

# Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion



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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 U.S. 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 milligram (mg) methylmercury per kilogram (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 that states, territories, and authorized tribes use the criterion and this guidance in establishing or updating water quality standards for waters of the United States and in issuing fish and shellfish consumption advisories. States and authorized tribes remain free to adjust EPA's recommended criterion, provided that their new or revised water quality criterion for methylmercury protect the designated uses and are based on scientifically defensible methodology.

The publication of the 2001 methylmercury criterion was the first time EPA 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 might pose implementation challenges. In the January 8, 2001 Federal Register 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 technical guidance to states, territories, and authorized tribes exercising responsibility under CWA section 303(c), which provides for state review and revision of water quality standards every three years, and adoption of criteria for toxic pollutants, such as mercury, for which EPA has published criteria under CWA section 304(a). The document provides guidance on how to use the new fish tissue-based criterion recommendation in developing water quality standards for methylmercury and in implementing those 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 into NPDES permits.

For more information on the methylmercury criterion, see the criteria page on EPA's Web site at <a href="http://www.epa.gov/waterscience/criteria/methylmercury/index.html">http://www.epa.gov/waterscience/criteria/methylmercury/index.html</a>. For more information on EPA's water quality standards program, see the standards page on EPA's Web site at <a href="http://www.epa.gov/waterscience/standards">http://www.epa.gov/waterscience/standards</a>. 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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NONROAD	
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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 milligram (mg) methylmercury per kilogram (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 1997a). As of 2008, 50 states, 1 territory, and 3 tribes had issued fish consumption advisories for mercury covering 16.8 million lake acres and 1.3 million river miles (USEPA 2009a). Mercury is widely distributed in the environment and originates from natural and human-induced (anthropogenic) sources, including combustion and volcanoes. Methylmercury is highly bioaccumulative, especially in aquatic food webs. Nearly 100 percent of the mercury that bioaccumulates in upper-trophic-level fish (predator) tissue is methylmercury (Akagi et al. 1995; Becker and Bigham 1995; Bloom 1992; Kim 1995).

Under section 303(c) of the Clean Water Act (CWA), states and authorized tribes must adopt water quality criteria that protect designated uses. Section 303(c)(1) provides that states and authorized tribes review their water quality standards every three years and modify and adopt water quality standards as appropriate. In light of the new science used to develop the 2001 methylmercury fish tissue criterion, EPA believes that states should consider reviewing and revising their mercury human health criteria during their next triennial review. This document provides technical guidance to states and authorized tribes that exercise responsibility under CWA section 303(c) on how to use the new fish tissue-based criterion recommendation as they develop water quality standards for methylmercury.

EPA expects that, as states adopt methylmercury water quality criteria and as monitoring of effluents, receiving waters, and fish tissue with the more sensitive methods recommended by EPA increases, the number of waterbodies that states report on CWA section 303(d) lists as impaired due to methylmercury contamination might increase. This guidance is designed to assist states and authorized tribes to address those impairments. Furthermore, this guidance addresses coordination across various media and program areas in implementing the criterion, which will be important because atmospheric deposition and multimedia cycling of mercury are significant in many waterbodies.

EPA recognizes the complexity and comprehensive nature of this guidance. As is always the case when EPA issues technical guidance, EPA will provide outreach and technical assistance to states and authorized tribes in implementing this guidance.

The following tables (tables 1a through 1d) provide a brief summary of the most important recommendations applicable to states and authorized tribes that are contained in the guidance.

NOTE: These tables are provided as a convenience to the reader, but are not comprehensive and are not a substitute for the full content of the guidance contained in the other chapters of this document.

Table 1a. Recommendations for water quality standards adoption

i dole 1d	i. Recommendations for water quality standards a	1	
		Most applicable to criteria expressed as	For a full discussion see section
Recomr	mended form of a methylmercury criterion		3.1.2 and
	A recommends that states and authorized tribes adopt a hylmercury criterion expressed as a fish tissue value.		3.1.3
	en adopting a fish tissue criterion, states and authorized es will need to decide whether to:		
•	Implement the fish tissue criterion without water column translation, or	FT (fish tissue value)	
•	Translate the fish tissue criterion to a water column value using bioaccumulation factors (BAFs). Three approaches include:  1. Site-specific BAFs  2. Modeled BAFs  3. BAFs derived using the results of field studies that are not site-specific (in limited circumstances); or	WC (water column value)	
•	Combination (fish tissue criterion for some or all waters, combined with water column criteria for some or all waters).	Both FT and WC	
•	States and authorized tribes may consider retaining their existing water column criteria, on a temporary basis, particularly for waters where there is a relatively high direct water input of mercury.	FT alone	
Adoptio	on considerations	FT or WC	
•	When adopting a fish tissue criterion, EPA encourages states and authorized tribes to develop implementation procedures.		3.1.2.1
•	This guidance does not supersede requirements in EPA's Great Lakes Initiative (GLI) regulation for waters in the Great Lakes system.		5.1
Criterio	n adjustments	FT or WC	3.2.1
•	Adjusting for local fish consumption rates. Adjusting for other sources of mercury (marine fish).		
Mixing 2	zones		5.3
•	Not relevant when applying a fish tissue criterion that has not been translated to a water column value.	FT alone	
•	If the fish tissue criterion is converted to water column values, EPA advises caution in the use of any mixing zones for mercury. Restricting or eliminating mixing zones may be appropriate.	WC	
Varianc	es	WC	3.2.2
•	Guidance on when variances are appropriate.		
•	Considerations before granting a variance.		

Table 1b. Recommendations for monitoring and assessment

	Most applicable to criteria expressed as	For a full discussion see section
Recommended analytical methods		4.1
<ul> <li>Methods 1631, revision E and 245.7 for mercury in water.</li> </ul>	WC	
<ul> <li>Draft Appendix A of Method 1631 for mercury in fish tissue.</li> </ul>	FT	
<ul> <li>Method 1630 for methylmercury in water.</li> </ul>	WC	
<ul> <li>Method 1630 (with draft modifications) for methylmercury in fish tissue.</li> </ul>	FT	
Other available methods are listed in appendix C of this guidance.	FT or WC	App. C
Field sampling recommendations	FT alone	4.2
<ul> <li>Select fish for monitoring that are commonly eaten in the study area.</li> </ul>		
<ul> <li>Choose large fish because these are typically highest in methylmercury.</li> </ul>		
<ul> <li>If local consumption data are not available, match assumed consumption pattern to sampled species, or sample trophic level 4 species.</li> </ul>		
<ul> <li>Use composite samples of fish fillets.</li> </ul>		
<ul> <li>EPA recommends biennial sampling if resources allow, otherwise waterbodies should be screened a minimum of every 5 years.</li> </ul>		
Assessing non-attainment of fish tissue criterion	FT alone	4.3
<ul> <li>Use statistical tests if enough data, or consider sample- by-sample comparisons if very limited data.</li> </ul>		

Table 1c. Recommendations for total maximum daily loads (TMDLs)

		Most applicable to criteria expressed as	For a full discussion see section
States'	States with comprehensive mercury reduction programs in place may defer TMDLs for waters impaired by mercury mainly from atmospheric sources. (Summarizing EPA's voluntary "5m" category for listing impaired waters.)  The greater the relative contribution to a waterbody from mercury sources other than air deposition, such as water point sources, the more appropriate it may be to use the TMDL process to characterize and address those sources sooner, rather than deferring TMDL development.	FT or WC	6.2 and 7.5.2.2
	ches in approved mercury TMDLs amples in guidance text and appendix D discuss:  Types of mercury sources; tools for assessing point sources, atmospheric deposition, past metals mining activity, sediments, and natural sources.  Example allocation scenarios involving waters where predominant sources are air deposition or mining.  Post-TMDL monitoring.	FT or WC	6.2
Des	phic scale scribes scales that have been used for developing recury TMDLs: Waterbody-specific. Watershed-level. Statewide or regional.	FT or WC	6.2.1
Availab •	le models and example TMDL applications  Example models for different situations (steady state, dynamic, detail geometry, regression).  Factors leading to model selection (methylation, BAFs, sodiments)	FT or WC	6.2.2.2
•	sediments).  Use of linked models without having explicit water column criteria or translations.  Other analytical approaches, e.g., proportionality approach: Where air deposition is the only significant mercury source and steady-state conditions apply, TMDLs have been developed to meet fish tissue targets by relying on a proportional relationship between mercury deposition and fish tissue methylmercury concentration.	FT alone	6.2.2.2.1

Table 1d. Recommendations for permitting procedures

	a recommendations for permitting procedures	Most applicable to criteria expressed as	For a full discussion see section
Two im	Two implementation approaches		
•	If a TMDL or a water column translation derived from a fish tissue criterion or site-specific data to translate is available at time of permit issuance, implement using the approaches described in the Technical Support Document (TSD) for Water Quality-based Controls (USEPA 1991).	WC	7.4
•	If a TMDL or water column translation or site-specific data to translate are not available, implement approaches described below.	FT alone	7.5
Finding	"reasonable potential" (RP) <sup>a</sup>	FT alone	7.5.1
Dep	pending on the particular facts, a permitting authority may sonably conclude that a facility has RP if:		
•	There is a quantifiable level of mercury in the discharge, using a sufficiently sensitive EPA-approved analytical method and		
•	Fish tissue from the receiving water is close to or exceeds the criterion.		
Where i	Where mercury effluent levels are unknown		7.5.1.1.1
EPA	A recommends that permitting authorities:		
•	Require effluent monitoring using a sufficiently sensitive EPA-approved analytical method.		
•	Include a reopener clause in the permit to allow permit to be modified if effluent data indicate a water quality-based effluent limit (WQBEL) is necessary.		
Where o	quantifiable amounts of mercury are not found	FT alone	7.5.1.1.2
•	If the permitting authority believes the monitoring data are representative of the discharge, no further permit conditions may be necessary.		
Where 1	fish tissue concentrations are unknown	FT alone	7.5.1.2.1
EPA	EPA recommends that permitting authorities:		
•	Include a special permit condition to conduct a mercury fish tissue survey for the receiving waterbody.		
•	Include a reopener clause in the permit to allow permit to be modified if fish tissue data become available indicating a WQBEL is necessary.		
•	Encourage the permittee to develop and implement a mercury minimization plan (MMP) tailored to the facility's potential to discharge mercury.		

Table 1d. Recommendations for permitting procedures (continued)

	Most applicable to criteria expressed as	For a full discussion see section
Permits with quantifiable mercury but without RP  Where a discharge contains a quantifiable amount of mercury but fish tissue in the receiving water does not exceed the criterion:	FT alone	7.5.1.2.2
<ul> <li>If the discharger will undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration         <ul> <li>Conduct tier 2 antidegradation analysis and develop appropriate permit conditions.</li> <li>Require permittee to implement an MMP tailored to the facility's potential to discharge mercury.</li> <li>Require effluent monitoring.</li> </ul> </li> <li>If the discharger will not undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration:         <ul> <li>Encourage the facility to develop and implement an MMP tailored to the facility's potential to discharge mercury.</li> </ul> </li> </ul>		
Other factors in determining RP	FT alone	7.5.1.2.2
<ul> <li>EPA recommends that the permitting authority account for other factors that may constitute the basis for a finding of RP. These include rising fish tissue concentrations and the impact on downstream waters.</li> </ul>		
Mercury in intake water	FT or WC	7.5.1.3
<ul> <li>Where the only source of mercury in a discharge may be the intake water taken directly from the same body of water, and where there are no known sources or additional contributions of mercury at the facility, the permitting authority may reasonably conclude, based on the particular facts, that there is no RP to exceed water quality standards.</li> </ul>		

Table 1d. Recommendations for permitting procedures (continued)

	Most applicable to criteria expressed as	For a full discussion see section
WQBELs where there is a finding of RP <sup>b</sup>	FT alone	7.5.2.1
EPA recommends that permitting authorities:		
<ul> <li>Require the permittee to implement an MMP tailored to its potential to discharge mercury.</li> </ul>		
<ul> <li>Depending on the particular facts, the permitting authority should consider including in an MMP an effluent trigger level, a mercury reduction goal, or an enforceable numeric level representing existing effluent quality or some increment of the mercury reduction determined achievable as a result of the measures and practices specified in the MMP.</li> </ul>		
<ul> <li>Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP.</li> </ul>		
<ul> <li>Include a reopener clause to modify the permit conditions if the MMP is found to be not effective or if a water column translation of the criterion is developed.</li> </ul>		
Other considerations and requirements may be necessary:		
<ul> <li>Where a discharger undertakes an activity that could result in an increase in receiving water or fish tissue mercury concentrations, it must be consistent with applicable antidegradation requirements. Additional requirements may also be necessary under the CWA and EPA's NPDES regulations.</li> </ul>		
<ul> <li>Include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1).</li> </ul>		
<ul> <li>For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements.</li> </ul>		7.2.4

Table 1d. Recommendations for permitting procedures (continued)

	Most applicable to criteria expressed as	For a full discussion see section
Permits with RP where direct water inputs are relatively high	FT alone	7.5.2.2
In addition to the above:		
<ul> <li>EPA recommends that states and authorized tribes specifically consider developing TMDLs in the short term.</li> </ul>		
<ul> <li>Where a state or tribe chooses not to develop a TMDL in the short term, the state or tribe should develop an analysis of sources and loading capacity similar to what a TMDL would provide, or a water column translation of the fish tissue criterion.</li> </ul>		
<ul> <li>EPA recommends that permitting authorities work together with mercury dischargers in the watershed to collect data necessary to develop:</li> <li>A TMDL, or</li> </ul>		
<ul> <li>An analysis of sources and loading capacity similar to what a TMDL would provide, or</li> </ul>		
<ul> <li>A water column translation of the fish tissue criterion for future permitting.</li> </ul>		
One approach is for the permitting authority to invoke its authority under CWA section 308 (or comparable state authority).		
Additional requirements that may apply	FT or WC	7.5.2.3
<ul> <li>Additional requirements for: POTWs with pretreatment programs; technology-based limits; anti-backsliding; permit documentation.</li> </ul>		
Mercury minimization plans (MMPs) This section provides guidance on appropriate MMPs.	FT	7.5.2.4

#### Notes:

<sup>&</sup>lt;sup>a</sup> "Reasonable potential" refers to the reasonable potential to cause or contribute to an excursion above a numeric or narrative criterion for water quality. 40 CFR 122.44(d)(1)(i). NPDES permits for discharges with "reasonable potential" must include water quality-based effluent limits (WQBELs).

<sup>&</sup>lt;sup>b</sup> As noted at the beginning of table 1d, this section refers to situations where neither a TMDL nor a water column translation is available at time of permit issuance. Where a TMDL has been developed, the WQBEL for that discharge must be consistent with the TMDL's wasteload allocation. Where a TMDL is not available at the time of permit discharge, but where a water column translation of the fish tissue criterion has been developed, or where site-specific data to do so are readily available, include a numeric WQBEL.

#### 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 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 therefore can be widely dispersed and transported thousands of miles from sources of emission (USEPA 1997b). 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). Inorganic mercury salts, when bound to airborne particles, are readily removed from the atmosphere by precipitation and are also dry deposited. Even after mercury deposits, it commonly returns to the atmosphere, as a gas or associated with particles, and then 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 (USEPA 1997b).

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 it is the form of mercury that presents the greatest environmental risks to human health (66 FR 1344; January 8, 2001). 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 methylmercury?

Exposure to methylmercury can result in a variety of health effects in humans. Children that 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 2002a). Mercury and its compounds are listed as a "toxic" pollutant under section 307(a) of the Clean Water Act (see 40 CFR 401.15).

In 2000 the National Academy of Sciences (NAS)/National Research Council (NRC) reviewed the health studies on mercury (NRC 2000). EPA's assessment of the methylmercury reference dose (RfD) relied on the quantitative analyses performed by the NRC (USEPA 2002a). The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure of the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 2002a). 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-day (0.0001 milligram of methylmercury per day for each kilogram of a person's body mass) (USEPA 2002a). EPA believes that exposures at or below the RfD are unlikely to be associated with an 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 nonappreciable. 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 2005a).

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 through maternal consumption of fish (rather than high-dose poisoning episodes) (USEPA 2005a).

In 2005 the National Health and Nutrition Examination Survey (NHANES) published the 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  $\mu$ g/L, a concentration associated with neurological 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  $\mu$ g/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 2005a).

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 (Salonen et al. 1995, as cited in USEPA 2001a). Other recent studies have not observed this association. The studies that have observed an association suggest that the exposure to methylmercury might offset the beneficial effects of fish consumption (USEPA 2005a). There also is some recent evidence that exposures to methylmercury might result in genotoxic or immunotoxic effects ([Amorim et al. 2000; ATSDR 1999; Silva at al. 2004], as cited in USEPA 2005a). 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 2005a).

Deposition of mercury to waterbodies can also have an adverse impact on ecosystems and wildlife. Plant and aquatic life, as well as 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; aquatic systems experience the greatest exposures because of bioaccumulation. *Bioaccumulation* refers to the net uptake of a contaminant from all possible pathways. It 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 consuming contaminated fish, and as a result they accumulate mercury to levels greater than those in their prey (USEPA 1997a).

EPA's mercury Web site, at <a href="http://www.epa.gov/mercury">http://www.epa.gov/mercury</a>, provides a broad range of information about mercury, including a full discussion of potential human health and ecosystem effects.

#### 2.1.2 How frequent are the environmental problems?

As of the 2008 listing of impaired waters (i.e.: water not attaining water quality standards) under section 303(d) of the clean Water Act, 43 states and Puerto Rico reported at least one waterbody as impaired due to mercury, and more than 8,800 specific waterbodies were listed as impaired due to mercury, either solely or in combination with other pollutants. All states have numeric criteria for mercury. About seven states, plus Washington D.C. and two territories have adopted a fish tissue criterion for methylmercury. Once additional states, tribes and territories begin to adopt EPA's recommended fish tissue criterion, the number of waterbodies listed as impaired for methylmercury is expected to increase since the revised criterion is more stringent than the water concentration criteria most states currently have in their water quality standards.

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 waters identified by the states as impaired) and compared them to the 2001 national recommended water quality criterion, 0.3 mg methylmercury/kg fish tissue wet weight. 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 2001b).

Figure 1 shows fish tissue mercury concentrations averaged by watershed (by 8-digit hydrologic unit code, or HUC).

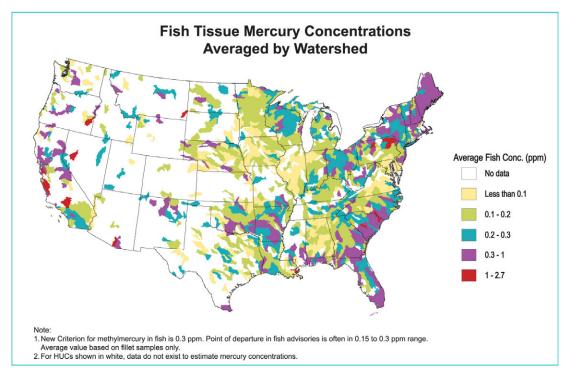


Figure 1. Average fish tissue concentrations by HUC watershed (USEPA 2005a).

In EPA's *Environmental Monitoring and Assessment Project (EMAP) Western Streams and Rivers Statistical Study* (USEPA 2005b), 626 streams and rivers were sampled in 12 states of the western United States. Mercury was detected at 100 percent of sites and samples in the study. The 0.3 mg/kg criterion (equivalent to 0.3 parts per million, ppm) was exceeded in 56.8 percent of waters surveyed, which represent 20–30 percent of all western rivers (Peterson et al. 2007). Results from the 2009 National Lake Fish Tissue Study, a statistically-based survey conducted by EPA, showed that 49% of the sampled population of lakes (76,559 lakes in the lower 48 states with surface areas greater than or equal to 1 hectare or about 2.5 surface acres) had mercury concentrations that exceeded the 0.3 ppm tissue-based mercury criterion (USEPA 2009b).

As of December 2008, 50 states, 1 territory, and 3 tribes had issued fish consumption advisories <sup>1</sup> for mercury covering 16.8 million lake acres and 1.3 million river miles (figure 2). Twenty-seven states had issued advisories for mercury in all freshwater lakes and rivers in the state, 13 states had statewide advisories for mercury in their coastal waters and one state had a deep sea advisory (USEPA 2009a). The thresholds for the levels of mercury in fish that trigger the issuance of an advisory for women of childbearing age vary among the states and authorized tribes, but generally range from 0.07 to 1 ppm, with most threshold values in the range of 0.1 to 0.3 ppm.

