solution onto gold-coated sand trap and thermally desorbed from trap for detection by CVAFS.	- EPA National Fish Tissue Study (>1000 samples over 4-year period) - EPA Cook Inlet Contaminant Study - Lake Michigan fish and invertebrates, Mason and Sullivan 1997 - NE Minnesota lake plankton, Monson and Brezonik 1998²⁷ - Method performance testing in freshwater and marine fish, Bloom 1989
Method 245.6 ²⁸	Total mercury in tissue	Total mercury in tissue	Sulfuric and nitric acid digestion, oxidation with potassium permanganate and potassium persulfate, SnCl ₂ reduction, CVAAS detection	unknown
Draft Method 7474 (SW-846) ²⁹	Total mercury in sediment and tissue	Total mercury in sediment and tissue	Microwave digestion of sample in nitric and hydrochloric acids, followed by cold digestion with bromate/bromide in HCl. Hg purged from sample and determined by CVAFS.	Reference materials cited in method. Niessen et al. 1999.

²⁶ Used similar techniques but used a methylene chloride extraction instead of the distillation.

²⁷ Used similar techniques but used a methylene chloride extraction instead of the distillation.

²⁸ Provided for reference purposes only. EPA recommends use of Method 1631 for mercury for analyzing water and fish tissue.

²⁹ Provided for reference purposes only. EPA recommends using Method 1631 for analyzing mercury for water and fish tissue.

Table C2. Analytical methods for determining mercury and methylmercury in water, sediment, and other nontissue matrices

Method	Forms/species and applicable matrices	Sensitivity	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1630	Methylmercury in water	0.02 ng/L	Distillation with heat and N ₂ flow, addition of acetate buffer and ethylation with sodium tetraethyl borate. Purge with N ₂ onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg followed by CVAFS detection.	• USEPA Cook Inlet Study • USEPA Savannah River TMDL study • Northern Wisconsin Lakes, Watras et al. 1995 • Lake Michigan waters, Mason and Sullivan 1997 • Anacostia River Study, Mason and Sullivan 1998 • NE Minnesota lakes, Monson and Brezonik 1998³⁰ • Poplar Creek, TN CERCLA Remedial Investigation of surface water, sediment, and pore water, Cambell et al. 1998³¹ • Scheldt estuary study of water, polychaetes, and sediments, Baeyens et al. 1998
UW-Madison SOP for MeHg Analysis	Methylmercury in water	0.01 ng/L	Distillation with heat and N ₂ flow, with potassium chloride, sulfuric acid, and copper sulfate. Ethylation with sodium tetraethyl borate. Purge with N ₂ onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg ⁰ followed by CVAFS detection.	• Lake Michigan tributaries to support GLNPO's LMMB Study • Fox River, WI waters and sediments, Hurley et al. 1998
USGS Wisconsin - Mercury Lab SOPs 004	Methylmercury in water	0.05 ng/L	Distillation (heat), APDC solution, N ₂ flow, potassium chloride, sulfuric acid, and copper sulfate. Ethylation with sodium tetraethyl borate. Purge with N ₂ onto Carbotrap. Thermal desorption and GC separation of ethylated species, reduction to Hg ⁰ , and CVAFS detection.	Aquatic Cycling of Mercury in the Everglades, (ACME) cofunded by USGS, EPA, and others
USGS Open-File Report 01-445:	Methylmercury in water	Detection limit cited as 0.04 ng/L	Distillation (heat) and N ₂ flow, HCl and copper sulfate. Addition of acetate buffer and ethylation with sodium tetraethyl borate. Purge with N ₂ onto Carbotrap. Thermal desorption and GC separation of ethylated mercury species, reduction to Hg(0) followed by CVAFS detection.	Formalized USGS method version of USGS Wisconsin Lab SOP 004. Report title is: <i>Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by GC Separation with CVAFS Detection.</i>

Note: The four methylmercury methods above are all based on the work of Bloom 1989 as modified by Horvat et al. 1993, and are virtually identical as a result.

³⁰ Used similar techniques but used a methylene chloride extraction instead of the distillation.