Although states, territories, tribes, and local governments continue to issue new fish advisories and most new fish advisories involve mercury, EPA believes that the increase in advisories is a result of increased monitoring and assessment of previously untested waters rather than increased domestic releases of mercury or increased levels or frequency of contamination. In fact, U.S. releases of mercury to the air have declined by more than 58 percent between 1990 and 2005 (USEPA 2008b).

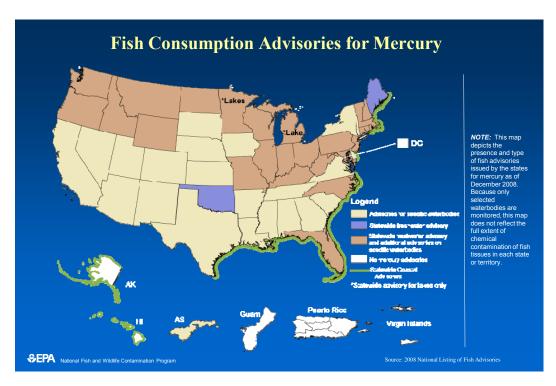


Figure 2. Fish Consumption Advisories for Mercury 2008 (USEPA 2009a).

<sup>&</sup>lt;sup>1</sup> States and tribes issue their advisories and guidelines voluntarily and have flexibility in which criteria they use and how they collect data. 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. Note that EPA does not issue fish advisories; states and tribes issue advisories (with the exception of national advisories, regional advisories, and Superfund-related advisories). EPA issues guidance on the level of contaminants in fish, which states and tribes may use in issuing their advisories.

#### 2.2 What are the sources of mercury in fish?

Mercury is emitted from both natural and anthropogenic sources. Its residence time in the atmosphere is much longer than that of most other metals because mercury can circulate for up to a year (USEPA 1997b). 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 from both U.S. and international sources (USEPA 2005c). 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 from natural and re-emitted sources. EPA's current air quality modeling indicates a substantial variation across the country: domestic sources influence mercury deposition much more in the East, and global sources are a more significant contributor to mercury deposition in the West, where relatively few domestic sources exist. This estimate was based on a modeling assessment of the atmospheric fate, transport, and deposition of mercury conducted by EPA for the Clean Air Mercury Rule<sup>2</sup> (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; hospital, medical, and infectious waste incinerators), manufacturing sources (e.g., chlor-alkali and cement manufacturers), and mining (USEPA 1997b).

U.S. anthropogenic emissions of mercury to the air have declined more than 58 percent from the passage of the 1990 Clean Air Act (CAA) Amendments to 2005 (most recent data available). These amendments provided EPA new authority 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 hospital, medical, and infectious waste incineration (figure 4, section 6.2.2.1). Regulations were issued in the 1990s to control mercury emissions from waste combustion. In addition, actions to limit the use of mercury—most notably voluntary and 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. Regulation of mercury emissions from chlorine production facilities that use mercury cells and regulation of industrial boilers will further reduce emissions of mercury.<sup>3</sup>

<sup>&</sup>lt;sup>2</sup> On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Section 112(n) Revision Rule and the Clean Air Mercury Rule.

<sup>&</sup>lt;sup>3</sup> Rules controlling mercury emissions, which implement the 1990 CAA amendments, include standards for municipal waste combustors (40 CFR part 60, subpart Da, and parts 72 and 75); standards for hospital, medical, and infectious waste incinerators (40 CFR part 60, subpart Ce); standards for chlor-alkali plants (40 CFR part 63, subpart IIIII); standards for existing and new hazardous waste-burning incinerators (40 CFR 63.1203 [a][2] and [b][2]); standards for existing and new hazardous waste-burning cement kilns (40 CFR 63.1204 [a][2] and [b][2]); and standards for existing and new hazardous waste-burning lightweight aggregate kilns (40 CFR 63.1205 [a][2] and [b][2]). See also section 8.3 of this document.

At present, the largest single source of anthropogenic mercury emissions to the air in the country 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 (70 FR 15994; March 29, 2005). In May 2005, EPA adopted the Clean Air Act Section 112(n) Revision Rule and the Clean Air Mercury Rule (CAMR). CAMR regulated mercury emissions from coal-fired utilities. On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Section 112(n) Revision Rule and CAMR. EPA is developing air toxics emissions standards for power plants under Clean Air Act (Section 112(d), EPA currently intends to propose and finalize air toxics standards for coal- and oil-fired electric generating units by the end of 2011. 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 ensure that permitted discharges achieve water quality standards (40 CFR 122.44(d)). Nonpoint source runoff is 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 from these sources for achieving the water quality standards.

Anthropogenic emissions, however, are only one part of the mercury cycle. 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 that govern methylmercury uptake in fish and shellfish tissue. The following is a synopsis of the current understanding of mercury cycling in the environment.

Mercury occurs naturally in the environment as several different chemical species. Most mercury in the atmosphere (95–97 percent) is present in a neutral, elemental state,  $Hg^0$  (Lin and Pehkonen 1999). In water, sediments, and soils, most 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 ( $CH_3Hg^{II}$ ) (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 emission 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 principal forms of mercury deposited onto terrestrial and aquatic systems because they are more efficiently scavenged from the atmosphere through wet and dry deposition than is  $Hg^0$  (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 the mercury 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<sup>II</sup> to Hg<sup>0</sup>, which might then escape back to the atmosphere (Carpi and Lindberg 1997, Frescholtz and Gustin 2004, Scholtz et al. 2003). Significant amounts of mercury can be co-deposited to soil surfaces in throughfall and litterfall of forested ecosystems (St. Louis et al. 2001), and exchange of gaseous Hg<sup>0</sup> by vegetation has been observed (e.g., Gustin et al. 2004). Hg<sup>II</sup> 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<sup>II</sup> 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 through 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; Bigham and Vandal 1994; Gbundgo-Tugbawa and Driscoll 1998; Gilmour et al. 1998; Mason et al. 1995). 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<sup>II</sup> and methylmercury accumulate in aquatic vegetation, phytoplankton, and benthic invertebrates. Unlike Hg<sup>II</sup>, methylmercury biomagnifies through each successive trophic level in the 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 pathways (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. Therefore, EPA makes this guidance available to fulfill that commitment to assist states and authorized tribes to adopt into their water quality standards the recommendations set forth in *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a), or other water quality criteria for methylmercury where such other criteria are based on scientifically defensible methods.

This nontraditional approach—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 presents many challenges because these activities have usually been based on a water concentration (e.g., as a measure of mercury levels in effluent or receiving waters). This guidance addresses issues associated with states' and authorized tribes' adoption of the new water quality criterion into their water quality standards programs and implementation of the revised water quality criterion in TMDLs and NPDES permits. Furthermore, because atmospheric deposition is a large source of mercury for many waterbodies, implementation of this criterion involves coordination across various media and program areas, which is also addressed in this guidance.

At this time, about seven states, plus Washington D.C. and two territories have adopted a fish tissue criterion for methylmercury with EPA approval. EPA expects that with the publication of this guidance, states and authorized tribes will include new or revised criteria for methylmercury in their waters as part of the next three year review of standards required by section 303(c) of the Clean Water Act. This expanded adoption of the 2001 methylmercury fish tissue criterion, together with a more sensitive method for detecting mercury in effluent and the water column and increased monitoring of previously unmonitored waterbodies, is expected to result in an increase in the number of waterbodies that states identify as impaired by mercury on CWA section 303(d) lists.

This guidance includes recommended approaches for relating a concentration of methylmercury in fish tissue to a concentration of mercury in ambient water (see chapter 3); a recommended approach for directly using the methylmercury tissue criterion as a basis for issuing NPDES permits (see chapter 7); and approaches that have been used in approved TMDLs for waterbodies impaired by mercury. This guidance includes examples of TMDL approaches for waterbodies where much of the mercury comes from atmospheric sources, as well as examples of TMDLs for waterbodies where the mercury

is predominantly from past mining activity. Finally, the guidance describes ongoing EPA efforts to address sources of mercury, such as programs under the CAA and pollution prevention activities.

EPA recognizes the complexity and comprehensive nature of this guidance. As is always the case when EPA issues technical guidance, EPA will provide outreach and technical assistance to states and authorized tribes in implementing this guidance.

#### 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 is not a 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 other scientifically defensible approaches that differ from this guidance. EPA may change this guidance in the future.

# 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 into state or tribal water quality standards. States and authorized tribes must adopt water quality criteria 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 are required to review standards every three years and submit changes to EPA for approval.

Whenever they review or revise standards, states and authorized tribes are to adopt numeric criteria for all toxic pollutants for which EPA has established national recommended ambient water quality criteria (AWQC) and where the discharge or presence of these pollutants could reasonably interfere with the designated uses (see CWA section 303(c)(2)(B)). Mercury and related compounds are identified as toxic pollutants in EPA regulations (40 CFR 401.15) and EPA published a criterion under 304(a) for methylmercury in 2001. EPA issued guidance on how states and authorized tribes may comply with CWA 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 pollutants 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 (e.g., a
  designated use of "fishing" is interfered with by nonattainment of the mercury
  water quality criterion).
- Option 3: States or authorized tribes may adopt a chemical-specific translator procedure<sup>5</sup> that can be used to develop numeric criteria as needed.

<sup>&</sup>lt;sup>4</sup> The term *water quality criteria* has two different definitions under the CWA. Under CWA section 304(a), EPA publishes recommended water quality criteria guidance that consists 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 recommended section 304(a) criterion. States may use these recommended 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).

EPA considers the 2001 methylmercury criterion a sound, scientifically based approach for meeting human health designated uses. In addition, this guidance addresses a range of complex technical issues and responds to the questions that states and authorized tribes have raised. Thus, EPA strongly encourages states and authorized tribes to adopt the 2001 methylmercury criterion or any sound, scientifically based approach for methylmercury or mercury, into their water quality standards at the upcoming triennial review of standards to fulfill the requirements of section 303(c) (2)(B) of the Clean Water Act and 40 CFR part 131. Numerical criteria for mercury in water, rather than fish tissue, published by EPA and in effect prior to 2001, may be included temporarily as part of revised mercury criteria at the next triennial review as provided for below.

### 3.1.2 What is the recommended form of the methylmercury criterion?

EPA's current recommended CWA section 304(a) water quality criterion for methylmercury is expressed as a fish<sup>6</sup> tissue concentration value (0.3 milligram methylmercury per kilogram of wet-weight fish tissue, or 0.3 mg/kg). With the publication of the fish tissue criterion, EPA withdrew the previous 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 2001c). These water column criteria, however, may be temporarily part of revised mercury criteria until the triennial review that follows the criterion adoption to help the transition in implementing the fish tissue criterion.

States and authorized tribes have several options for adopting a new or revised methylmercury criterion into their water quality standards. They may:

- Adopt the 2001 criterion or other scientifically defensible criterion as a fish tissue residue concentration, and implement it without water column translation; or
- Adopt a water column concentration, using the translation methodologies outlined in section 3.1.3.1, and implement it using traditional approaches; or
- Use a combination of the above approaches. For example, states and tribes could adopt a fish tissue criterion and implement it without water column translation for some or all waters, and translate the criterion to water column values for some or all waters.

Site-specific data for translating the fish tissue criterion to water column concentration, where needed, may take time to collect. Accordingly, states and authorized tribes may consider retaining their existing water column criteria, on a temporary basis, particularly for waters where there is a relatively high direct water input of mercury. In such a case,

<sup>&</sup>lt;sup>5</sup> A *translator procedure* is simply the detailed process adopted 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.

<sup>&</sup>lt;sup>6</sup> The criterion applies to both finfish and shellfish. For purposes of simplifying language in this document, the term *fish* means both finfish and shellfish.

where the state has retained the existing water column criteria, permits must include both a limit based on the existing numeric water column criterion and other requirements based on the fish tissue criterion (see chapter 7).

Where a water column translation of the fish tissue criterion has been developed or where site-specific data to do so are readily available using one of the options in Section 3.1.3.1, states and authorized tribes should translate the fish tissue criterion, and implement using traditional approaches. If site-specific data are not available to translate, the state or authorized tribe may design data collection activities to obtain the necessary data. States and authorized tribes should focus data collection activities on water bodies where methylmercury impairments are high priorities for action because of high direct water inputs. EPA recommends that states and tribes not only focus on data collection but also on the development of translators for waters with high direct water inputs of mercury. Additionally, EPA recommends that states and tribes include such translators in their criterion implementation plans.

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 and local or statewide fish consumption. EPA will evaluate criteria submitted by states and authorized tribes case by case.

If states and authorized tribes decide to adopt the tissue criterion expressed as a fish tissue concentration without translating it to a traditional water column concentration, this decision will lead to choices on how to implement the tissue criterion. A state or authorized tribe could decide to develop TMDLs and to calculate WQBELs in NPDES permits directly without first measuring or calculating a BAF. This guidance provides options for such approaches in chapters 6 and 7.

EPA does not require states and tribes to translate the fish tissue criterion into water column criteria. For waters with relatively high direct water inputs of mercury (mercury from point sources and nonpoint sources other than air deposition), EPA does recommend developing TMDLs, an analysis of sources and loading capacity similar to what would be provided in a TMDL, or a water column translation of the fish tissue criterion, to provide important information for developing appropriate permit limits. See section 7.5.2.2 for a further discussion of this situation.

#### 3.1.2.1 Developing a methylmercury criterion implementation plan

Regardless of the approach a state decides to use to implement its criterion, EPA encourages states and authorized tribes to develop a methylmercury criterion implementation plan to ensure environmentally protective and effective administration of all water quality related programs with respect to methylmercury. Developing a methylmercury implementation plan can facilitate adoption of the tissue-based criterion and provide transparency on state or tribal approaches to the numerous implementation issues associated with this type of criterion. This benefits not only the state or tribe but the regulated community and the public.

Examples of potential implementation issues the plan could cover include criterion adoption into the water quality standards (e.g., tissue or water column value with translators, BAF development methods), reasonable potential and permitting decisions, ambient monitoring strategies, and impairment determinations.

Developing an implementation plan could also facilitate subsequent regulatory decisions. Working with stakeholders and the public to develop an appropriate implementation plan concurrent with adoption of a tissue-based criterion could facilitate subsequent implementation decisions (e.g., application of the criterion in the context of 303(d) listing decisions or NPDES permitting actions) and decrease the likelihood of legal challenges.

It may be most useful to states and tribes to develop such an implementation plan prior to the adoption of the fish tissue criterion. States and tribes could propose draft plans when they are developing updates or revisions to their water quality standards. Additionally, EPA encourages states and tribes to take public comment on their draft plan during the time when the state or tribe is proposing to adopt the fish tissue criterion.

If a state or tribe develops a methylmercury implementation plan during adoption of its criterion, the state or tribe should submit the plan to EPA with the state's new criterion. Although the plan itself is not subject to EPA review and approval, the plan could facilitate EPA's review of the new criterion.

#### 3.1.2.2 Why is the fish tissue concentration criterion recommended?

EPA recommends that when states and authorized tribes adopt new or revised methylmercury water quality criteria, they adopt the criteria in the form of a fish tissue methylmercury concentration. This is the preferred form for the following reasons:

- A criterion expressed as a fish tissue concentration 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) through which humans are exposed to methylmercury.
- A fish tissue concentration value is more consistent with how fish advisories are issued.
- At environmentally relevant concentrations, methylmercury is currently easier to detect in fish tissue than in water samples.

#### 3.1.2.3 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 residue criterion (TRC) for the protection of human health is calculated as:

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

Where:

TRC = fish tissue residue criterion (in mg/kg) for freshwater and estuarine fish

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 consumed<sup>7</sup>), 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<sup>8</sup>

This equation and all values used in the equation are described in *Water Quality Criterion* for the Protection of Human Health, Methylmercury (USEPA 2001a). This equation is essentially the same equation used in the 2000 Human Health Methodology (USEPA 2000b) 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 2001c)).

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 rate of 17.5 g fish/day of freshwater or estuarine fish.

EPA encourages states and authorized tribes to collect, as quickly as possible, local or regional data to modify the fish consumption rate rather than using the default values if the state or authorized tribe believes that such a fish consumption rate would be more appropriate for its target population. This gives states and tribes the flexibility to develop criteria that provide additional protection appropriate for highly exposed populations that may be at greater risk than the general population protected by the 304(a) criterion (USEPA 2000b). Where states do not have site-specific data, but intend to collect this

<sup>&</sup>lt;sup>7</sup> 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 FR 1354–1355; January 8, 2001.

<sup>&</sup>lt;sup>8</sup> The consumption rate 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 2000a). 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 2000b).

data over time to develop a more appropriate criterion, states should use EPA's default fish consumption rate on a temporary basis to be able to adopt and implement the fish tissue criterion in a timely manner.

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 approach is conservative in that it assumes that all fish consumed are at the highest trophic level, and it will likely protect 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 information on determining consumption patterns, see chapter 4.) This approach might be more precise and is less likely to be overprotective; however, developing it could be resource-intensive.

# 3.1.3 What approaches should states or authorized tribes consider when developing a water column concentration criterion?

As described in section 3.1.2 above, there may be situations where it is appropriate to adopt a criterion expressed as a water column concentration. 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 programs. Water quality standards, water quality-based effluent limits<sup>9</sup> (WQBELs), total maximum daily loads (TMDLs), and other activities generally employ a water column value. This section provides information for states and authorized tribes that decide to adopt a water concentration criterion derived from a fish tissue criterion.

Alternatively, a state or authorized tribe may decide to adopt a fish tissue criterion with a site-specific procedure for translating the tissue criterion to a water column concentration. Because methylmercury bioaccumulation can vary substantially from one location to another, this option allows for the tissue criterion to be translated to a water concentration using site-specific information on methylmercury bioaccumulation (i.e., site-specific BAFs). Administratively, this option might be more efficient compared to adopting a water concentration criterion for an entire state or tribal jurisdiction or adopting or approving site-specific criteria on an individual waterbody basis. Approaches for translating a tissue concentration-based criterion to a water concentration are provided in the following section (section 3.1.3.1).

Developing a water column translation of the fish tissue criterion requires assessment of methylmercury bioaccumulation at an appropriate geographic scale. The uncertainty associated with differential bioaccumulation of methylmercury across sites within a state or tribal jurisdiction will be embedded in the state or tribal water-based criterion.

<sup>&</sup>lt;sup>9</sup> 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)).

Reducing such uncertainty is one of the primary reasons EPA chose to express its national recommended criterion for methylmercury as a tissue concentration rather than as a water concentration.

To express the methylmercury tissue concentration-based criterion as a water concentration, a state or authorized tribe would translate the methylmercury criterion concentration in fish tissue to methylmercury concentrations in the water column. To accomplish this, the state or authorized tribe would develop BAFs. In the 2001 *Federal Register* notice of the methylmercury criterion, EPA identified three different possible 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.

The following equation may be used to translate the tissue concentration-based human health AWQC to a water concentration-based methylmercury criterion using a BAF as

$$AWQC = TRC / BAF$$
 (Equation 2)

Where:

AWQC = water concentration-based ambient water quality criterion for methylmercury in milligrams per liter (mg/L)

TRC = tissue residue concentration; the water quality criterion for methylmercury in fish tissue 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 liters per kilogram (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

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

Where:

BAF = bioaccumulation factor, derived from site-specific field-collected samples of tissue and water in L/kg

Ct = concentration of methylmercury in fish tissue in mg/kg, wet tissue weight

Cw = concentration of methylmercury in water in mg/L

When such data are unavailable, other approaches for deriving BAFs may be used, as outlined in section 3.1.3.1.

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 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. 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 (through 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 that influence bioaccumulation and by limitations in the data parameters necessary to run the models.

The bioaccumulation of nonionic organic chemicals <sup>10</sup> such as methylmercury can also be affected by a number of these same physicochemical 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 2003). Normalizing to the age or size (length, weight) of fish has been shown to reduce variability in measures of bioaccumulation (Brumbaugh et al. 2001; Glass et al. 2001; Sonesten 2003; Sorensen et al. 1990; Wente 2004).

The United States Geological Survey (USGS) developed a procedure called the National Descriptive Model for Mercury in Fish Tissue (NDMMF) (Wente 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.

<sup>&</sup>lt;sup>10</sup> Nonionic organic compounds are those organic compounds that do not ionize substantially when dissolved in water and therefore are more likely to associate with sediment compounds, lipids, or other compounds in water (USEPA 2000b).

### **Mercury Terminology**

For the purposes of this document, the following definitions apply:

**Mercury (or total mercury):** The sum of all forms of mercury, including methylmercury, other organic forms, inorganic, and elemental mercury. All of these are toxic, and inorganic and elemental mercury can be methylated in the environment.

**Methylmercury:** The organic form of mercury, that bioaccumulates in the food chain. (Other organic forms of mercury exist, but exposure to them through environmental pathways is not significant.)

**Dissolved mercury (or filtered mercury):** The portion of mercury that passes through a filter

**Dissolved methylmercury (or filtered methylmercury):** The portion of methylmercury which passes through a filter.

**Total recoverable mercury (or unfiltered mercury):** The dissolved portion plus the particulate portion of mercury in a water sample.

**Total recoverable methylmercury (or unfiltered methylmercury):** The dissolved portion plus the particulate portion of methylmercury in a water sample.

Taking into account the previous discussion, EPA has outlined in this document three different approaches that could be considered for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water, should a state decide to develop or implement its standard in this manner:

- 1. Use site-specific methylmercury BAFs derived from field studies.
- 2. Use a scientifically defensible bioaccumulation model.
- 3. Where appropriate, use BAFs derived using the results of field studies that are not site-specific. Appropriate situations for using such BAFs include waters where direct water inputs are relatively high and where ambient fish tissue data are unavailable, where deriving site-specific, field-measured BAFs is not feasible, or where using a model is not feasible. Such BAFs may include the draft national BAFs presented in appendix A of Water Quality Criterion for the Protection of Human Health: Methylmercury (USEPA 2001a) and discussed in more detail below. Alternatively, BAFs may be derived using other approaches, such as a combination of national and site-specific data in conjunction with other, non-site-specific data, to create better estimates.

Of these approaches, 1 and 2 are preferred over 3. Because of the significant uncertainties inherent in non-site-specific estimates of BAFs (including the draft national BAFs), they should be used as defaults only in limited circumstances such as:

- When a state determines that use of the draft national BAFs are appropriate (for example, where direct water inputs are relatively high, where no other data are available to derive site-specific field-measured BAFs, and use of an appropriate BAF model is not feasible)
- When a state can show that such BAFs are appropriate for its situation (e.g., a state
  has data or analyses that demonstrate that the draft national BAFs would be
  appropriate)

• As an interim approach until more appropriate BAFs can be developed using other data and/or an alternate approach

The reasons for preferring approaches 1 and 2 are discussed in more detail below. However, the hierarchy assigned to the approaches is not intended to be inflexible. For example, in some cases, the site-specific information available may be so limited in quality or quantity that BAFs derived using other data may be preferable. In other cases, there might be enough site-specific information to indicate that the local conditions approximate the draft national values.

In situations where the state or tribe has some data available on fish tissue and water column levels in its jurisdiction, but data are insufficient to support broad development of site-specific translations, the state or tribe may be able to use these data in combination with an evaluation of the draft national BAFs to help develop water column translations. For example, California's Office of Environmental Health Hazard Assessment compiled mercury concentration data for water and biota, and calculated state-specific BAFs for different types of waters and different trophic levels. The office found enough similarities between the state-specific BAFs and EPA's draft national BAFs that it recommended using EPA's draft national values as an interim approach until more complete state-specific data becomes available (Sanborn and Brodberg 2006). The state is in the process of deciding whether to adopt this approach.

If the state or tribe chooses to derive BAFs using the third approach above, the state or tribe should provide an accompanying rationale that acknowledges an understanding of the potential limitations of the approach.

Developing site-specific data to support approaches 1 and 2 can be facilitated by efforts involving stakeholders, states, and authorized tribes. Developing site-specific data is one possible approach EPA recommends permitting authorities consider to help develop NPDES permits in watersheds where mercury loadings from point sources are relatively high. See section 7.5.2.2.

#### 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 2000b) and the Technical Support Document for developing national BAFs (USEPA 2003). 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 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). Although a BAF can be measured for the aggregate of fish in a location, site-specific BAFs are often specific to trophic level and species of fish. The BAF can also be measured based on a predatory indicator species with a high propensity

for bioaccumulation, such as largemouth bass. A field-measured site-specific BAF also reflects biotic and abiotic factors that influence the bioavailability and metabolism of a chemical that might occur in the aquatic organism or its food web at a given location. By incorporating these factors, field-measured site-specific BAFs account for the actual uptake and accumulation of the chemical.

States and authorized tribes should exercise caution, however, in developing a site-specific BAF for a migratory fish because its exposure to methylmercury occurred in part in areas other than where the fish was caught and therefore might not accurately predict the water column mercury concentrations associated with the fish tissue concentration of mercury. States and tribes should consider the life history of the migratory fish and the consumption patterns of the local population when considering BAFs for migratory species. States and tribes should also review how the applicable RSC considers migratory fish when considering including those species in BAF calculations (see section 3.2.1.1).

For the purposes of developing a criterion expressed as a water concentration, states and authorized 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 <sup>11</sup> (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 (Equation 2). 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.

As an example, California is currently employing a site-specific BAF approach in its Central Valley Region. In this approach, the state 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 et al. 2004). California linearly regressed fish tissue methylmercury concentrations for specific trophic level (TL) 3 and 4 fish against aqueous methylmercury concentrations (P < 0.001, P = 0.98, and P < 0.01, P = 0.98, respectively) and determined methylmercury concentrations in unfiltered water that correspond to the fish tissue criteria used in the TMDL analyses (0.15 ng/L for TL3 fish and 0.14 ng/L for TL4 fish) (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 for such sites 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

<sup>&</sup>lt;sup>11</sup> Although BAFs are sometimes calculated to represent the relationship between methylmercury in fish tissue and dissolved methylmercury in the water column, data can be collected to determine the relationship between methylmercury in fish tissue and total recoverable methylmercury or dissolved or total recoverable mercury in the water column. The Great Lakes Water Quality Initiative (GLI) used site-specific BAFs to convert directly from methylmercury in fish to total recoverable mercury in the water column. See 40 CFR part 132, and appendix B to part 132, Methodology for Deriving Bioaccumulation Factors.

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, these 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 at a specific 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 increase 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-, waterchemistry-, and 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., Brumbaugh et al. 2001; Kamman et al. 2004; Sorensen et al. 1990). 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, percentage of 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 in 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 because of 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, using 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 methylmercury bioaccumulation. The process of methylation itself is incompletely understood, and general models for reliably predicting rates of methylation do not exist, although EPA's WASP model might be useful in some environments. Three examples of mechanistic bioaccumulation models are the Dynamic Mercury Cycling Model, or D-MCM (EPRI 2002); the Bioaccumulation and Aquatic System Simulator, or BASS (Barber 2002), and the Quantitative Environmental Analysis Food Chain model, or QEAFDCHN (QEA 2000). A conceptual advantage of mechanistically based bioaccumulation models is that methylmercury bioaccumulation can be predicted under different conditions (e.g., different growth rates of fish, different water chemistry conditions, and different mercury loading scenarios) because the models include mathematical representations of 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 been applied to lotic systems (i.e. streams, rivers, estuaries) and therefore probably should be used only for static environments (lakes) at this time. The other models have been developed more generally, for nonionic organic chemicals that bioaccumulate, and require substantial modification and validation for application to mercury.

Most mechanistic bioaccumulation models use a chemical mass balance approach to calculate bioaccumulation in 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. Because of the need for site-specific data and calibration, these models are likely to cost as much to implement as a site-specific BAF. Their value comes from the ability to represent a wider range of explanatory and policy-relevant variables.

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 2000b) and *Technical Support Document Volume 2: Derivation of National Bioaccumulation Factors* (USEPA 2003). 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 the 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 as defaults. EPA used *Technical Support Document Volume 3: Development of Site-Specific Bioaccumulation Factors* of the 2000 Human Health Methodology (USEPA 2000b, 2003) and the BAF methods in volume III, appendix D, of the *Mercury Study Report to Congress* (USEPA 1997c) 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. The 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 2001a). The draft national BAFs (50th percentile values) are listed by trophic level in table 2.

Table 2. Draft national BAFs for dissolved methylmercury

BAF trophic	BAF trophic	BAF trophic
level 2	level 3	level 4
(L/kg)	(L/kg)	(L/kg)
120,000	680,000	2,700,000

Source: USEPA 2001a.

Note: Expressed as milligrams methylmercury/kilogram fish tissue per milligram methylmercury/liter water, or liters per kilogram (L/kg).

To develop the draft 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. Specifically, the data presented in *Water Quality Criterion of the Protection of Human Health: Methylmercury* (USEPA 2001a) indicate that BAFs for trophic levels 3 and 4 vary by a factor of 100

(two orders of magnitude) between the 5th and 95th percentiles. EPA does not recommend basing an AWQC on BAF values associated with the extremes of the distribution (e.g., 10th or 90th percentile), unless supported by site-specific data. Such values might introduce an unacceptable level of uncertainty into the calculation of a water column-based AWQC. States and authorized tribes should consider the magnitude of the potential error when proposing to use the draft national BAFs.

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). For more information on the draft national BAFs, see chapter 6 and appendix A, section I, of EPA's 304(a) water quality criterion for methylmercury (USEPA 2001a). 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 2,700,000 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 / 2,700,000 L/kg) to indicate attainment of the water quality column criterion. Using the BAF based on site-specific data, however, 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 reductions or permits using the draft national BAF of 2,700,000 L/kg would be underprotective.

#### • Overprotective scenario

A state uses the draft national BAF of 2,700,000 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 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 / 2,700,000 L/kg) to indicate attainment of the water quality criterion. Using the BAF based on site-specific data, however, attainment of the water quality criterion could be achieved at a higher water column concentration, 0.33 ng/L. Thus, load reductions or permits using the draft national BAF of 2,700,000 L/kg would be overprotective.

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 2001a), which 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 age (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 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, although the concentration of methylmercury in fish tissue is presumably a function of these varying concentrations, published BAFs are typically 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.

Peer reviewers expressed concerns about the use of the draft national BAFs as defaults 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 draft 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. States and tribes should also consider whether more recent data and/or data that are more reflective of local conditions are available to supplant or supplement the limited database used to derive the draft national BAFs.

Risk managers should also understand that in using the draft national BAFs as defaults, 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. A state's or tribe's decision to use the draft national BAFs would be a risk management decision. The decision would reflect the state's or tribe's judgment that, for specific reasons, translating the fish tissue criterion to a water column value using such a BAF is preferable to implementing the fish tissue criterion directly (e.g., using the approaches discussed in this guidance), or conducting studies to develop a site-specific BAF (e.g., site-specific field studies or bioaccumulation modeling).

# 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 water or fish in 40 CFR part 136. A discussion of analytical methods for mercury and methylmercury can be found in section 4.1. For fish tissue, however, states and authorized tribes can estimate methylmercury concentrations and determine attainment by using the same analytical method used to measure for mercury, at least for upper-trophic-level fish (levels 3 and 4). This is because 80 to 100 percent of the mercury found in the edible portions of freshwater fish greater than three years of age from these two trophic levels is in the form of methylmercury (USEPA 2000c). In fish greater than approximately three years of age, mercury has had sufficient time to bioaccumulate to roughly steady levels in the fish. Appendix A summarizes eight 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 eight studies, methylmercury on average accounted for more than 90 percent of the mercury concentration in fish tissue. In the remaining two studies, methylmercury on average accounted for 80 to 90 percent of the mercury concentration in trophic level 3 and 4 fish.

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 by using

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 using the National Descriptive Model for Mercury in Fish Tissue, or 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 2005a).

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 are correlated with the magnitude of methylmercury accumulation, the types and sizes of aquatic organisms being consumed should be considered when determining which fish to sample for deriving BAFs. States and tribes should consider the fish being consumed by various subpopulations (e.g., sport anglers, subsistence fishers) as well as culturally and economically diverse communities. 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 authorized tribes should review site-specific data used to calculate field-measured BAFs and thoroughly assess the quality of the data and the overall uncertainty in the BAF values. States and authorized tribes should also consider the following general factors when determining the acceptability of field-measured BAFs reported in the published scientific literature. The same general issues and questions should also be addressed when designing a field study to generate site-specific field-measured BAFs.

- Calculate a field-measured BAF using aquatic organisms that are representative of
  the aquatic organisms 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, its 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 the 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 2001a). 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) because of 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 1997d). 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 2003). A publication by Burkhard (2003) is also a good source of information on designing BAF field studies and on deriving field-measured site-specific BAFs.

# 3.1.3.3 How is methylmercury in water translated into its mercury equivalent in water?

Given that permit limits are often derived using a mercury water column concentration criterion, a state or tribe may wish to take another step after using a BAF to determine a methylmercury water concentration criterion to derive a mercury water column concentration criterion. Although not necessary to develop a water quality criterion, a state can translate a methylmercury water concentration into a mercury water concentration criterion by converting the concentration of methylmercury in water to the equivalent concentration of mercury in water. This step might be necessary because although the BAF is typically based on the concentration of methylmercury in water, the assessment of water quality is typically based on an evaluation of mercury concentrations since other forms of mercury are converted to methylmercury in the environment. As a result, a relationship between (dissolved or total recoverable) methylmercury and (dissolved or total recoverable) mercury in the water needs to be developed. NPDES permits and other water quality-based pollution control activities traditionally rely on the total recoverable concentration of mercury, not the dissolved methylmercury form.

Many of the issues surrounding the uncertainty in predicting and transferring methylmercury BAFs across different waterbodies also apply to translating methylmercury concentrations to mercury concentrations. As with BAFs, one approach for translating between methylmercury and mercury concentrations is for states and

authorized tribes to measure site-specific concentrations of methylmercury and mercury to determine the relative amounts of each form. This field-measured, site-specific approach is the most direct and the most appropriate approach to the translation.

Where a site-specific approach is not feasible, states and authorized tribes may consider applying EPA's draft national methylmercury-to-mercury translator factors. In the 2001 methylmercury criterion document (USEPA 2001c), EPA derived these translator factors for rivers/streams and lakes as geometric means from data collected from the literature reporting concentrations of mercury in aquatic environments. Thus, like the draft national BAFs, the methylmercury-to-mercury translators were empirically derived based on various water data from across the United States. As with the draft national BAFs, the draft national methylmercury-to-mercury translator factors vary greatly across ecosystems and are subject to many of the same uncertainties. Therefore, EPA suggests that states and tribes that may be considering using the draft national translator values as defaults carefully review the discussion in the 2001 criterion document, particularly the discussions concerning uncertainty and limitations, before deciding to apply them in a regulatory context (see appendix A, section II, USEPA 2001a). States and tribes should consider whether more recent data and/or data that are more reflective of local conditions are available to supplant or supplement the limited database used to derive the draft national translators.

Alternatively, states and tribes that choose to develop water column criteria can consider collecting data to develop BAFs that relate methylmercury in fish tissue directly to total mercury in the water column. See the footnote to section 3.1.3.1.1 for more information.

# 3.2 What options are available to address 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 2000b) describes how states and authorized tribes can adopt site-specific modifications of a section 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, it 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, are 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 for the consumption rate of the population surveyed. When defining a target population, a state or authorized tribe should focus on protecting populations with high rates of fish consumption from the local area.

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

• Use an alternative RSC factor or

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 the former would better
reflect the target population.

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

#### 3.2.1.1 How does one modify the RSC?

Section 5 of the methylmercury criterion document (USEPA 2001a) 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 RfD 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.

If a state or tribe proposes to change the RSC, it should document the modifications with data supporting the modifications and share the proposed modifications to the RSC with EPA prior to recalculating the criterion. See appendix B for the tables from the methylmercury criterion document. States and authorized tribes should review section 5 of the methylmercury criterion document and modify the media-specific exposure estimates using local data that reflect the exposure patterns of their populationsTo modify this factor, states and authorized tribes should review the amount of marine fish and shellfish estimated to be consumed (table 5-1, USEPA 2001a) and the concentration of methylmercury in the commonly consumed marine species (table 5-14, USEPA 2001a).

#### 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/day<sup>12</sup>, uncooked (USEPA 2001a). States and authorized tribes may use a different intake rate based on local or regional consumption patterns and are encouraged to use consumption rates that are protective of a range of culturally and economically diverse communities. The fish consumption value in the TRC equation may 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 equation 1 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

<sup>&</sup>lt;sup>12</sup> This value represents the 90th percentile of freshwater and estuarine finfish and shellfish consumption reported by the 1994–1996 *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 2000b).

their target population. However, states and authorized tribes should consider whether the fish consumption rates reflect existing public concern about contamination of fish when collecting survey data, rather than local preference for fish consumption (i.e., the presence of fish advisories limits the consumption of fish). In this instance, the state or authorized tribe should take this into account and try to conduct surveys in a manner that accounts for the effects of fish advisories on the consumption of fish. Where there is afish consumption advisory, surveys should be designed to evaluate how much fish a local population would consume if the fish were safe to eat and incorporate that consumption level into the criterion.

EPA suggests that states and authorized tribes follow a hierarchy when deriving fish intake estimates (USEPA 2000b). From highest preferred to lowest preferred, this hierarchy is as follows (1) use local data protective of culturally and economically diverse communities 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.

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, states and authorized tribes might want to include EPA in the development of the study plan and submit the data supporting the site-specific criterion for EPA's consideration when EPA approves or disapproves state or tribal water quality standards under CWA section 303(c). Including EPA at the study plan development stage may help to avoid problems and facilitate development of a defensible site-specific criterion.

#### 3.2.1.2.1 Use local data

If a state or authorized tribe believes a fish consumption rate other than the default would be appropriate for their target population, EPA's first preference is that they use fish intake rates derived from studies of consumption of local fish. Such studies could include 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. When estimating the fish intake rate, all freshwater fish, whether caught recreationally or bought commercially, should be included. States and authorized tribes may choose to develop either fish intake rates for the local population as a whole, or individual fish intake rates for various subpopulations (e.g., sport anglers, subsistence fishers) as well as culturally and economically diverse consumers.

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 that eat local fish. EPA's consumption survey guidance offers recommendations on how to develop appropriate quality assurance and quality control procedures to help ensure the quality of the survey. Results of studies of the broader geographic region in which the state or authorized tribe is located can also be used, but they might not be as applicable as study results for local watersheds. Because such studies would ultimately form the basis of a state's or authorized tribe's methylmercury criterion, EPA would consider any surveys of

fish intake as part of its review of the methylmercury criterion's scientific defensibility 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 tribes should ensure that the distribution is based on survey respondents that 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 other Agency positions such as that of the 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 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 fishers, minority populations). A state or authorized tribe in a region of the country might consider using rates from studies that surveyed the same region; for example, a state or authorized tribe that has a climate that allows year-round fishing might underestimate consumption if it uses rates from studies taken in regions where people fish for only one or two seasons per year. A state or authorized tribe that has a high percentage of an age group (such as older persons, who have been shown to have higher rates in certain surveys) might wish to use age-specific consumption rates, which are available from some surveys. For additional information on the use of fish consumption rates, see EPA's 2000 Human Health Methodology (USEPA 2000b). 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 1994–1996 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 1994–1996 and 1998 CSFII surveys, the statistical methodology, and the results and uncertainties of the EPA analyses (USEPA 2002b). The estimated fish consumption rates

in the CSFII report are presented 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 (rates based on consumers and nonconsumers of fish from the survey period), (2) by consumers-only rates (rates based on respondents that reported consuming finfish or shellfish during the 2-day reporting period), and (3) per capita consumption by body weight (per capita rates reported as mg/kg-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.

The CSFII surveys (USDA/ARS 1998, 2000) 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 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 shortterm 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 American Indians on reservations and certain ethnic groups. Although these persons 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 2002b).

#### 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, default rates on the basis of the 1994–1996 CSFII data for the U.S. population, which EPA believes are representative of freshwater and estuarine fish and shellfish intake for different population groups. The 1994–1996 CSFII data for U.S. fish consumption among both consumers and nonconsumers of fish is delineated below in table 3.

Because the combined 1994–1996 CSFII survey is national in scope, EPA uses the results from it to estimate fish intake for deriving national criteria. EPA applies a default rate of 17.5 grams/day for the general adult population. EPA selected an intake rate that is protective of a majority of the population (the 90th percentile of consumers and nonconsumers, according to the 1994–1996 CSFII survey data) (USEPA 2000b). EPA also recommends a default rate of an average of 17.5 grams/day for sport fishers.