³¹ Used similar techniques but omitted the distillation procedure

Table C2. (continued)

Method	Forms/species and applicable matrices	Sensitivity	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1631 (CVAFS)	Total or dissolved mercury in water	MDL=0.2 ng/L ML=0.5 ng/L	Oxidize all Hg compounds to Hg(II) with BrCl. Sequentially pre-reduce with hydroxylamine hydrochloride to destroy the free halogens and reduce with SnCl ₂ to convert Hg(II) to Hg(0). Hg(0) is purged from solution with N ₂ onto gold coated sand trap and thermally desorbed from trap for detection by CVAFS.	• USEPA Cook Inlet Study • State of Maine studies • USEPA Savannah River TMDL study • USEPA/U.S. Navy study for development of Uniform National Discharge Standards • Watras et al. 1995 • Anacostia River Study, Mason and Sullivan 1998 • Northeastern Minnesota lakes, Monson and Brezonik 1998 • Poplar Creek, TN CERCLA Remedial Investigation Study, Cambell et al. 1998 • Scheldt Estuary Study, Baeyens et al. 1998
EPA 245.1 (CVAAS)	Total or dissolved mercury in wastewater	200 ng/L	H ₂ SO ₄ and HNO ₃ digestion, KMnO ₄ , K ₂ S ₂ O ₈ oxidation + heat, cool +NaCl-(NH ₂ OH) ₂ H ₂ SO ₄ , SnSO ₄ , aeration. Detection by CVAAS.	Effluent guideline development studies for the Meat Products Industry, Metal Products and Machinery Industry, and Waste Incinerators
EPA 245.2 (CVAAS)	Total or dissolved mercury in wastewater and sewage	200 ng/L	H ₂ SO ₄ and HNO ₃ added, SnSO ₄ , NaCl-(NH ₂ OH) ₂ H ₂ SO ₄ , KMnO ₄ , K ₂ S ₂ O ₈ , heat. Detection by CVAAS.	MPM Industry effluent guideline development study
EPA 245.5 (CVAAS)	Total or dissolved mercury in soils, sludge and sediment	200 ng/L	Dry sample, aqua regia, heat, KMnO ₄ added, cool +NaCl-(NH ₂ OH) ₂ H ₂ SO ₄ , SnSO ₄ , aeration. Detection by CVAAS.	Pharmaceutical industry effluent guideline development study
EPA 245.7 (CVAFS)	Total or dissolved mercury in water	ML = 5 ng/L; MDL = 1.8 ng/L	HCl, KBrO ₃ /KBr, NH ₂ OH·HCl, SnCl ₂ , liquid-vapor separation. CVAFS detection	Interlaboratory validation completed.
EPA 7470A (CVAAS)	Total or dissolved mercury in liquid wastes and Ground water	200 ng/L (IDL)	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ added, K ₂ S ₂ O ₈ added + heat, cool +NaCl-(NH ₂ OH) ₂ H ₂ SO ₄ , SnSO ₄ , aeration of sample. CVAAS detection.	Method is similar to and cites performance data given in EPA 245.5
EPA 7471B (CVAAS)	Total or dissolved mercury in solid wastes semisolid wastes	200 ng/L (IDL)	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ added, K ₂ S ₂ O ₈ added + heat, cool +NaCl-(NH ₂ OH) ₂ H ₂ SO ₄ , SnSO ₄ , aeration of sample. CVAAS detection.	Method is similar to and cites performance data given in EPA 245.5
EPA 7472 (Anodic Stripping Voltametry)	Total or dissolved mercury in water	100-300 ng/L	Acidify and chlorinate sample, GCE electrode	Unknown
EPA 7473 (Thermal decomposition, amalgamation, and CVAA)	Mercury in water, soil, and sediment	estimated to be as low as 20 ng/ L or 20 ng/kg	Sample aliquot decomposed at 750EC in oxygen atmosphere. Decomposition products carried into catalytical furnace for completed oxidations, then to amalgamated trap. Mercury is thermally desorbed and determined by AA.	Unknown

Table C2. (continued)

Method	Forms/species and applicable matrices	Sensitivity	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1620 (CVAAS)	Mercury in water, sludge, and soil	200 ng/L	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ , K ₂ S ₂ O ₈ + heat, cool +NaCl-(NH ₂ OH) ₂ ·H ₂ SO ₄ , SnSO ₄ , aeration. CVAAS detection.	Industry effluent guideline development studies
SM 3112B (CVAAS)	Total or dissolved mercury in water	500 ng/L	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ added, K ₂ S ₂ O ₈ added + heat, cool +NaCl (NH ₂ OH) ₂ ·H ₂ SO ₄ , SnCl ₂ or SnSO ₄ , aeration. CVAAS determination.	Unknown
*ASTM D3223-91(CVAAS)	Total or dissolved mercury in water	500 ng/L	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ added, K ₂ S ₂ O ₈ added + heat, cool +NaCl (NH ₂ OH) ₂ ·H ₂ SO ₄ , SnSO ₄ , aeration. CVAAS determination.	Unknown
*AOAC 977.22 (Atomic absorption spectrometry)	Total or dissolved mercury in water	200 ng/L	H ₂ SO ₄ and HNO ₃ added, KMnO ₄ added, K ₂ S ₂ O ₈ added + heat, cool +NaCl (NH ₂ OH) ₂ ·H ₂ SO ₄ , SnSO ₄ , aeration. Determine mercury by CVAA.	Unknown