Table 3. Estimates of freshwater and estuarine combined finfish and shellfish consumption from the combined 1994–1996 and 1998 CSFII surveys (U.S. population)

	Mean	Median	90th percentile	95th percentile	99th percentile
All ages	6.30	N/a	11.65	41.08	123.94
Age 18 and over	7.50	0.00*	17.53	49.59	142.41
Women ages 15-44	5.78	N/a	6.31	32.37	109.79
Children age 14 and under	2.64	0.00	0.00	13.10	73.70

Note: All values expressed as grams per day for uncooked fish.

Similarly, EPA believes the 99th percentile of 142.4 grams/day is within the range of consumption estimates for subsistence fishers, according to the studies reviewed, and that it represents an average rate for subsistence fishers. EPA knows that some local and regional studies indicate greater consumption among American Indian, 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 the 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 1994–1996 CSFII are representative, the state or tribe may choose these recommended rates.

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. States and authorized 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 (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 2000b).

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<sup>\*</sup> The median value of 0 grams/day might reflect the portion of persons in the population that never eat fish, as well as the limited reporting period (2 days) during which intake was measured.

<sup>&</sup>lt;sup>13</sup> See the discussion of the RSC in sections 3.1.2.3 and 3.2.1.1.

# 3.2.2 How do water quality standards variances apply?

Where a discharger or waterbody cannot meet a water quality standard, a state or authorized tribe may adopt a temporary water quality standard through a variance process. 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 revision to the otherwise applicable water quality standard (designated use and criteria), water quality standards variances must be supported by one of the six justifications under 40 CFR 131.10(g) (see section 3.2.3.4 below). Variances are generally determined based on the discharger's ability to meet a WQBEL and, therefore, are considered after an evaluation of controls necessary to implement water quality standards. In addition, EPA recommends that the permitting authority require the facility seeking a variance to develop and implement a mercury minimization plan (MMP) to both reduce mercury loading and to determine the highest level of water quality achievable to inform future permit decisions (see section 7.5.2.4 for more discussion of MMPs).

Variances typically apply for a limited period but may be reviewed at the time of the state triennial review of water quality standards, and require the same procedural steps that are required of a change in the standards. Where the term of a variance extends beyond three years, as for example in an NPDES permit, the variance must still be reassessed as part of the state's three year triennial review to confirm that the underlying attainability analysis remains relevant and accurate. A variance must continue to protect "existing uses" (defined in 40 CFR 131.3(e) as uses actually attained in the waterbody on or after November 28, 1975). Typically, variances apply to specific pollutants and facilities, which would mean that a water quality standards variance for mercury would apply to only the new methylmercury criterion in a stated waterbody and specifically to the discharger requesting the variance. The state or authorized tribe, however, 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). See section 3.2.3 for a discussion of the requirement to conduct a use attainability analysis for changes to water quality standards, including the prohibition on removing existing uses.

#### 3.2.2.1 When is a variance appropriate?

Some regulated point sources discharging mercury might apply for variances for their discharges into impaired waters where the largest source of mercury is atmospheric deposition. In other cases, limits to technology or naturally elevated levels of methylmercury in a waterbody could preclude attainment of standards. To address these types of issues, the following scenarios are examples of demonstrations that could satisfy the requirements under 40 CFR 131.10(g). The demonstrations are more thoroughly explained below and in the *Water Quality Standards Handbook* (USEPA 1994).

- Economic or social impacts (131.10(g)(6)). 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 (131.10(g)(3)). Demonstrate that, in the short term, none of the present technologies for improving the quality of

an effluent are capable of bringing methylmercury levels in the discharge down to a level as stringent as necessary to meet the criterion (i.e., there is no technological remedy or it is technologically infeasible).

• Natural conditions that preclude attainment (131.10(g)(1)). Demonstrate that local conditions of an aquatic system result in high methylmercury levels. For example, elevated methylmercury concentrations might occur naturally in a system because of a short-term condition.

During the period the variance applies, any permit issued must be consistent with applicable water quality standards (40 CFR 122.44(d)(1)(vii)), which in this case would be the temporary standard approved in the variance. The permit would need to be modified to derive from and comply with the underlying standard if the variance is not re-issued.

# 3.2.2.2 What should a state or tribe consider before granting a variance?<sup>14</sup>

In general, the temporary revised standard established by a variance should be set at a level representing the highest attainable water quality (like all water quality standards). Variances may not interfere with existing uses, and variances should ensure progress toward ultimate attainment of the designated use for the waterbody. 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 to 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.

- Variance protocols. If a state or authorized tribe anticipates receiving a number of variance requests for mercury discharges, it could consider establishing a mercury variance protocol, with EPA's participation and agreement. The protocol would govern the development and processing of variance requests. It would specify the information needed and the criteria the state would use in considering whether to adopt the variance. Although the state or tribe would need to submit each variance to EPA for approval (40 CFR 131.20), EPA's advance agreement to the protocol could streamline EPA's review of any variances developed in accordance with the protocol. Public notice requirements for variances could be satisfied through the process of issuing the NPDES permit that incorporates limits based on such temporary standards, as long as the variance is identified and all the necessary information pertaining to the variance is included.
- Time frames. A variance is typically a time-limited change in the water quality standards. Although EPA part 131 regulations do not specify a time limit for variances, EPA's triennial review regulations at 40 CFR 131.20 require that variances, as part of water quality standards, are reexamined every three years to

<sup>&</sup>lt;sup>14</sup> Federal or state regulations also govern the granting of a variance. For example, regulations promulgated under 40 CFR part 132, appendix F, procedure 2, specify the conditions for granting variances in the Great Lakes and prohibit the granting of variances to new dischargers or recommending Great Lakes dischargers.

determine if new information has become available and modified as appropriate. Variances that extend longer than three years are traditionally revisited in the context of a triennial review. Once a variance has expired, to justify the continuation of the variance, the state must demonstrate that meeting the standard is still unattainable based on one of the factors at 131.10(g). The state should also ensure that the permittee has made reasonable progress to control mercury in the discharge during the period of the previously approved variance (i.e. has adopted a mercury minimization plan.)

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, but may do so where the permit contains a reopener condition to address such revised water quality standards. In the Great Lakes, however, permits with limits based on variances must include a provision enabling the permitting authority to reopen and modify the permit based on triennial revisions to water quality standards. (40 CFR part 132, appendix F, procedure 2, section F.4). Any new or reissued permit must implement the water quality standards applicable at time of permit issuance. 40 CFR 122.44(d)(1).

- Antidegradation. Permits with effluent limits based on a variance for methylmercury must conform, as do all permits, to the state or authorized tribe's antidegradation policy.
- Mercury Minimization Plans (MMPs). EPA recommends that states and authorized tribes require dischargers receiving a variance to adopt and implement an MMP as described in section 7.5.2.4. By reducing mercury sources up front, as opposed to traditional reliance on treatment at the end of a pipe, diligent implementation of MMPs might mitigate any adverse effects of a variance by improving the water quality. As noted above, MMPs also serve to inform the evaluation of controls needed to grant a variance and to determine the highest attainable 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, states and authorized tribes may 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 facilities with similar discharge processes, a watershed basis, particularly for states that issue NPDES permits on a watershed basis, or a broader geographic basis, analogous to a general NPDES permit.

For example, Ohio adopted a statewide mercury variance applicable to point source dischargers in the state that meet specified criteria. In addition, Michigan has authorized multiple discharger variances for mercury with permit requirements, including development and implementation of an MMP.

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 use attainability analysis (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)).

Where a UAA indicates that the current use is unattainable, the state or tribe will need to identify and assign the "highest attainable use," which should reflect the factors and constraints on the attainability of a use that were evaluated as part of the UAA process. Once the state or tribe has determined the highest attainable use, it should propose adopting this designated use in place of the designated use deemed unattainable. For example, to the extent allowed by state or tribal law, the state or tribe could refine its designated use from "fish consumption" to "mercury-limited fish consumption." That way the waterbody would still be expected to meet other pollutant criteria designed to protect fish consumption.

#### 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 these goals as providing for the protection of aquatic communities and human health related to the consumption of fish and shellfish. In other words, EPA views "fishable" 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) 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 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. An existing use is 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, EPA considers designated uses 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 for nonpoint sources. The federal regulations at 40 CFR 131.10(g) further establish 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 (40 CFR part 131.10(b)). States and tribes 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.

# 3.2.3.4 What conditions justify changing a designated use?

EPA's regulations at 40 CFR 131.10(g) list 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 guide analysis and decision-making with respect to establishing an attainable use.

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. These documents are at <a href="http://www.epa.gov/waterscience/standards/uaa/info.htm">http://www.epa.gov/waterscience/standards/uaa/info.htm</a>. 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).

EPA recognizes that there may be naturally occurring concentrations of methylmercury which may exceed the national recommended 304(a) criterion. However, EPA policy, whereby criterion may be set at ambient conditions if contaminant levels are due only to non-anthropogenic sources, applies only to aquatic life uses. The policy does not apply to human health uses. The policy states that for human health uses, where the natural background concentration is documented, this new information should result in, at a minimum, a re-evaluation of the human health use designation (USEPA 1997e).

# 4 Monitoring and Assessment

Water quality monitoring and assessment are essential elements in implementing the CWA at the local, state, and national levels. In implementing the water quality-based approach, the most obvious uses of monitoring information are in determining attainment of water quality standards and in developing TMDLs and permits. In the case of mercury, analyzing for mercury and methylmercury in water and fish is particularly important for states and tribes that choose to develop BAFs and methylmercury-to-mercury translators. This chapter provides guidance on analytical methods, field sampling, and assessment considerations for mercury. Additional information on developing site-specific BAFs and translators is provided in section 3.1.3 of this guidance.

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

Over the past two 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 analytical methods and to determine which of the analytical methods would be most useful for implementing the new methylmercury criterion. After the 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).

To assist states and authorized tribes in selecting an analytical method to use, this chapter describes selected analytical methods available (sections 4.1.1 and 4.1.2), and identifies five specific methods that EPA recommends for use in implementing this guidance (section 4.1.3). In addition, appendix C of this document presents a list of available methods in more detail. Table C1 of the appendix summarizes 4 methods to analyze mercury and methylmercury in fish tissue, and table C2 summarizes 18 methods for the analysis of mercury and methylmercury in water and other nontissue matrices. Each table identifies the forms and species of mercury 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.

The CWA establishes an EPA approval process for certain methods used in the NPDES program and for section 401 certifications. As described in section 4.1.2 below, EPA has approved two of the above methods for analysis of mercury in water under 40 CFR part 136: method 1631, revision E and method 245.7. EPA's regulations generally require that these methods be used whenever such analyses are required for the NPDES program and for CWA section 401 certifications issued by states and authorized tribes (40 CFR 136.1). Sections 7.4 and 7.5.1.1 of this guidance provide additional information on appropriate analytical methods for measuring mercury in water for NPDES permitting purposes.

There are no regulatory requirements for the use of particular methods in setting water quality standards, evaluating the attainment of standards, or developing TMDLs,

although any methods used need to be scientifically defensible. Although this chapter provides recommendations for methods that can be used for these purposes, states and tribes are not precluded from using other methods, including those in appendix C.

# 4.1.1 Analytical Methods for Methylmercury

For measuring methylmercury in water, EPA method 1630 (USEPA 2001d), developed by EPA's Office of Water, reflects the techniques developed by Bloom and Crecelius (1983) and refined by Bloom and Fitzgerald (1988), Bloom (1989), Mason and Fitzgerald (1990), and Horvat (1993). This method has a quantitation level of 0.06 ng/L.

Draft modifications to method 1630, described in table C1 (see appendix C) and in Horvat et al. (1993), allow for measurement of methylmercury in fish 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 using these techniques when direct measurements of methylmercury in fish tissue are desired.

Three additional methods for measuring methylmercury in water are listed in table C2 (see appendix C). These methods are UW-Madison's standard operating procedure, or SOP (Hurley et al. 1996), used by the Great Lakes National Program Office for its Lake Michigan Mass Balance Study; USGS Wisconsin-Mercury Lab SOPs 004 (DeWild et al. 2002), used by USGS and EPA in the Aquatic Cycling of Mercury in the Everglades study; and a recently released USGS method (DeWild et al. 2002). All these procedures are based on the same techniques and have detection limits of 0.01 ng/L, 0.05 ng/L and 0.04 ng/L, respectively.

Because the four methods are nearly identical test procedures, they are expected to produce very similar results with sensitivity as low as 0.01 to 0.06 ng/L in water. These levels are well below the expected range of water column concentrations associated with the methylmercury fish tissue criterion.

# 4.1.2 Analytical Methods for Mercury

For measuring low level mercury in water, EPA method 1631, revision E (USEPA 2002c), developed by EPA's Office of Water, reflects the techniques developed by researchers mentioned previously. It has a quantitation level of 0.5 ng/L. EPA made this revision to clarify method requirements, increase method flexibility, and address frequently asked questions. The revision includes recommendations for using the clean techniques contained in EPA's *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (USEPA 1996a). The benefits of using method 1631 are that it has been fully validated, numerous laboratories are routinely using the method, and it is sensitive enough to measure at the water concentrations expected to be associated with the criterion. This method was approved in 2002 under 40 CFR part 136 for NPDES permitting and other purposes under the CWA (67 FR 65876).

In addition, EPA method 245.7 (USEPA 2005e), which has a quantitation level of 5.0 ng/L, was approved under part 136 in 2007 (72 FR 11200). Developed by EPA's Office of Water, method 245.7 is similar to EPA method 1631E because both methods require use of a cold-vapor atomic fluorescence spectrometry (CVAFS) detector to measure low levels of mercury. Method 245.7 has been validated in two EPA

laboratories, one university laboratory, and an interlaboratory validation study. Results from these studies indicate that the method is capable of producing reliable measurements of mercury at some toxic criteria levels (40 CFR 136).

Appendix A to method 1631 (64 FR 10596) details the researcher's techniques for determining total and dissolved mercury in tissue, sludge, and sediments. The appendix 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 0.002 to 5.0 mg/kg.

EPA recognizes that some users might find Method 1631 (appendix A) costly or difficult to implement. Appendix C summarizes three other methods available for analyzing mercury in fish tissue that are less costly and less difficult to implement, but they have not undergone the same extensive interlaboratory validation studies as Method 1631 (appendix A). Two are listed in table C1 (Methods 245.6 and 7474). The third—Method 7473 for analyzing mercury in water, listed in table C2—has been adapted by some users for analyzing mercury in fish tissue; this approach has been used to measure mercury in fish tissue to support state fish consumption advisories.

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, might be 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.

# 4.1.3 Summary of Recommended Analytical Methods

In summary, on the basis of the available information, EPA believes that the most appropriate methods for measuring low levels of mercury concentrations in the water column are method 1631, revision E (mercury in water by CVAFS) and method 245.7 (mercury in water by CVAFS). Likewise, EPA believes that the most appropriate method for measuring methylmercury concentrations in the water column is method 1630 (methylmercury in water by CVAFS), and the most appropriate methods for measuring mercury concentrations in fish tissue are appendix A to method 1631 (mercury in tissue by CVAFS) and modifications to method 1630 for handling tissues. EPA recommends these procedures for the following reasons:

- EPA developed methods 1631 and 1630 to support implementation of water quality criteria for mercury and methylmercury, respectively. Both are already in the appropriate EPA format and include all standardized quality control elements needed to demonstrate that results are reliable enough to support CWA implementation.
- EPA developed method 245.7 specifically to address state needs for measuring
  mercury at ambient water quality criteria levels, when such measurements are
  necessary to protect designated uses. In addition, it has been validated in two EPA
  laboratories, one university laboratory, and an interlaboratory validation study.
- EPA developed appendix A to method 1631 to support its National Study of Chemical Residues in Lake 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 was used by Battelle Marine Sciences to analyze more than a thousand tissue samples collected during EPA's national study (USEPA 2000d). 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 2001e) and the Savannah River TMDL study (USEPA 2001f). 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. Furthermore, the procedures in method 1630 are nearly identical to those given in the USGS method and in the University of Wisconsin SOP (Hurley et al., 1996), listed in table C2. The University of Wisconsin SOP was used in EPA's Lake Michigan Mass Balance Study (USEPA 2001g).

Table 4 summarizes the recommendations discussed above.

Table 4. Recommended analytical methods for detecting and measuring low levels of methylmercury and mercury in fish tissue and water

Recommended for analysis of:	Methylmercury (see section 4.1.1)	Mercury (see section 4.1.2)
in fish tissue (for additional available methods, see appendix C, table C1)	Method 1630 with draft modifications for tissue	Method 1631, draft Appendix A
in water (for additional available methods, see appendix C, table C2)	Method 1630	Method 1631, revision E* Method 245.7*

<sup>\*</sup>Approved under 40 CFR part 136. See sections 7.4 and 7.5.1.1 for further information on appropriate methods for NPDES permitting purposes.

# 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*, 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 can be applied for obtaining a representative sample for determining attainment. The guidance also includes recommendations for quality control and quality assurance considerations. In all cases, states and authorized tribes should develop data quality objectives for determining the type, quantity, and quality of data to be collected (USEPA 2000e).

# 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 for selecting fish is that the species are commonly eaten in the study area and have commercial, recreational, or subsistence fishing value. States and tribes also should ensure that the species monitored reflect the fish species consumed by culturally and economically diverse communities. Fish creel data (from data gathered by surveying recreational fishers) from state fisheries departments are a 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 that eat fish.

The fish sampling guidance also identifies recommended target species for inland fresh waters and for Great Lakes waters. Walleye and largemouth bass have been identified as freshwater fish that accumulate 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 consumption of contaminated prey.

The fish sampling guidance further recommends that the size range of the sampled target fish ideally should include the larger fish individuals harvested at each sampling site because larger (older) fish within a population are usually the most contaminated with methylmercury (Phillips 1980, Voiland et al. 1991). 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 that neither spawning populations nor undersized juvenile stages be sampled in fish contaminant monitoring programs (USEPA 2000c). States and authorized tribes should consider the life history of migratory species and the consumption patterns of the local population when including migratory species in their fish sampling protocols. Sampling of target finfish species during their spawning period should be avoided because contaminant tissue concentrations might decrease at that time.

If states and authorized tribes do not have local information about the types of fish 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 or by individuals in another target population, a monitoring sample could be composited to reflect this knowledge. For example, a state might decide that 75 percent of the fish consumed are trophic level 4 species, 20 percent are trophic level 3 species, and 5 percent are trophic level 2 species. A composite sample (see section 4.2.2) would reflect the determined trophic level breakout.
- *Use trophic level 4 fish only*. Predator species (e.g., trout, walleye, largemouth bass, and 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 larger (older) individuals correlates with greater risks to human health. Increasing mercury concentrations also correlate with higher trophic levels, and thus consumption of higher-trophic-level species would provide greater risks to human health. Therefore, targeting trophic level 4 species should serve as a conservative approach (depending on the species most frequently consumed by recreational fishers) 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 that people in the local area eat because methylmercury is found primarily in fish muscle tissue (USEPA 2002c). 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 typically eat the fillets without skin. 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. Some fish consumers, however, do eat fish with the skin on. In areas where the local population eats fish with the skin or eats other parts of fish, the state or authorized tribe should consider including these parts of fish 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. 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 on 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?

Ideally, states and authorized tribes should collect samples 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, those 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 those areas but not included if the areas are not used for fishing.

Once the state or tribe identifies the geographic area, EPA recommends that they use a probabilistic sampling design to select individual sites or sampling locations. Use of a

probabilistic design can address the spatial variability of methylmercury levels in fish. This approach allows statistically valid inferences to be drawn about tissue levels in the area as a whole. EPA's *Guidance on Choosing a Sampling Design for Environmental Data Collection, for Use in Developing a Quality Assurance Project Plan* (USEPA 2002d) contains information about probabilistic site selection.

# 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 program resources are sufficient, 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 five 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 (August to October). Water levels are typically lower during that time, simplifying collection procedures. Also, the fish lipid content is generally higher, allowing the 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 that period. 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 authorized tribes sample consistently in a season to eliminate seasonal variability as a confounding factor when analyzing fish monitoring data. Moreover, 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 the mercury concentrations in fish fillet muscle 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 than in warm seasons by as much as two to three times. 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 of mercury concentrations in fish 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 levels. 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 (Burrows and Krenkel 1973; Giblin and Massaro 1973; Huckabee et al. 1979 [literature review]; McKim et al. 1976; Rodgers and Beamish 1982). Such slow depuration rates are expected to dampen strongly any fluctuations in methylmercury concentrations in fish. Instead, seasonal variations in fish tissue are likely linked to seasonal nutrition variability that affects fish body conditions but not mercury body burden.

# 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 6.1.2.7.2, provides information to help determine the number of composite samples needed for comparing fish tissue information to a target value. The guidance does not recommend a single set of sample size requirements (e.g., number of replicate composite samples per site and 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's preventing the site-specific statistical analysis, at least 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 that for mercury analysis), one approach for the states and authorized tribes could be to first measure mercury in fish tissue. States and tribes may find that more labs have the capability for mercury analysis and that the analysis time may be quicker.

When measuring only mercury, the state or authorized tribe might make the conservative assumption that all mercury in fish tissue is methylmercury. Appendix A summarizes eight 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 eight studies, methylmercury, on average, accounted for more than 90 percent of the mercury concentration in fish tissue. In the remaining two studies, methylmercury, on average, accounted for 80 to 90 percent of the mercury concentration in trophic level 3 and 4 fish. If the measured mercury level exceeds the methylmercury criterion, states and tribes may wish to repeat the sampling (if sufficient tissue is not left) and analyze for methylmercury.

# 4.2.7 Other sampling considerations

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 Hinners (2004) reported a negative correlation between fish body condition (a ratio of weight to cubed length) and fish tissue mercury concentration. Regardless of the exact mechanism, body condition offers a useful method to explain variability in fish mercury.

## 4.3 How should waterbody impairment be assessed for listing decisions?

Section 303(d)(1) of the CWA and EPA's implementing regulations require 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. In accordance with 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, or in category 5 of the Integrated Report under sections 303(d) and 305(b)<sup>15</sup>, 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 and narrative AWQC (40 CFR 130.7 (b)(3)). Where a fish tissue criterion has been adopted, states and tribes should consider observed concentrations in fish tissue in comparison to the criterion. Where a water column translation of the fish tissue criterion has been developed and is adopted as part of the state's or tribe's water quality standards, states and tribes should consider ambient water concentrations in comparison to the translation.

For assessment of concentrations in fish tissue, resources may typically be unavailable to collect an adequate number of replicate composite samples to support rigorous statistical testing, especially where it is desirable to evaluate each individual target species separately. In these situations, states should make direct comparisons between composite sample concentrations and the criterion, as each composite effectively represents the average concentration observed in several fish.

Statistical tests for comparing the average concentration from multiple replicate composite samples to the criterion may be conducted where a sufficient number of replicates have been collected. EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*, volume 1 (USEPA 2000c), at section 6.1.2.7.2, recommends using the t-test to determine whether the mean concentration of mercury in composite fish tissue samples exceeds the screening value. This test involves a statistical comparison of the mean of all fish tissue data to the criterion. States and authorized tribes can evaluate whether the t-test statistic of the mean exceeds the water quality standards. This procedure could also be used to determine impairment, provided it is consistent with a state's water quality standards. States and authorized tribes might also want to consider the guidance in appendixes C and D of the *Consolidated Assessment and Listing Methodology: Toward a Compendium of Best Practices* (USEPA 2002e). Ultimately, the method that states and authorized tribes choose depends on how they express their water quality standards and apply their water quality assessment methodology.

#### 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

<sup>&</sup>lt;sup>15</sup> See EPA's guidance for Integrated Reports described at http://www.epa.gov/owow/tmdl/2006IRG/.

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 is no need to mathematically compute an average. Second, the newer analytical methods 1630 and 1631 can quantify mercury at 0.002 mg/kg, which should be lower than the observed mercury in most fish tissue samples being analyzed.

If, however, a state or authorized tribe is mathematically computing an average of a data set that includes 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). The 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 the 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 authorized 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 2001h).

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 by first using the value of the detection level to quantify samples below the detection level and then using a zero value for samples below the detection level. If both calculated means are 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 level 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 2001h) 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. Again, the selected methodology must be consistent with the state's water quality standards and their published assessment method.

#### 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 could perform 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 5 and equation 4.

Table 5. 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 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 have been 0.18 mg/kg and would have given more weight to the methylmercury concentrations in brown bullhead than to 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:

$$C_{\text{avg}} = \underbrace{3.8 * C_2 + 8.0 * C_3 + 5.7 * C_4}_{(3.8 + 8.0 + 5.7)} = 0.23 \text{ mg/kg}$$
 (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 fish<sup>16</sup>). As noted throughout this document, however, the consumption pattern of the target population should be used if available.

If fish tissue concentration 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 tissue concentration data for trophic level 2 fish in the previous example, equation 5 shows the revised calculation:

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

This revised calculation preserves the relative contribution of each trophic level to consumption patterns. This approach (i.e., dropping a trophic level from Equation 4), however, should not be used if there are no fish tissue data for trophic level 4 fish. Since level 4 fish are the type of fish that people most often consume, dropping trophic level 4 from Equation 4 may result in underprotection if trophic level 4 fish are actually consumed at the site. 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 state or tribe may drop trophic level 4 from Equation 4.

If the state or authorized tribe has developed a site-specific fish consumption rate for the criterion, the state or authorized tribe should incorporate this site-specific rate into equation 4. 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 is representative of the risk considerations of the state. Regression models

<sup>&</sup>lt;sup>16</sup> The values for each trophic level are the same as those discussed in section 3.2.1.2; they can be found in *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000b).

have been developed for this purpose (Rae 1997; Wente 2003). 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 to be lognormally 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 for Mercury in Fish Tissue in various analyses (USEPA 2005a). This model is a statistical model related to covariance, and it 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. The 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 or category 5 of the Integrated Report, 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 past five years, as recommended in section 4.2.4. Such recent information might not always be available, however, and the available data often includes mercury samples collected and analyzed several years in the past. When the state or authorized tribe evaluates this information, it should take into account the reliability of this information and its compliance with applicable data collection or quality assurance/quality control program requirements.

## 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 2000j). 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 or in an Integrated Report, EPA considers a fish consumption advisory and the supporting data existing and readily available data and information.

When listing waters under CWA sections 303(d) or in the Integrated Reporting format on the basis of a fish advisory for a migratory fish species, the state or authorized tribe should include the waters the migratory fish are known to inhabit because those are the waters where the fish potentially would be 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 inclusion is appropriate.

A state or authorized tribe should include on its section 303(d) list or in its Integrated Report, at a minimum, those waters for which waterbody-specific data that were the basis of a fish or shellfish consumption advisory demonstrate nonattainment of water quality standards. EPA believes that a fish or shellfish advisory demonstrates 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.<sup>17</sup>

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 not to 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 exceedance and that the waterbody should be placed on the 303(d) list or in the Integrated Report. In contrast, if this same state or authorized tribe finds the level of mercury in fish in another waterbody is at a level at which it would advise people to eat no more than three 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 might not need to be listed.

<sup>&</sup>lt;sup>17</sup> 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.

#### 5 Other Water Quality Standards Issues

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

The 2001 recommended methylmercury fish tissue criterion and EPA's recommendations for its implementation do not supersede the requirements applicable to the Great Lakes at 40 CFR part 132. The Great Lakes regulatory requirements, known as the Great Lakes Initiative, or GLI, apply to all the streams, rivers, lakes and other bodies of water within the U.S. portion of the Great Lakes drainage basin. For those waters, a state or authorized tribe must adopt requirements (including water quality criteria) that are consistent with (as protective as) regulations EPA promulgated on March 23, 1995. See 60 FR 15366 and 40 CFR 132.1(b) and 132.4.

Under these regulations, if a state or authorized tribe adopts a fish tissue residue methylmercury criterion for the protection of human health, EPA, in its review of the new state or tribal criterion, must determine whether it is as protective as the mercury water column criterion for human health protection promulgated at 40 CFR 132.6, table 3, and whether all implementation procedures are as protective as the implementation procedure. See 40 CFR 132.5(g).

As described below, it is unlikely that adoption of EPA's 2001 recommended methylmercury fish tissue-based criterion of 0.3 mg/kg to protect human health would result in TMDLs or NPDES permit limits addressing mercury impairments in the Great Lakes basin less stringent than those that would be required under the existing GLI regulations. The reasons for this include the following:

- The GLI requires all states and authorized tribes to adopt the GLI wildlife water column criterion. The GLI wildlife criterion has a significantly more stringent methylmercury fish tissue basis than either the 2001 criterion or the GLI human health criteria and would therefore likely be the controlling basis for any TMDLs or NPDES permit limits addressing mercury pollution.
- Even if that were not the case, the 2001 criterion is more stringent than the methylmercury fish tissue basis for the GLI human health water column criteria for mercury.

Furthermore, using the 2001 fish tissue criterion would not necessarily result in lower transaction costs than the GLI. The GLI implementation procedures (e.g., the mixing zone prohibition, 40 CFR part 132, appendix F, procedure 3) require the use of water column criteria, so the 2001 methylmercury fish tissue criterion would need to be converted to a water column criterion following the GLI site-specific modification procedures before it could be approved by EPA and implemented using other GLI implementation procedures.

The human health criterion for mercury established by the GLI is 3.1 ng/L<sup>18</sup>. This water column criterion for mercury is equivalent to a methylmercury fish tissue residue value of 0.35 mg/kg using the Great Lakes-specific BAFs for mercury—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). Because EPA's 2001 methylmercury criterion (0.30 mg/kg) is more stringent than the GLI fish tissue residue value, the 2001 criterion would result in more stringent water column concentrations than the GLI human health criteria unless other, site-specific factors were significantly less stringent. This could occur, for example, if a state or authorized tribe applied the GLI site-specific modification procedures and found that the current, local BAF is significantly lower than the one used to develop the GLI criterion. In that case, the state or tribe could use the lower, local BAF and EPA's recommended fish tissue-based criterion to recalculate the water column criterion using the GLI site-specific modification procedures and submit it to EPA for review and approval. If the site-specific water column criterion was approved by EPA, the state or authorized tribe could use it and the GLI implementation procedures to develop TMDLs and NPDES permits.

Finally, as indicated above, if a state or authorized tribe were to adopt the 2001 human health criterion in the Great Lakes basin, this action most likely would not result in a change to TMDLs or NPDES permits. The GLI also includes a 1.3 ng/L criterion for the protection of wildlife, and in most instances, this more stringent criterion will 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 the 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 National Toxics Rule (40 CFR 131.36) and the California Toxics Rule, or CTR (40 CFR 131.38). 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).

 $<sup>^{18}</sup>$  EPA promulgated the GLI human health criteria of 1.8 ng/L in 40 CFR part 132, table 3, in March 1995, based on an RfD of 0.06 μg/kg/d. In May 1995 EPA revised the RfD to the current 0.1 μg/kg/d, which would result in GLI criteria of 3.1 ng/L. In October 1996 EPA issued guidance indicating that the 3.1 ng/L criteria were considered as protective as the promulgated 1.8 ng/L.

#### 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 may be 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 and fully protect the designated use of the waterbody as a whole. 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 for later application to NPDES point source 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 the water column and food over the life of the fish, and thus it 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.

Some states and authorized tribes, however, might choose to adopt a water column criterion based on the fish tissue criterion and thus have a criterion for which a mixing zone might apply. In this situation, a state or authorized tribe should follow its existing procedures for determining appropriate mixing zones. EPA advises caution in the use of mixing zones for mercury. While fish tissue contamination tends to be a far field problem affecting entire waterbodies, rather than a narrow scale problem confined to mixing zones, EPA's guidance recommends restricting or eliminating mixing zones for bioaccumulative pollutants such as mercury so that they do not encroach on areas often used for fish harvesting (particularly for stationary species such as shellfish). Restriction or elimination might also be used to compensate for uncertainties regarding the ability of aquatic life or the aquatic system to tolerate excursions above the criteria, uncertainties inherent in estimating bioaccumulation, or uncertainties in the assimilative capacity of the waterbody. See the *Water Quality Standards Handbook*, section 5.1.3 (USEPA 1994).

# 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). The 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.

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 therefore they 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 tribe would have determined a site-specific BAF in this process and therefore would 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 whether they are as protective as the Great Lakes procedures for human health protection (40 CFR 132.5(g)(3)). Specifically, EPA would determine whether 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 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 state and tribal Fish Advisory Programs?

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 for 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*, volumes 1 and 2 (USEPA 2000c, 2000f). This guidance describes the two main equations necessary to derive meal consumption limits on the basis of the methylmercury RfD. Basically, the first equation is used to calculate the daily consumption limits of grams of edible fish (in g/day); 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.

In the absence of site-specific fish consumption data, EPA recommends using a fish consumption rate of 17.5 grams/day of fish (uncooked) eaten from the local water as a screening level. 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 ([0.001 mg/kg-day x 70 kg bw]/0.0175 kg fish/day). This means that you can safely consume approximately two 8-ounce meals per month of locally-caught fish, where concentrations in such fish are 0.4 mg/kg or lower, and where there is no additional exposure (i.e., consumption of store bought or marine-caught fish).

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 (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 the fish advisory default screening value for mercury is that the criterion includes an RSC <sup>19</sup> and the screening value does not. In deriving the criterion, EPA assumed an RSC value of  $2.7 \times 10^{-5}$  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 those from noncommercially caught fish, but the guidance may be applied without using an RSC. The RSC guidance in the 2000 Human Health Methodology (USEPA 2000b) 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 assessing criterion attainment and issuance of a fish consumption advisory?

In many states and authorized tribes, numeric water quality criteria and fish and shellfish consumption limits differ because of inherent differences in the technical and risk assumptions used to develop them. 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 in which the presence of an advisory might not imply an exceedance of the water quality standard (USEPA 2005f) 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 might not demonstrate that a CWA section 101(a) "fishable" use is not being attained in an individual waterbody and might not be appropriate for determining attainment based on exceedance of water quality criteria.
- Local advisory. States have issued local advisories using a higher fish consumption value than that which they use in establishing water quality criteria for protection of human health. Again, in this case the fish consumption advisories might not

<sup>&</sup>lt;sup>19</sup> See discussion on the RSC in section 3.1.2.3 and 3.2.1.1.

demonstrate that a section 101(a) "fishable" use is not being attained in an individual waterbody and might not be as appropriate as comparison with 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 8-ounce 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 four 8-ounce meals a month. In this case, because the fish consumption advisory uses a higher fish consumption value than that 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 2005f).

In the case where a local advisory is based on a higher fish consumption value which is considered representative of local consumption, 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 and may reflect local fish consumption patterns, and it might identify more representative fish species. The information gathered in developing the advisory might 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 fish advisory studies and the recommended 304(a) criterion for mercury are based on similar methodologies and are intended to protect people who consume 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. However, recognizing that differences in consumption advisories and waterbody impairment for the methylmercury criterion can be confusing to the public, states may wish to consider explaining the differences in the information that these two types of listings provide. 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 fish tissue and fish consumption data that are representative and of acceptable quality. Alternatively, states may wish to consider issuing a fish consumption advisory, where appropriate, if a waterbody is considered impaired based on the methylmercury 304(a) criterion and no such consumption warning exists.

#### 5.4.6 What federal agencies issue advisories?

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; it does not include food that is caught locally by recreational or subsistence fishers. FDA also issues fish consumption advice on fish and shellfish sold in commerce in cases where contaminants have been detected at levels that may pose public health concerns for some consumers.

As described in section 5.4.2, EPA provides guidance to states, tribes, local governments and others on scientifically sound, cost-effective methods for developing and managing noncommercial fish consumption advisories on local waters. See EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA 2000c, 2000f). In addition, EPA has issued advice under CWA section 104(b)(6) to supplement state and/or tribal advice on local waters.

In March 2004, EPA and FDA issued a joint national fish advisory about mercury in fish and shellfish. The purpose of the advisory is to inform women who may become pregnant, pregnant women, nursing mothers, and parents of young children how to get the positive health benefits from eating fish and be confident that they have reduced their exposure to the harmful effects of mercury. The 2004 advisory lists fish sold in interstate commerce that are known to be high in mercury as well as fish that that are low in mercury to help consumers choose the most appropriate fish. The advisory also contains recommendations about eating fish harvested from local waters where no advice has been provided by state or tribal authorities. Information regarding the national advisory is at http://www.epa.gov/waterscience/fish/.

#### 5.4.7 How is the criterion related to FDA action levels?

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 members of the general population who consume fish and shellfish typically purchased in supermarkets or fish markets that sell products 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 or tribe'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 rely heavily on 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?

CWA section 303(d)(1) and EPA's implementing regulations require states and authorized tribes to identify and establish priority rankings 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 the 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 the 2008 303(d) listing cycle, 43 states and Puerto Rico reported at least one waterbody as impaired due to mercury, and more than 8,800 specific waterbodies were listed as impaired due to mercury, either solely or in combination with other pollutants. As mentioned previously in section 2.4, with the implementation of the new methylmercury fish tissue criterion, monitoring of previously unmonitored waterbodies, and use of more sensitive analytical methods, EPA expects that the number of waterbodies listed as impaired due to mercury might increase.

## **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 past metalmining activity 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 and the 303(d) listing process to provide a basis for reducing mercury releases to water, including consideration of air deposition, to meet applicable

water quality standards and CWA 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. As of April 2010, mercury TMDLs have been approved for more than 6,700 waterbodies, including a "statewide" mercury TMDL in Minnesota and a multi-state mercury TMDL for the Northeast states (see below).

On March 8, 2007, EPA issued a memorandum describing a voluntary approach for listing waters impaired by atmospheric mercury under CWA section 303(d) and managing the development of mercury TMDLs. (USEPA 2007) (http://www.epa.gov/owow/tmdl/mercury5m/Mercury5m.pdf). EPA recommends this approach for states that have in place a comprehensive statewide mercury reduction program with elements recommended by EPA. These states may separate their waters impaired by mercury predominantly from atmospheric sources in a subcategory of their impaired waters list ("5m") and defer the development of TMDLs for those waters. A state using the 5m subcategory may continue to defer the development of mercury TMDLs where the state demonstrates continuing progress in reducing in-state mercury sources. Recommended elements of a mercury reduction program include identification of air and multimedia sources within a state and programs to address those sources; mercury reduction goals and target dates; multimedia monitoring; public reporting on the state's mercury reduction efforts; and multistate coordination. The 5m subcategory is intended to recognize states with comprehensive mercury programs and to allow states to focus on early implementation actions.

Because the 5m subcategory is focused primarily on waterbodies impaired by mercury from air deposition, EPA recommends that the 5m subcategory include waters where the proportion of mercury from air deposition is high compared to other mercury sources. In the 5m memorandum, EPA recommends that states describe how such waterbodies were identified. Such information will help determine whether the 5m approach is appropriate. EPA also believes that, as the relative contribution to a waterbody from sources other than air deposition increases, such as water point sources, it may be more appropriate to use the TMDL process to characterize and address those sources sooner, rather than deferring TMDL development. As stated in the 5m memorandum, states have the option to continue developing mercury TMDLs sooner, whether or not they place waterbodies in subcategory 5m.

On September 29, 2008, EPA issued a document titled *Elements of Mercury TMDLs Where Mercury Loadings Are Predominantly from Air Deposition*, to assist states, EPA regional staff, and other stakeholders in identifying approaches for the development of mercury TMDLs (USEPA 2008a). Compiled in a checklist format, approaches described in the document are drawn largely from approaches and best practices used in approved mercury TMDLs. The checklist summarizes considerations in addressing the required and recommended TMDL elements described in the *Guidelines for Reviewing TMDLs under Existing Regulations Issued in 1992* (USEPA 2002f) when developing mercury TMDLs on geographic scales ranging from waterbody-specific to multi-state.

While the checklist is based on existing guidance for reviewing TMDLs, this guidance document supplements the checklist by providing additional information and case studies on approaches that have been used in approved mercury TMDLs to date, and examples of

technical tools available to assist in mercury TMDL development. 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.

EPA recommends that states continue to develop TMDLs for mercury-impaired waters where appropriate, taking into account the considerations and approaches described in this guidance. States may also consider using the 5m subcategory for waters impaired by mercury predominantly from air deposition if the state has a comprehensive mercury reduction program as described in the 5m memorandum.