Notes: (1) CVAAS = cold vapor atomic absorption spectrometry
 (2) CVAFS = cold vapor atomic fluorescence spectrometry
 (3) ASTM and AOAC analytical methods are available from the respective organization

Appendix D. Examples of National Deposition Monitoring Networks

There are a number of national deposition monitoring networks that may be useful for developing TMDLs. Networks include the National Atmospheric Deposition Program - National Trends Network (NADP/NTN) and the MDN (a subset of the NADP network). The NADP/NTN is a nationwide network of precipitation monitoring stations. Operating since 1978, it collects data on the chemistry of precipitation for monitoring of geographical patterns and temporal long-term trends. NADP/NTN measures weekly average concentrations of sulfate, nitrate, ammonium, base cations, and acidity at approximately 230 monitoring stations across the United States. The MDN measures concentrations of total mercury in precipitation at approximately 45 monitoring stations across the United States. NADP/NTN results for 2003 are shown in Figure D-1. For more information about NADP see <http://nadp.sws.uiuc.edu>.

Used in conjunction with NADP/NTN, the Clean Air Status and Trends Network (CASTNET) is the nation's primary source of atmospheric data on the dry deposition component of total acid deposition, ground-level ozone, and other forms of atmospheric pollution that enters the environment as particles and gases. CASTNET measures weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid, and hourly concentrations of ambient ozone levels in rural areas. Dry deposition rates are calculated using the measured atmospheric concentrations, meteorological data, and information on land use, surface conditions, and vegetation. Seventy-nine monitoring stations operate across the United States. For more information about CASTNET, see <http://www.epa.gov/castnet> and <http://nadp.sws.uiuc.edu>.

Note that these national monitoring networks generally provide only estimates of wet deposition; estimates of dry deposition can be obtained from the literature. For more information on deposition monitoring networks, see *Deposition of Air Pollutants to the Great Waters: Third Report to Congress* (USEPA 2000f) (<http://www.epa.gov/oar/oaqps/gr8water/3rdrpt>) and the Air-Water Interface Plan (http://www.epa.gov/owow/oceans/airdep/airwater_plan16.pdf).