#### 6.2.1 What geographic scales have been used for mercury TMDLs?

Many mercury TMDLs approved to date were developed on a waterbody-specific basis. They include some of the first approved mercury TMDLs, such as those developed for waterbodies in middle and south Georgia. Other examples include TMDLs developed for waterbodies in Louisiana, such as the Ouachita River, the Narraguinnup and McPhee reservoirs in Colorado, and Pena Blanca and Arivaca lakes in Arizona. Various aspects of these TMDLs are described further in appendix D.

In areas of the country where many waterbodies are listed as impaired due to mercury primarily from atmospheric sources, some states have begun to explore the development of mercury TMDLs on a watershed scale or on the basis of a large geographic area, such as a state or region. 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. Because of the large geographic extent of mercury in the coastal waters and the similar extent of mercury contributions from air deposition, the TMDL was developed on a watershed basis rather than waterbody by waterbody. The TMDL used air deposition modeling results from the Regional Modeling System for Aerosols and Deposition (REMSAD) to estimate wet and dry deposition of mercury for the six segments. The 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 that is subsequently transported to the waterbody via runoff and erosion. Additional information on this TMDL can be found on EPA's TMDL webpage at http://iaspub.epa.gov/tmdl/waters list.tmdl report?p tmdl id=11642.

A "statewide" mercury TMDL developed by Minnesota was approved by EPA on March 27, 2007. The TMDL report covers 998 mercury impairments and is the first approved mercury TMDL covering such a large number of waterbodies and large geographic area. (Note: Although called statewide, the TMDL does not cover all mercury-impaired waterbodies in the state.) Minnesota used a statewide approach because the predominant mercury source in those waterbodies—air deposition—is relatively uniform across the state. The final TMDL report includes two TMDLs—one for the northeast region of the state and the other for the southwest region of the state. Waterbodies were grouped into the two regions on the basis of differences in fish tissue concentrations, with higher fish mercury concentrations in the northeast region compared to the southwest region. The difference in mercury concentrations is thought to be due to the effect of land use and other factors on the methylation of mercury. For example, the

northeast region is dominated by wetlands, where mercury tends to be methylated more readily; the southwest is dominated by cultivated lands. A summary of the Minnesota mercury TMDL approach is provided in appendix D, and the allocation approach is described further below. The final TMDL and EPA decision document are at <a href="http://www.pca.state.mn.us/water/tmdl/tmdl-ercuryplan.html#approval.">http://www.pca.state.mn.us/water/tmdl/tmdl-ercuryplan.html#approval.</a>

On December 20, 2007, EPA approved the Northeast Regional Mercury TMDL covering waterbodies in Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island and Vermont. In using a regional approach, the TMDL document provides aggregate wasteload allocations and load allocations for the region. The regional approach was based on an analysis of data showing similar levels of mercury in fish throughout waterbodies in the region, and the states' finding that air deposition is the predominant mercury source. The TMDL document focuses on waters impaired by mercury primarily from atmospheric sources; it excludes coastal and marine waters and a few areas of high localized deposition and high fish mercury levels. The number of individual waterbodies covered by the regional TMDL document amounts to over 5,300 (the specific number of waterbodies covered by the TMDL document vary from state to state and are cited in EPA's approval documents). The TMDL target is EPA's recommended fish tissue criterion of 0.3 ppm methylmercury for each of the states except for Connecticut and Maine, where the targets are 0.1 ppm and 0.2 ppm, respectively. The TMDL allocates approximately 2.0 percent of the loading capacity to point sources and 98 percent to nonpoint sources (predominantly atmospheric deposition). The TMDL assumes that most of the reductions would need to come from atmospheric sources. The Northeast Regional Mercury TMDL are at http://www.epa.gov/region1/eco/tmdl/assets/pdfs/ne/Northeast-Regional-Mercury-TMDL.pdf, and the EPA approval documents for each of the states are at http://www.epa.gov/region1/eco/tmdl/approved.html.

#### 6.2.2 What are the 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 (40 CFR 130.2(i)). EPA guidance further notes that a TMDL should identify the pollutant sources, both point and nonpoint, including the location of the sources and quantity of the loading. Where feasible, states are encouraged to consider waterbodies affecting disadvantaged communities and tribal issues in setting priorities for TMDL development. Some of the considerations in developing a mercury TMDL and approaches used in approved mercury TMDLs are described in more detail in the text below.

#### 6.2.2.1 What are potential mercury sources to waterbodies?

An important step in TMDL development is an evaluation of the loadings from various sources. The potential sources of mercury to waterbodies include the following: (1) direct discharges of mercury from water point sources, including industrial dischargers and wastewater treatment plants; (2) 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, including via stormwater; (3) 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; (4) sediments, which might have mercury contamination or hot spots resulting from past discharges; and (5) "naturally occurring" mercury in soils and geologic materials. Sediments containing mercury from past discharges might continue to contribute mercury to the overlying waterbody. Further discussion of each of these types of sources follows.

**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, as well as a study of domestic mercury sources by the Association of Metropolitan Sewerage Agencies (AMSA 2000), now called the National Association of Clean Water Agencies (NACWA). 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. NPDES-permitted stormwater sources might also include mercury discharges, which in turn might include mercury originating from atmospheric deposition.

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 their total loading from atmospheric deposition, either directly or indirectly via runoff and erosion. (See Ochlockonee, Georgia, TMDL in appendix D.) The mercury in atmospheric deposition originates from anthropogenic sources, including U.S. and international sources, as well as natural sources. Examples of specific anthropogenic sources that emit mercury to the air include medical and municipal waste incinerators, electric utilities, chlor-alkali plants, and active metals mining, among others.

Mercury is emitted to the air in several chemical forms or species. Common measurements of mercury in air differentiate between reactive gaseous mercury (RGM), elemental mercury (Hg<sup>0</sup>), and particulate mercury (Hg<sub>p</sub>). 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 determines 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. It shows that in many parts of the United States, the source of deposited mercury is not a U.S. source.

Of the 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 2005 and shows a 58 percent overall decrease.

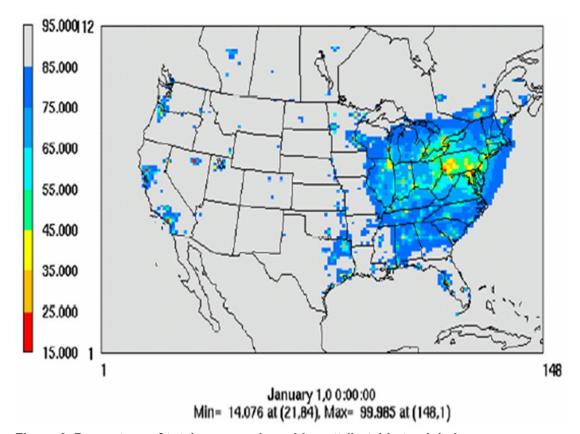
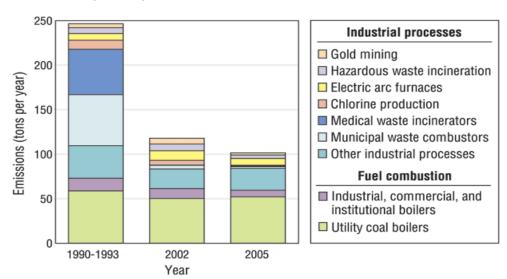


Figure 3. Percentage of total mercury deposition attributable to global sources (USEPA 2005a).



**Exhibit 2-39.** Mercury emissions in the U.S. by source category, 1990-1993, 2002, and 2005<sup>a,b</sup>

Data source: U.S. EPA, 2009

Figure 4. Trends in mercury air emissions between 1990 and 2005 (USEPA 2008b).

Additional decreases in mercury air emissions may have occurred since 2005 as the result of EPA's regulatory efforts under the CAA. At the same time, however, global emissions might have increased.

The 2005 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 those in construction equipment and agricultural equipment), 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 generated using EPA's latest models such as the MOBILE and NONROAD models. More information on the 2005 NEI is at

http://www.epa.gov/ttn/chief/net/2005inventory.html.

<sup>&</sup>lt;sup>a</sup>1990-1993 is considered the baseline period for mercury emissions. The baseline period spans multiple years due to the availability of emissions data for various source categories. The data presented for the baseline period are annual emissions (tons per year) and are therefore comparable to the 2002 and 2005 data.

<sup>&</sup>lt;sup>b</sup>Mercury emissions from mobile sources are not depicted because they have been estimated only for inventory years 2002 (0.8 tons) and 2005 (1.1 tons), not for the baseline period.

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 <a href="http://gaepd.org/Documents/TMDL">http://gaepd.org/Documents/TMDL</a> page.html). 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. To estimate the total contributions from air deposition, data from the Mercury Deposition Network (MDN) were used. Modelers also used the existing Regional Langrangian Model of Air Pollution (RELMAP) deposition results developed for the 1997 Mercury Report to Congress to estimate the relative contributions from local sources within a 100-kilometer airshed.

EPA has evaluated water and air deposition modeling tools as part of two mercury TMDL pilot projects in Wisconsin and Florida. In particular, the pilots examined approaches for combining the results of air deposition and water quality modeling, which in turn might be used in a TMDL context. In the Florida pilot, air modelers used a combination of modeling tools to predict the amount of mercury deposition to the study area from local sources in southern Florida. Using the Mercury Cycling Model, aquatic modelers then used results from the atmospheric modeling and other data to examine how mercury levels in fish might respond to reductions in deposition. The Florida pilot report is complete (see <a href="ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf">ftp://ftp.dep.state.fl.us/pub/labs/assessment/mercury/tmdlreport03.pdf</a>) (Atkeson et al. 2002).

In the Wisconsin pilot project, EPA evaluated modeling tools such as the Regional Modeling System for Aerosols and Deposition (REMSAD) for identifying the sources or categories of sources contributing mercury deposition to a waterbody, as well as how to use the deposition results as input to aquatic models, similar to the approach used in the Florida pilot. REMSAD is a three-dimensional grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (ICF International 2006). REMSAD simulates both wet and dry deposition of mercury. (See appendix E for further information on REMSAD.) In the Wisconsin pilot, the results of the air deposition modeling were used as input to the Mercury Cycling Model to examine how mercury levels in fish might respond to potential changes in deposition.

Other TMDLs in which the results of REMSAD modeling were used include the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana approved in 2005. The results of earlier air modeling for the *Mercury Study Report to Congress* were used in the mercury TMDLs for middle and south Georgia approved in 2002 (see Ochlockonee TMDL in appendix D). EPA 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 develop TMDLs and determine the appropriate strategies for addressing mercury deposition from sources within their jurisdictions.

Additional tools available for determining mercury deposition loadings include the Community Multi-Scale Air Quality (CMAQ) model. 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 with a number of science attributes that are critical for simulating the oxidant precursors and nonlinear chemical relationships associated with mercury formation. Version 4.3 of CMAQ (Bullock and Brehme 2002; Byun and Schere 2006) reflects updates to earlier versions in a number of areas to improve the underlying science and address comments from peer review. Further information on the CMAQ model is provided in appendix E.

As with any analysis based on limited data, uncertainty is inherent 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 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 MDN. Examples of these tools are provided in appendix F. 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 of EPA's Web site at <a href="http://www.epa.gov/oar/oaqps/gr8water/handbook/">http://www.epa.gov/oar/oaqps/gr8water/handbook/</a>.

An analysis of deposition should take into account both direct deposition to the waterbody, as well as mercury deposited within the watershed (indirect deposition). In addition, fires, flooding, and other landscape disturbances could re-mobilize mercury previously deposited within the watershed and cause an increase in mercury transported to the waterbody. Studies are underway to examine the extent to which mercury deposited to a watershed is transported to a waterbody. For example, the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) project is a mercury loading experiment to examine the timing and magnitude of the relationship between mercury loading to ecosystems and mercury concentrations in fish (Harris et al. 2006). Using stable mercury isotopes, researchers are examining the fate of mercury deposited to uplands, wetlands, and directly to lakes. It is being carried out at the Experimental Lakes Area (ELA) in northwestern Ontario by U.S. and Canadian researchers. A discussion of factors affecting mercury transport and bioavailability is included in chapter 2 of this guidance.

As part of a source evaluation, EPA encourages states to conduct a careful analysis to verify and quantify the contributions of air deposition as compared to other sources. Such information is important for determining the appropriate management approaches. For example, an analysis of the contribution from air sources is the basis for determining whether it may be appropriate to defer TMDLs under the 5m approach, or whether it is more appropriate to develop TMDLs to address significant local sources.

Although not required for a TMDL, states may wish to examine the contributions to the watershed from local air sources within the state as compared to out-of-state sources. Such information provides a basis for determining the appropriate allocations. In turn, such source information can help to develop a meaningful TMDL implementation plan and identify the extent to which state and local programs may be appropriate for addressing the mercury sources.

Metals mining activity. Loadings from metals mining activities might reflect 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 such as 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 E), 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 might 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 E.

Sediments. A TMDL analysis should account for any mercury present in sediments as a result of current and past mercury loadings. Mercury in sediments may be the result of past metals mining activity as described above, past industrial activity, and historical air deposition. Data on levels of mercury in sediments are important in determining which sources are most significant, the most appropriate approach for addressing the sources and how long it will take to achieve water quality standards. For example, development of appropriate allocations, and in turn development of management strategies, may need to address both current sources of deposition as well as legacy sources. An examination of past industrial practices in the watershed could include whether sediments might serve as a reservoir for mercury. Various national databases, such as the National Sediments Database (USEPA 2002g) and data collected by USGS might help to identify isolated locations of elevated mercury in sediments. EPA has also developed a detailed guide on sediment source analysis in the first edition of *Protocol for Developing Sediment TMDLs*: http://www.epa.gov/owow/tmdl/sediment/pdf/sediment.pdf.

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 whether loadings from a location were contributing to water quality standards violations
- Screening modeling to identify other potential sources of sediment contamination (see the TMDL at <a href="http://www.epa.gov/waters/tmdldocs/1991">http://www.epa.gov/waters/tmdldocs/1991</a>
   Bellingham%20Bay%20TMDL.pdf)

Other examples of TMDLs involving an analysis of mercury contributions from sediments include the TMDLs for Pena Blanca, Arizona, and the Cache Creek watershed in California (see appendix D). As described in the section on allocations, the Cache Creek watershed TMDL also accounts for methylmercury production in sediments.

Natural or background levels of mercury in soils. Soils and sediments can include mercury of geologic origin or mercury produced by the weathering of geologic materials, together with mercury of anthropogenic origin (mercury emitted over time from human sources and then deposited on soils). Mercury in soils can also re-emit or become resuspended 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.

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

When developing a TMDL, states and authorized 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 typically link models of atmospheric deposition, watershed loading, and mercury cycling with bioaccumulation. For example, a watershed model (e.g., Grid Based Watershed Mercury Model, GBMM) might be linked with a receiving water mercury model (e.g., Water Quality Analysis Simulation Program, WASP) and a bioaccumulation model (e.g., Bioaccumulation and Aquatic Simulator, BASS). These models are described further in appendix E. Linking models together can enable a translation between the endpoint for the TMDL (expressed as a fish tissue concentration of methylmercury) and the mercury loads to the water without having explicit water column criteria or translations. The analysis determines the loading capacity as a mercury loading rate consistent with meeting the endpoint fish tissue concentration. This section describes some of the modeling tools available for use in mercury TMDLs.

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 might 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 the accuracy of predicted future fish concentrations?
- Could other pollution-control activities reduce mercury loads to the waterbody or affect the mercury bioaccumulation rate?
- After regulatory controls are implemented, how long will it take for fish tissue levels to meet the criterion?

Depending on the types of questions states and authorized 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. In addition, models are often used in TMDL analyses but are not required. For more information on the specific models described here, see <a href="http://www.epa.gov/athens">http://www.epa.gov/athens</a> and <a href="http://www.epa.gov/crem">http://www.epa.gov/crem</a>.

#### 6.2.2.2.1 Steady state models and the proportionality approach

Steady state modeling describes the dynamic equilibrium between environmental media established in response to constant loads over the long term. Consequently, complex mercury cycling processes can be compressed into simple equations. One such approach, 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, often referred to as the proportionality approach and explained in detail in the Mercury Maps report (USEPA 2001b), assumes that where air deposition is the sole significant source, factors affecting methylation remain unchanged. As a result, the ratio of current to future fish tissue concentrations can be assumed to equal the ratio of current to future air deposition loads in this situation. Mercury Maps, and the situations in which the proportionality assumption may or may not apply, are described further in appendix E.

A number of mercury TMDLs where air deposition is the predominant mercury source have been developed using an assumption of proportionality between mercury deposition and fish tissue methylmercury concentration. Specifically, such TMDLs have reasoned that a reduction in deposition will result in a proportional reduction in mercury concentrations in fish over time. Such an approach applies to situations where air deposition is the only significant mercury source and relies on steady-state conditions. This approach may also be used to estimate the reductions needed to meet a fish tissue target without necessarily calculating a water column target.

Mercury TMDLs which applied a proportional relationship between reductions in deposition and reductions in fish tissue methylmercury concentration include TMDLs for waterbodies in Louisiana, such as the Ouachita Basin (FTN 2002), the Mermentau and Vermillion-Teche River Basins (USEPA 2001i, 2001j) and the Coastal Bays and Gulf Waters of Louisiana (Parsons 2005). Using the Everglades Mercury Cycling Model, the pilot mercury TMDL study in the Florida Everglades also reported a linear relationship between mercury deposition and the concentrations of mercury in largemouth bass (Atkeson et al. 2002).

More recently, the Minnesota statewide mercury TMDL applied the proportionality approach. As described in section 6.2.1 above, waterbodies within the state were grouped into two regions, and a TMDL developed for each region. Minnesota calculated a reduction factor for each region, or the percent reduction in total mercury load needed in each region to achieve the fish tissue target of 0.2 mg/kg for the 90th percentile of the standard-length fish (MPCA 2007). Using the proportionality assumption, Minnesota applied the regional reduction factor (51 percent for the southwest region and 65 percent for the northeast region) to the total source loadings to determine the load reduction goal. The Minnesota TMDL explains in further detail the basis for using the proportionality approach.

Mass balance models are somewhat more complex implementations of the steady state approach. In place of a simple ratio, such models describe fluxes of mercury in and out of the model domain (e.g., impaired segment) and, optionally, balance fluxes (e.g., methylation and demethylation) within the model domain. The advantage provided by this approach is that individual fate processes 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 a watershed and waterbody remain unchanged, steady state models can produce as accurate an estimate of the necessary load reductions as a dynamic model, generally with less-intensive data collection and analysis. In addition, such simple approaches might be less prone to calculation error and are much easier for the public to understand.

#### 6.2.2.2.2 Continuous-simulation and dynamic models

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

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 2000g) simulated the amount of time necessary to attain equilibrium in response to reduced mercury loads using the Everglades Mercury Cycling Model. The model results predicted that sediments would continue to supply as much as 5 percent of the mercury load 100 years after air deposition reductions occurred. The Dynamic Mercury Cycling Model (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 D) (Tetra Tech 2001).

The SERAFM model incorporates more recent advances in scientific understanding and implements an updated set of the IEM-2M solids and mercury fate algorithms described in the 1997 *Mercury Study Report to Congress* (USEPA 1997c).

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.

#### 6.2.2.2.3 Spatially detailed models

Spatially detailed models, such as that used in the Savannah River mercury TMDL (USEPA 2001j), 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 Water Quality Analysis Simulation Program (WASP) model. WASP is a dynamic, mass balance framework for modeling contaminant fate and transport in surface water systems. The model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. Another model that has been used for mercury TMDLs is the EPA Region 4 Watershed Characterization System (WCS). WCS is a geographic information system (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 a 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 occurs predominantly through soil erosion, erosion control might be identified as a useful nonpoint source control on mercury to waterbodies (Balogh et al. 1998). As another example, controls on acid deposition and, thus, changes in lake pH and their effect on fish tissue mercury concentrations can also be modeled (Gilmour and Henry 1991, Hrabik and Watras 2002). Finally, spatially detailed landscape models hypothetically could be used to reflect the local effects of wetlands and their impacts on mercury methylation rates.

#### 6.2.2.2.4 Regression models

In general, a regression model is a statistical model describing how a parameter, such as mercury levels in fish, is related to one or more variables. Regression models provide only approximations of real trends.

One example of a regression model for mercury is the regression-based model under development for New England. The model, known as MERGANSER (Mercury Geospatial Assessments for the New England Region), is being developed by EPA and several partners. The partners include USGS, the Biodiversity Research Institute, the State of Vermont, the Clean Air Association of the Northeast States, and the New England Interstate Water Pollution Control Commission. The model will integrate recent atmospheric mercury-deposition models with many databases on mercury sources, mercury levels in fish and bird tissue, and ecosystem features that might be associated with the risk of mercury contamination in biota and, ultimately, humans.

The intent of the project is to identify, by using regression modeling, explanatory variables that contribute to elevated mercury levels in fish and wildlife in New England. The model can then be applied in a predictive mode to lakes throughout New England

that have no mercury fish tissue or loon blood data. Specifically, the model will (1) identify watershed and other factors associated with high mercury levels in fish and wildlife; (2) identify likely sources of mercury; (3) provide estimates of mercury levels in fish and wildlife at any lake or stream in New England; (4) provide estimates of mercury reductions needed from air deposition to meet water-quality criteria; and (5) identify optimal locations for long-term monitoring. Modeling will be done within a GIS environment so that the spatial distribution of data is retained and results can be displayed watershed by watershed. Maps from MERGANSER will show the areas in New England that are susceptible to high mercury levels in biota and that are, therefore, areas where human health impacts (through fish consumption) and ecological impacts (bird tissue mercury levels) are potentially occurring. In addition, the model can be used to produce maps that identify mercury sources and show the relative magnitude of mercury loading from those sources.

#### 6.2.2.2.5 Model selection

When selecting a model, a state or authorized tribe should be aware of the assumptions inherent in each type of model and consider the potential effects of those assumptions on relationships between loadings and fish tissue levels or water quality. The first consideration for model assumptions is methylation. Several factors, including pH, redox, potential sulfate concentrations, temperature, dissolved organic carbon (DOC) concentrations, salinity, and microbial populations, influence the speciation of mercury (Ullrich et al. 2001). If these factors fluctuate seasonally around an average condition, a waterbody could be at a dynamic equilibrium and the steady state assumption would still apply over the long term. If these factors change over time such that they might have a significant impact on fish tissue concentrations, the equilibrium assumptions inherent in steady state modeling might not hold, and a dynamic model like 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 non-equilibrium state.

The second consideration for model assumptions is the BAF. As discussed in section 3.1.3.1, 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 because of 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 for model assumptions 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.

#### 6.2.2.2.6 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 an 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., sulfate, 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 scales.

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.

#### 6.2.2.3 What are the allocation approaches in mercury TMDLs?

A requirement for an approvable TMDL is that the state or authorized tribe allocate the pollutant load necessary to achieve water quality standards among point and nonpoint sources. EPA's regulations, however, leave the decision regarding how to allocate loadings to the state or authorized tribe developing the TMDL. States and authorized tribes have discretion in selecting a 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 might 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 and allocation scenarios have occurred in mercury TMDLs, each with a different mix of point and nonpoint sources. The scenarios have ranged from situations where mercury loadings are predominantly from air deposition, with small loadings from point sources or other sources, to situations where mercury loadings are predominantly from past mining activity. In addition, allocation approaches in mercury TMDLs have included allocations to individual sources as well as allocations to sectors and regions where appropriate. Examples of scenarios involving different source mixes and allocation approaches in approved mercury TMDLs are provided below.

### Mercury loadings predominantly from air deposition, with very small loadings from point sources or other sources

Contributions from air deposition, such as direct deposition to the waterbody and deposition to the watershed transported to the waterbody by runoff and erosion, are typically included as part of the load allocation. As discussed in EPA guidance on reviewing TMDLs, allocations for nonpoint sources may range from reasonably accurate estimates to gross allotments (USEPA 2002f). TMDLs where air deposition is the predominant mercury source have usually allocated only a small portion of the reductions to the point sources or wasteload allocation, as described in the examples below. Many mercury TMDLs have included an allocation to air deposition as a whole; in some mercury TMDLs, the contributions from air deposition are further allocated to within-state and out-of-state sources, and contributions from anthropogenic and natural contributions are distinguished.

The Savannah River mercury TMDL is one of the first examples of an approach to allocating loadings where the predominant mercury source is atmospheric deposition. Many of the TMDLs developed to date are for situations where air deposition is the predominant mercury source. The Savannah River mercury TMDL indicated that NPDES point sources contribute 1 percent of the mercury loadings, while atmospheric deposition contributes 99 percent of the loadings. The TMDL identified only one point source on the Georgia side of the river that has a permit to discharge mercury to the Savannah River. It identified 28 point sources in Georgia that might have the potential to discharge larger amounts of mercury in their effluent according to the nature of the discharge or the mercury levels that have been found in their effluents above the water quality standard level.

The Savannah River mercury TMDL assigned 99 percent of the load reductions to the air sources and 1 percent of the reductions to point sources. The TMDL provides specific wasteload allocations for these 28 sources on the basis of meeting the water quality criterion at the end of a pipe or, alternatively, implementing a pollutant minimization program. In addition, the TMDL identifies about 50 other point sources expected, on the basis of their size and nature, to discharge mercury at levels 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 their holding their effluents at current levels. The wasteload allocations for these point sources are expressed in the TMDL as a sum or aggregate allocation.

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. EPA believes, however, that the decisions, policies, and interpretations set forth in the TMDL are still valid and provide an example of a possible approach to mercury TMDLs. The Savannah River mercury TMDL is at <a href="http://www.gaepd.org/Files\_PDF/techguide/wpb/TMDL/Savannah/EPA\_Savannah\_River\_Watershed\_Hg\_TMDL.pdf">http://www.gaepd.org/Files\_PDF/techguide/wpb/TMDL/Savannah\_River\_Watershed\_Hg\_TMDL.pdf</a>.

The series of mercury TMDLs issued February 28, 2002, for watersheds in middle and south Georgia, such as the Ochlockonee watershed, also illustrate the first scenario. In

these basins, point source loadings contribute very little to the mercury loadings (the 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.

The Ochlockonee mercury TMDL assigns most of the load reductions to the air sources, with a load allocation of 1.16 kg/yr and a wasteload allocation of 0.06 kg/yr. Although point sources collectively contribute a very minute share of the mercury load, the Ochlockonee and other mercury TMDLs for middle and south Georgia include 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 TMDL was written so that all NPDES-permitted facilities would achieve the wasteload allocation through discharging mercury at concentrations below the applicable water quality standard or through implementing a pollutant minimization program. A summary of the Ochlockonee mercury TMDL is provided in appendix D and is at <a href="http://gaepd.org/Files\_PDF/techguide/wpb/TMDL/Ochlockonee/EPA\_Ochlockonee\_River\_Hg\_TMDL.pdf">http://gaepd.org/Files\_PDF/techguide/wpb/TMDL/Ochlockonee/EPA\_Ochlockonee\_River\_Hg\_TMDL.pdf</a>.

The Minnesota "statewide" mercury TMDL document takes a regional approach to allocations, providing a single wasteload allocation and a single load allocation that applies to each region rather than to individual waterbodies. The TMDL document indicates that such a regional allocation serves as a regional "cap." The predominant source is atmospheric deposition, with a small contribution (about 1.2 percent of the total source load for both regions combined) from point sources. The wasteload allocation is set at 1 percent of the TMDL or the 1990 baseline load, whichever is lower, with the remainder allocated to nonpoint sources. Point sources, including NPDES-permitted stormwater sources, municipal treatment facilities, and industrial dischargers that impact the waterbodies covered by the TMDL, are subject to the wasteload allocation. For the load allocation, the Minnesota TMDL estimates the contributions to air deposition from within-state and out-of state sources, as well as from global sources and anthropogenic sources. A summary of the Minnesota mercury TMDL is included in appendix D. The TMDL and related documents can be found at <a href="http://www.pca.state.mn.us/water/tmdl/tmdl-mercuryplan.html">http://www.pca.state.mn.us/water/tmdl/tmdl-mercuryplan.html</a>.

### Mercury loadings predominantly from past mining activity, with small or no contributions from atmospheric deposition and/or NPDES point source contributions

One example of a TMDL for this scenario is the Cache Creek Watershed TMDL. Cache Creek is a tributary to the Sacramento-San Joaquin Delta in California. Sources of mercury entering the Cache Creek watershed include leaching from waste rock and tailings from historical mercury and gold mines, erosion of naturally mercury-enriched soils, geothermal springs, and atmospheric deposition. There are multiple inactive mercury and gold mines in the Cache Creek watershed and no NPDES-permitted discharges. Methylmercury is also produced *in situ* in the streambed of Cache Creek. The TMDL analysis provides load allocations for Cache Creek, as well as each of the tributaries. For each waterbody, load reductions are provided for both methylmercury and total mercury. Allocations are expressed as a percentage of the existing methylmercury

loads. Estimated atmospheric contributions of mercury, from direct deposition and runoff after deposition, are very small compared to loads of mercury from mine sites or erosion of the stream bed and banks, and thus no allocations are made to air deposition. Reducing the methylmercury loads will require a multifaceted approach that includes controlling inorganic mercury loads and limiting the entry of inorganic mercury into sites with high rates of methylmercury production. The Cache Creek watershed mercury TMDL and the allocation approach are summarized further in appendix D.

## Mercury loadings from a combination of different sources, including atmospheric deposition, past mining, and point sources

The Mercury TMDL for the Willamette Basin, Oregon, identifies atmospheric deposition (direct plus indirect deposition: 47.7 percent) and erosion of mercury-containing soils (47.8 percent) as the top sources, along with small contributions from legacy mining (0.6 percent) and NPDES-permitted point sources (3.9 percent). The point source loadings consist of 2.7 percent from POTWs and 1.2 percent from industrial discharges. The TMDL assigns interim allocations to each of the source categories or sectors, rather than individual sources, based on the considerable uncertainty in the loading estimates and other factors. The TMDL specifies an across-the-board reduction of 27 percent in each source. After the 27 percent reduction to each source, the allocations for the Willamette mainstem are approximately similar to their relative contribution to the total loadings: 44.7 kg/yr for air deposition, 44.8 kg/yr for erosion, 0.6 kg/yr for legacy mine discharges, 2.6 kg/yr for POTWs, 1.1 kg/yr for industrial discharges, and 0.8 kg/yr for reserved capacity. Allocations are also provided for other waterbodies in the basin. The TMDL is at <a href="http://www.deq.state.or.us/wq/tmdls/docs/willamettebasin/willamette/chpt3mercury.pdf">http://www.deq.state.or.us/wq/tmdls/docs/willamettebasin/willamette/chpt3mercury.pdf</a>.

### Mercury loadings from point sources predominate or are not insignificant compared to other sources

A small number of approved TMDLs have been developed for situations where mercury is primarily or exclusively from point sources, including TMDLs for waterbodies in Colorado. Examples of such TMDLs can be found at <a href="http://iaspub.epa.gov/tmdl">http://iaspub.epa.gov/tmdl</a> waters10/attains impaired waters.control?p state=CO&p pollutant id=693.

### 6.2.2.4 What kinds 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 the criteria-end-of-pipe (i.e., apply the TMDL water quality target to a discharger's effluent at the outfall point).
- Monitor for mercury in the facilities' influent and effluent using more sensitive analytical techniques (e.g., EPA 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.

Other facilities expected to discharge at levels below the water quality target will be expected to verify through monitoring whether or not 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, including an assessment of all mercury sources. (See the TMDL and supporting documents at <a href="http://iaspub.epa.gov/tmdl/waters-list.tmdl">http://iaspub.epa.gov/tmdl/waters-list.tmdl</a> report?p tmdl id=11642.)

TMDLs involving past mining activity have also included follow-up monitoring; examples include three of the TMDLs described in appendix D (Clear Lake, California; Arivaca Lake, Arizona; and Cache Creek, California). The mercury TMDL for Arivaca Lake lists several follow-up actions and monitoring activities, such as 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 <a href="http://www.epa.gov/waters/">http://www.epa.gov/waters/</a> tmdldocs/17.pdf). The Clear Lake, California, mercury TMDL also identifies the need for follow-up monitoring of fish tissue and sediment (see appendix D, and the TMDL at http://www.swrcb.ca.gov/rwqcb5/water issues/tmdl/central valley projects/ clear lake hg/cl final tmdl.pdf. The Cache Creek TMDL indicates that monitoring will be conducted to determine whether mercury loads have been reduced and to measure progress toward the TMDL target, as well as to better characterize areas of methylmercury production and mercury loadings from tributaries. Monitoring will include fish tissue, sediment, and water monitoring.

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 on the success of implementation activities are collected. States may refine information on the contributions from sources such as runoff from abandoned mining sites, sediment loading of mercury-laden sediments, and air deposition as data and modeling tools improve. States should consider the application of adaptive implementation in determining load allocations for these sources. Although a monitoring plan is not required in a TMDL, EPA guidance documents recommend using a monitoring plan to track the effectiveness of a TMDL; see *Guidance for Water Quality-Based Decisions: the TMDL Process* (EPA 440/4-91-001). Post-TMDL monitoring is an important tool for evaluating implementation success and, if necessary, refining the TMDL. Follow-up monitoring may include monitoring of water quality, fish tissue, air deposition, and sediments.

### 7 National Pollutant Discharge Elimination System (NPDES) Implementation Procedures

## 7.1 What are the general considerations in NPDES permitting?

Section 301(a) of the CWA prohibits the discharge of any pollutant, including mercury, from a point source into waters of the United States except in compliance with certain enumerated provisions of the CWA, among them section 402. CWA section 402 establishes the NPDES program, under which EPA or states and tribes authorized to administer the program issue permits that allow the discharge of pollutants into waters of the United States, notwithstanding the general prohibition established by section 301(a). 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 water quality-based effluent limitations (WQBELs), when necessary to ensure that the receiving waters achieve applicable water quality standards (see CWA section 301(b)(1)(C)).

Most WQBELs are expressed as numeric limits on the amounts of specified pollutants that may be discharged. However, WQBELs may also be expressed in narrative form such as best management practices (BMPs) or pollutant minimization measures (e.g., practices or procedures that a facility follows to reduce 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 CWA (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" analysis. 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 exceedance of any applicable water quality standard." Thus, if a pollutant discharge has the reasonable potential to cause or contribute to an exceedance 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)(iii)). The procedure specifies only

<sup>&</sup>lt;sup>20</sup> When developing WQBELs, the permitting authority must ensure that the level of water quality achieved by such limits derives from and complies with water quality standards (see 40 CFR 122.44(d)(1)(vii)(A)).

whether a discharge must have a WQBEL; it does not specify the actual permit limits. The NPDES regulations at 40 CFR 122.44(d)(1)(vii) specify that the level of water quality to be achieved by the WQBEL must derive from and comply with water quality standards, as required by CWA section 301(b)(1)(C) (requiring "any more stringent limitation... necessary to meet water quality standards"). This would necessarily be a permit-by-permit determination.

## 7.2 What is the EPA-recommended NPDES permitting approach for methylmercury?

The recommendations below assume that an approved TMDL is not available at the time of permit issuance. If EPA has approved or established a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate), the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)).

EPA believes, depending on the particular facts, that a permit writer may reasonably conclude that limits on point sources consistent with this guidance are likely to be as stringent as necessary to achieve water quality standards. As described in more detail below, the permit writer should conduct a reasonable potential analysis to determine whether a discharger will cause or contribute to the exceedance of applicable water quality standards. Once such a determination is made, limits can be imposed consistent with this guidance. In circumstances where waters are not yet impaired, the permit writer should consider other factors or conditions when determining whether a facility has reasonable potential with the goal of preventing future impairments. (See Sections 7.2.2, 7.5.1.2.2 and 7.5.1.2.3).

### 7.2.1 Developing NPDES permit limits based on the fish tissue criterion

The first component of the recommended NPDES permitting approach for methylmercury is to determine how the methylmercury criterion is expressed in the applicable water quality standard and to determine whether a water column translation of the fish tissue criterion or site-specific data to translate are available at the time of permit issuance. This will inform the selection of the appropriate recommended implementation option. If the methylmercury criterion is expressed as a water column value, the permit writer should develop permit limits based on this criterion according to procedures described in section 5.4.4 of the *Technical Support Document for Water Quality-based Toxics Control*, or TSD (USEPA 1991). If the criterion is expressed as a fish tissue value and a water column translation of the fish tissue criterion or site-specific data to translate are available at the time of permit issuance, the permit limits based on the translated water concentration value should again be developed according to procedures described in section 5.4.4 of the TSD.

If, however, the criterion is expressed as a fish tissue value and a water column translation of the fish tissue criterion or site-specific data to translate are not available at the time of permit issuance, the permitting authority may reasonably conclude that a numeric WQBEL is infeasible to calculate. In that instance, EPA recommends that the permitting authority develop NPDES permit limits based on the criterion using the

procedures described below. Section 7.3 contains additional information about expressing and developing permit limits based on the methylmercury criterion.

#### 7.2.2 Determining reasonable potential

The second component of the recommended NPDES permitting approach for methylmercury is to conduct a reasonable potential analysis to determine whether the discharge will cause or contribute to an exceedance of applicable water quality standards. The recommended reasonable potential analysis consists of two steps. Step one is to determine whether there is a quantifiable amount of mercury in the discharge using a sufficiently sensitive analytical method (see sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.) If this information is unknown, EPA recommends including a monitoring requirement in the permit to collect this information and a reopener clause to allow establishment of appropriate requirements if the permitting authority determines that the discharge has reasonable potential. If, using a sufficiently sensitive analytical method, there is not a quantifiable amount of mercury in the discharge, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential and that no water qualitybased limits are necessary. If there is a quantifiable amount of mercury, however, the permitting authority should move to step two of the reasonable potential analysis. Section 7.5.1.1 contains additional information on step one of the reasonable potential analysis.

Step two of the reasonable potential analysis is to determine whether the fish tissue concentration of methylmercury in the receiving water is close to or exceeds the criterion.

If the fish tissue concentration of methylmercury in the receiving water is below and not close to the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential, but tier 2 antidegradation provisions should be considered. This situation is described below in the third component of the NPDES permitting approach.

If the fish tissue concentration of methylmercury in the receiving water is close to or exceeds the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharger has reasonable potential, and a WQBEL must be included in the permit. Recommended WQBELs for this situation are described below in the fourth component of the NPDES permitting approach. Section 7.5.1.2 contains additional information on step two of the reasonable potential analysis. If information for step two is unknown, EPA recommends including in the permit a special permit condition to conduct a fish tissue survey of the receiving waterbody and a reopener clause so that reasonable potential can be determined when the fish tissue data become available. EPA further recommends that in this situation the permitting authority encourage permittees to develop and implement mercury minimization plans (MMPs) to reduce mercury loading to the waterbody.

In order to prevent future impairments, EPA recommends that a state or authorized tribe consider other factors or conditions such as rising fish tissue concentrations or the relative contribution of mercury or methylmercury from the source when determining whether a facility has reasonable potential in waters that are not yet impaired. Section

7.5.1.2.2 contains additional examples of other factors, such as downstream impacts, that should be considered in a reasonable potential analysis.

#### 7.2.3 Implementing antidegradation

The third component of the recommended NPDES permitting approach for methylmercury is to determine whether the discharger will undertake an activity that can increase mercury loading to the waterbody. If the discharger will not undertake such an activity, no additional permit conditions are necessary. EPA recommends, however, that in this situation the facility voluntarily develop and implement an MMP to reduce the facility's mercury loading to the receiving water. If the discharger will undertake such an activity, EPA recommends that a tier 2 antidegradation analysis be conducted in accordance with the state or tribe's antidegradation policy and that permit conditions consistent with the analysis be included in the permit.

As part of conducting a tier 2 antidegradation analysis, the state or authorized tribe would evaluate the activity's potential to lower water quality, whether there are alternatives that would avoid lowering water quality, and whether lowering of water quality would be necessary to accommodate important economic or social development in the area of the discharge. EPA considers analyses of potential pollution prevention and enhanced treatment alternatives as an appropriate starting point for the antidegradation review for both industrial and municipal dischargers. See 67 FR 68971, 68979. The results of such an analysis of potential alternatives could provide the basis for developing an MMP.

EPA further recommends that the permit contain a special condition requiring the permittee to implement an MMP and conduct effluent monitoring to allow for evaluation of the effectiveness and implementation of the MMP. Section 7.5.1.2.2 contains additional information on antidegradation considerations.