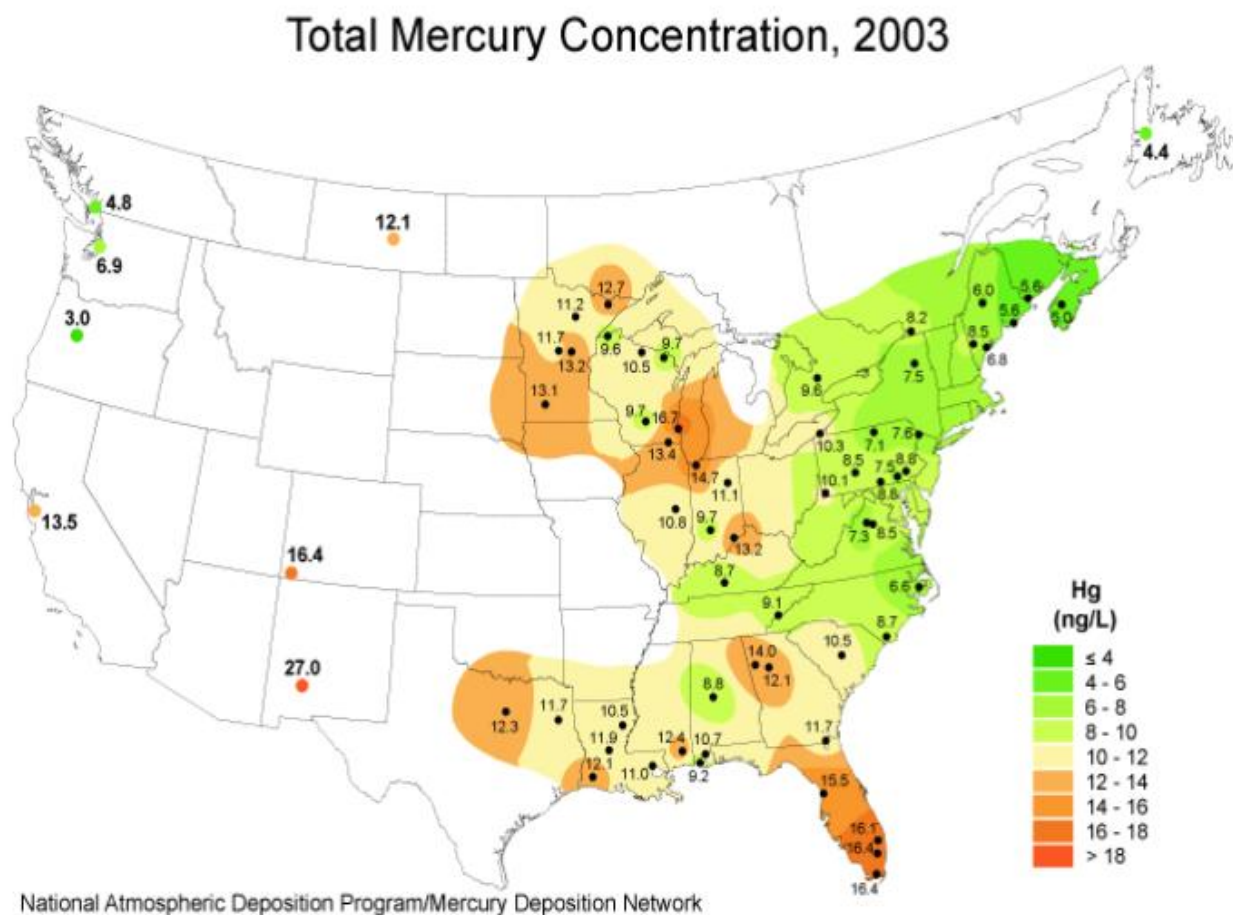


Figure D-1 MDN data for 2003

Appendix E. Methylmercury/Mercury Ratio Exhibited in Muscle Tissue of Various Freshwater Fish Species

Source	Ecosystem type	Fish species	MethylHg/ total Hg ratio
C.R. Hammerschmidt, J.G. Wiener, B.E. Frazier and R.G. Rada (1999)	Freshwater lakes in Wisconsin, USA	Yellow perch (<i>Perca flavescens</i>)	mean 0.95; range from 0.84 to 0.97
D.S. Becker and G.N. Bigham (1995)	Onondaga Lake, a chemically-contaminated lake in New York, USA	Gizzard shad (<i>Dorosoma cepedianum</i>) White perch (<i>Morone americana</i>) Carp (<i>Cyprinus carpio</i>) Channel catfish (<i>Ictalurus punctatus</i>) Bluegill (<i>Lepomis macrochirus</i>) Smallmouth bass (<i>Micropterus dolomieu</i>) Walleye (<i>Stizostedion vitreum</i>)	> 0.90 Note: authors did not provide specific percentages for individual species
T.M. Grieb, C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie, and D.B. Porcella (1990)	Lakes in the Upper Michigan Peninsula, USA	Yellow perch (<i>Perca flavescens</i>) Northern pike (<i>Esox lucius</i>) Largemouth bass (<i>Micropterus salmoides</i>) White sucker (<i>Catostomus commersoni</i>)	0.99 Note: authors did not provide data for each species separately—only mean value observed over all species
N.S. Bloom (1992)	Freshwater fish species collected from remote midwestern lakes and one mercury contaminated site USA	Yellow perch (<i>Perca flavescens</i>) Northern pike (<i>Esox lucius</i>) White sucker (<i>Catostomus commersoni</i>) Largemouth bass (<i>Micropterus salmoides</i>)	0.99 1.03 0.96 0.99
B. Lasorsa and S. Allen-Gil (1995)	3 lakes in the Alaskan Arctic, USA	Arctic grayling Lake trout Arctic char Whitefish	1.00 all for species Note: authors did not provide species specific information on MeHg/Total Hg ratio
T. A. Jackson (1991)	Lakes and reservoirs in northern Manitoba, Canada	Walleye (<i>Stizostedion vitreum</i>) Northern pike (<i>Esox lucius</i>) Lake whitefish (<i>Coregonus clupeaformis</i>)	range: 0.806 to 0.877% range: 0.824 to 0.899% range: 0.781 to 0.923% Note: author sampled the 3 fish species at 4 lake locations
R. Wagemann, E. Trebacz, R. Hunt, and G. Boila (1997)	Sampling location not provided; presumed to be from Canadian waters	Walleye (<i>Stizostedion vitreum</i>)	mean 1.00 Note: authors did not provide more specific information

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Note: Bold numbers indicate where the term is defined (if applicable). If the term has been broken into subcategories, this is noted with a “defined” entry.

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