#### 7.2.4 Establishing appropriate WQBELs

The fourth component of the recommended NPDES permitting approach for methylmercury is to develop appropriate WQBEL requirements. Where a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate) has been developed, the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)). Where a TMDL is not available at the time of permit issuance, to satisfy 122.44(d)(1)(vii)(A), EPA recommends the following WQBEL requirements, which are explained in greater detail in section 7.5.2.1:

- Where a water column translation of the fish tissue criterion has been developed, or where site-specific data to do so are readily available, include a numeric water quality-based limit.
- Where a water column translation or site-specific data are not available and the permit writer determines that a numeric limit is infeasible to calculate:
  - Require the permittee to implement an MMP tailored to the facility's potential to discharge mercury. Depending on the particular facts, the permitting authority may include in the MMP a trigger level, reduction goal, or

- enforceable numeric level (e.g., existing effluent quality) to further manage mercury discharges.
- Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP. (See sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.)
- Include a reopener clause to modify the permit conditions if the MMP is not found to be effective or if a water column translation of the fish tissue criterion is developed.

Since permitting authorities need to establish and maintain WQBELs as stringent as necessary to meet water quality standards, if a state or tribe has yet to complete the transition from an existing water column criterion to a fish tissue-based criterion, states may consider retaining their existing water column criteria until translators are developed. Alternatively, until a translator is available, EPA recommends that one of the approaches outlined in this document for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water be considered, especially for waters with relatively high direct water inputs of mercury. (See section 3.1.3.1.)

In modifying or reissuing permits with existing WQBELs for mercury, permit writers must also ensure compliance with CWA anti-backsliding requirements. As described elsewhere in this Guidance, CWA section 402(o)(1) prohibits the revision of WQBELs to make them less stringent than existing permit limits unless a specific exception applies under 402(o)(2) or 303(d)(4).

Exceptions under Section 402(o)(2), which would allow for the establishment of less stringent limits are:

- (1) There have been material and substantial alterations or additions to the permitted facility which justify the less stringent limit.
- (2) New information (other than revised regulations, guidance, or test methods) is available that was not available at the time of permit issuance, and that would have justified a less stringent limit.
- (3) Good cause exists due to events beyond the permittee's control (e.g., natural disasters) and for which there is no reasonably available remedy.
- (4) The permit has been modified under 301(c), 301(g), 301(h), 310(i), 301(k), 301(n), or 316(a).

CWA section 303(d)(4) provides additional exceptions to the anti-backsliding prohibition: paragraph (A), which applies to "non-attainment waters," and paragraph (B), which applies to "attainment waters".

• Non-attainment water: CWA section 303(d)(4)(A) allows the establishment of a less stringent effluent limitation when the receiving water does not meet applicable water quality standards (i.e., a "non-attainment water") if the permittee meets two conditions. First, the existing effluent limitation must have been based on a total maximum daily load (TMDL) or other wasteload allocation established under

CWA section 303. Second, relaxation of the effluent limitation is allowed only if the cumulative effect of all revised limitations would assure the attainment of water quality standards, or the designated use not being attained is removed in accordance with the water quality standards regulations.

• Attainment water: CWA section 303(d)(4)(B) applies to waters where the water quality equals or exceeds levels necessary to protect the designated use, or to otherwise meet applicable water quality standards (i.e., an "attainment water"). Under CWA section 303(d)(4)(B), a limitation based on a TMDL, wasteload allocation, other water quality standard, or any other permitting standard may only be relaxed where the action is consistent with the state's antidegradation policy.

The application of these exceptions is limited under 402(o)(3), which prohibits the relaxation of effluent limitations in all cases if a revised effluent limitation would result in a violation of applicable effluent limitation guidelines or water quality standards, including antidegradation requirements.

In establishing WQBELs for mercury, permit writers will need to ensure that the CWA anti-backsliding requirements are met. The first step of the inquiry is to determine whether the WQBEL based on the fish tissue criterion is "less stringent" than the WQBEL in the previous permit. If the new permit limit is not less stringent (e.g., if the prior numeric WQBEL is included in the MMP as an enforceable numeric level (see section 7.5.2.4 for additional information)), then the anti-backsliding prohibition should not be triggered and it should be appropriate to include the new limit in the permit. If the WQBEL based on the new fish tissue criterion is in fact less stringent than the prior WQBEL, then the permit writer must retain the existing numeric WQBEL unless there is an available exception to the anti-backsliding prohibition.

Because CWA section 402(o)(2)(B)(i) does not allow backsliding solely because regulations are revised (e.g., adoption of the fish tissue criterion), any applicable exceptions to the anti-backsliding prohibition for impaired waters would be found under section 303(d)(4)(A). In this case, permit limits based on TMDLs or other wasteload allocations established under section 303 can be made less stringent only if: a) the cumulative effect of all loadings meets the WQS or b) the designated use is removed.

Anti-backsliding requirements are further described in EPA's *NPDES Permit Writers' Manual* (USEPA 1996a) and in EPA's *Technical Support Document for Water Quality-Based Toxics Control* (USEPA 1991).

Other considerations and requirements may be necessary in developing permits. They include the following:

• Where a discharger undertakes an activity that could increase mercury loading to the receiving water, the WQBEL must be consistent with applicable antidegradation requirements (see section 7.5.1.2.2). Additional requirements may also be necessary under the CWA and EPA's NPDES regulations (see section 7.5.2.3).

• The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1) (see section 7.5.2.3).

The entire recommended NPDES permitting approach is summarized in figure 5 and explained in greater detail in the following sections.

## 7.3 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 into their water quality standards as a fish tissue concentration, a traditional water column concentration, or both. If states or authorized tribes choose to use both approaches, they should clearly describe in their standards how each will be used for specific applications and describe applicable implementation procedures.

EPA recommends two 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 expresses the criterion—as a fish tissue concentration or as a water column concentration. In addition, states and authorized tribes that adopt the recommended criterion as a fish tissue value may choose to implement it through NPDES permitting as a water column translation of the fish tissue value. Each of these approaches is summarized in figure 6 and discussed in more detail in sections 7.4 and 7.5.

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 (and methylmercury where appropriate), the WQBEL for that discharge must be consistent with the wasteload allocation (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 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 relevant to determining reasonable potential and establishing effluent limits, where appropriate. If a state or authorized tribe develops its own such permitting procedures, EPA recommends that states and authorized tribes 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' permitting procedures, the CWA, and applicable federal regulations.

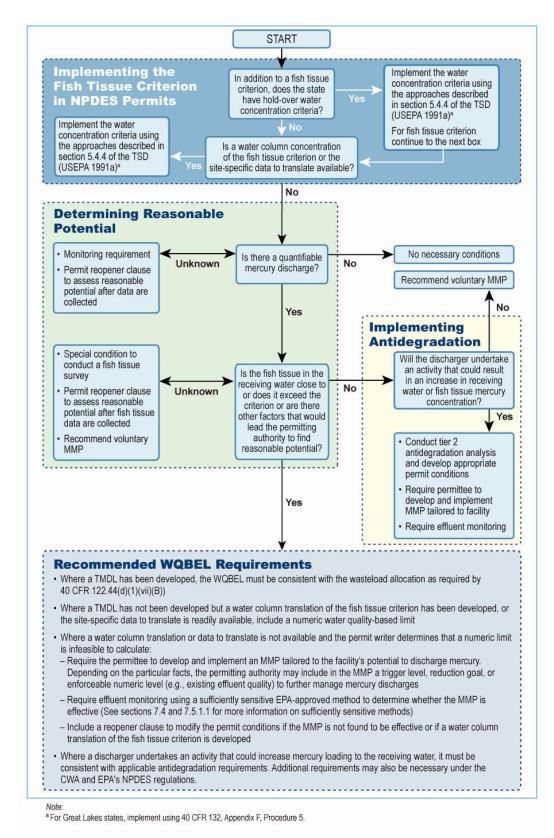


Figure 5. NPDES permitting approach for methylmercury.

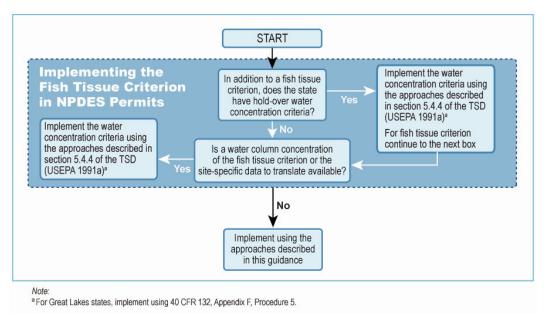


Figure 6. Implementing the fish tissue criterion in NPDES permits.

# 7.4 What are the procedures for developing permit limits when the criterion is adopted as a water column value or when the criterion is adopted as a fish tissue value and the permitting authority uses 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 one of the following forms:

- Water column concentration value. Expressing a criterion as a water column value is very common, and permitting authorities have considerable historical experience in developing permit limits based on such criteria in NPDES permits.
- Fish tissue concentration value that is translated into a water column value.
   Sections 3.1.3.1 through 3.1.3.3 of this guidance discuss 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 determining reasonable potential and for deriving numeric WQBELs.

In either case described above, the permitting authority should determine reasonable potential and calculate numeric WQBELs using the procedures described in section 5.4.4 of the TSD (USEPA 1991) to derive a numeric WQBEL.

This approach relies on the measurement of mercury in effluent, often at concentrations below the quantitation levels of some analytical methods. Therefore, the permitting authority should specify that the NPDES regulated discharger use a sufficiently sensitive EPA-approved method for the measurement of mercury in the discharge. An analytical method is sufficiently sensitive when (1) its method quantitation level is at or below the

level of the applicable water quality criterion or (2) its method quantitation level is above the applicable water quality criterion, but the amount of mercury in a discharge is high enough that the method detects and quantifies the level of mercury in the discharge. To illustrate the latter, if the water column criterion or water column translation of a fish tissue criterion for mercury in a particular waterbody is 2.0 parts per trillion (ppt), method 245.7 (with a quantitation level of 5.0 ppt) would be sufficiently sensitive when it reveals that the level of mercury in a discharge is 5.0 ppt or greater. In contrast, method 245.7 would not be sufficiently sensitive when it resulted in a level of nondetection for that discharge because it could not be known whether mercury existed in the discharge at a level between 2.0 and 5.0 ppt (less than the quantitation level but exceeding the water quality criterion).<sup>21</sup>

The selection of a sufficiently sensitive method relates method quantitation levels to the water column criterion value. If a water column criterion or a water column translation of a fish tissue criterion is not available to allow for selecting an alternate sufficiently sensitive method, EPA recommends the use of the most recent version of method 1631 to characterize discharges from all facilities for which the mercury levels are unknown or undetected. Method 1631 is relatively new, and the facilities may not have used it to analyze their effluent discharges. As a result, previous monitoring may show undetectable levels of mercury when use of method 1631 shows detectable or quantifiable amounts. Therefore, EPA recommends monitoring using the most recent version of method 1631 to help identify all facilities that contribute to mercury water quality impairment, unless another EPA-approved method can be justified as being sufficiently sensitive.

EPA's regulations require that measurements included on NPDES permit applications and on reports required to be submitted under the permit must generally be made using analytical methods approved by EPA under 40 CFR part 136. Because EPA has approved methods for analyzing mercury in water, these approved methods must be used in water analyses for NPDES permits involving mercury. See 40 CFR sections 122.21(g)(7), 122.41(j), 136.1, 136.3, and 136.6. Selection of an approved method should take into account the above discussion of method sensitivity. For metals, such as mercury, the federal regulations at 40 CFR 122.45(c) generally require effluent monitoring for the total form of the metal.

The discussion above describes analytical methods for measuring mercury in water. Refer to section 4.1 and appendix C for information on analytical methods for measuring mercury in fish tissue and for measuring methylmercury in water or fish tissue.

<sup>&</sup>lt;sup>21</sup> For more information on choosing a sufficiently sensitive method, see the memorandum *Analytical Methods for Mercury in National Pollutant Discharge Elimination System (NPDES) Permits* from James A. Hanlon, Director of the Office of Wastewater Management, dated August 23, 2007, at <a href="http://www.epa.gov/npdes/pubs/mercurymemo">http://www.epa.gov/npdes/pubs/mercurymemo</a> analyticalmethods.pdf.

# 7.5 What are the procedures for developing permit limits 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 a fish tissue concentration and that a TMDL, water column translation of the fish tissue criterion, or site-specific data to translate are not available at the time of permit issuance. As a result, the permitting authority will use a different approach than it has previously used for determining reasonable potential and expressing WQBELs. EPA recommends the approach described below, which is summarized in figure 7.

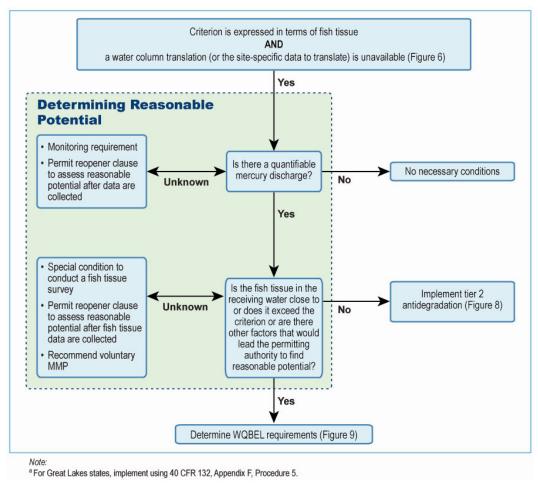


Figure 7. Determining reasonable potential.

### 7.5.1 How to determine the need for permit limits to control mercury (how to determine reasonable potential)

As discussed in section 3.1.2.2 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 concentration. When a criterion is adopted into standards as a fish tissue value, states and authorized tribes may not have sufficient data to translate from a fish

tissue value to a traditional water column value using BAFs or translators. This section provides recommendations for how a permitting authority can determine reasonable potential in the absence of site-specific data to translate the fish tissue value into 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 exceedance of 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 40 CFR 122.44(d)(1)(ii) with respect to a water quality criterion for methylmercury expressed as a fish tissue value in the absence of a TMDL and a water column translation of that value at the time of permit issuance.

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) the methylmercury level in fish tissue from the receiving waterbody is close to or exceeds the fish tissue water quality criterion. Under these circumstances, the effluent data indicate that the mercury load in the effluent contributes to the mercury load in the waterbody, and the fish tissue concentration indicates that the mercury load in the waterbody causes or has the potential to cause an exceedance of the water quality criterion. This approach is consistent with federal regulations pertaining to the Great Lakes Basin, which contained an approach for determining reasonable potential using fish tissue data (see 40 CFR part 132, appendix F, procedure 5.F.4). The reasonable potential approach for mercury described in this guidance 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 methylmercury present in fish tissue at levels close to or above the fish tissue criterion, and therefore the discharge may be found to exhibit the reasonable potential to cause or contribute to the exceedance of 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 water quality criterion integrates spatial and temporal complexity and the cumulative effects of mercury loading from point and nonpoint sources that affect methylmercury bioaccumulation in aquatic systems. As discussed further in section 7.5.1.2.2, EPA believes that comparing the fish tissue concentration in steady state systems directly to the applicable fish tissue criterion appropriately accounts for the

factors specified in 40 CFR 122.44(d)(1)(ii) for a criterion expressed as a fish tissue value.

Finally, EPA further notes that because of the sensitivity of Method 1631E or other sufficiently sensitive methods (as described in section 7.4), it is reasonable to conclude that a discharge below quantitation does not have reasonable potential to exceed the criterion.

# 7.5.1.1 Step one of the reasonable potential analysis: Determining whether the NPDES-permitted discharger has mercury in its effluent at quantifiable levels

The first step in the reasonable potential analysis is to determine whether the discharge contains a quantifiable amount of mercury. To determine this, EPA recommends that permitting authorities require monitoring using a sufficiently sensitive analytical method approved for use by EPA under 40 CFR part 136. Section 7.4 contains additional information about sufficiently sensitive EPA-approved methods. If an alternate EPA-approved method cannot be justified as being sufficiently sensitive, EPA recommends monitoring using the most recent version of method 1631 to help identify all facilities that contribute to mercury water quality impairment. EPA recognizes that using method 1631 will likely result in a large majority of facilities showing quantifiable mercury discharges. This approach, however, is intended to allow permitting authorities to determine that facilities without quantifiable levels of mercury may not need step two of the reasonable potential analysis (determining whether the fish tissue criterion is being attained).

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

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

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?

In this situation, EPA recommends that the permitting authority include permit conditions that include the following elements:

- Effluent monitoring using a sufficiently sensitive EPA-approved analytical method to characterize the discharger's effluent for mercury (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods)
- A reopener clause to identify the actions that the permitting authority may take should the monitoring information indicate that a WQBEL for mercury is necessary

EPA recommends that permitting authorities require monitoring, using a sufficiently sensitive EPA-approved method, by all facilities for which the mercury levels are unknown or previously undetected (using less sensitive methods) to characterize the discharger's effluent for mercury. EPA recommends this monitoring to help identify all facilities that contribute to mercury loads in the waterbody. The permitting authority could obtain these monitoring data as part of the permit application, by requiring periodic (e.g., quarterly to annually) monitoring as part of the permit, or by invoking its authority under CWA section 308 (or equivalent state authority) to require NPDES facilities to collect information necessary for developing NPDES permit limits. The permit should include a reopener clause so 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 TSD (USEPA 1991). This section acknowledges that EPA has not recommended a specific monitoring frequency. However, the TSD recognizes that the choice of a monitoring frequency is a site-specific decision and provides the permitting authority with a number of factors to consider when making these decisions.

Until the permitting authority has sufficient data to determine whether the discharge has reasonable potential, and depending on the particular facts, the permit writer may reasonably conclude that the permit conditions described in this section are as stringent as necessary to achieve 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 does not include quantifiable amounts of mercury?

In this situation, EPA recommends that the permitting authority first review the monitoring data to determine whether they are representative of the effluent. If the permitting authority believes the monitoring data are representative of the discharge, no further permit conditions may be necessary. 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.

### 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 move to step two of the reasonable potential analysis and evaluate data on the concentrations of methylmercury in the fish tissue from the receiving waterbody to determine appropriate permit conditions (see section 7.5.1.2).

# 7.5.1.2 Step two of the reasonable potential analysis: Determining whether the fish tissue concentration of methylmercury in the receiving waterbody exceeds the fish tissue criterion

In step two of EPA's recommended fish tissue criterion reasonable potential procedure, the permitting authority has concluded that the first condition of the two-part reasonable potential analysis has been satisfied (i.e., the NPDES-permitted discharger has mercury in

its effluent at a quantifiable level). The permitting authority should then address the second condition of the reasonable potential analysis—determining whether the fish tissue from the receiving waterbody exceeds (or is close to exceeding) the fish tissue water quality criterion.

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

- The fish tissue concentration of methylmercury is unknown.
- The fish tissue concentration of methylmercury does not exceed the criterion or is not close to the criterion.
- The fish tissue concentration of methylmercury exceeds the criterion or is close to exceeding the criterion.

For discharges with quantifiable levels of mercury, the recommended reasonable potential determination and recommended permit conditions for each outcome 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 document.

# 7.5.1.2.1 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury but the fish tissue concentrations of methylmercury in the receiving waterbody are unknown?

In waterbodies for which there are insufficient fish tissue data available, a permitting authority cannot determine whether there is reasonable potential using a fish tissue approach. Therefore, in this case, EPA recommends that the permitting authority take the following actions:

- Include a special permit condition to conduct a mercury fish tissue survey for the receiving waterbody, unless such information will be available from another source in a timely manner.
- Include as a permit condition a reopener clause to identify the actions that the permitting authority may take should fish tissue monitoring information become available and indicate that a WQBEL for mercury is necessary.
- Encourage the permittee to develop and implement an MMP tailored to the facility's potential to discharge mercury.

In this instance, the permitting authority should start a process for collecting fish tissue data in the waterbodies where point source discharges of mercury exist. 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 study design be

consistent with the recommendations on conducting ambient monitoring in section 4.2 of this guidance.

EPA also recommends that the permitting authority require only one study per waterbody. The permitting authority could do this by contacting all facilities that discharge into the waterbody and encouraging them to work jointly to conduct the study, because the outcomes of the study may affect the permit limits of those facilities. For example, the State of Idaho has developed a statewide fish tissue monitoring program for mercury that provides a standardized approach for collecting reliable data while recognizing limited resources for monitoring.

In waterbodies where the permitting authority expects to find high mercury concentrations in the water column or believes it will need a site-specific BAF to finish issuing the permits, the permitting authority should consider requiring the facility to include measurement of water column concentrations of mercury as part of the study.

EPA further recommends that the permit include a reopener clause so that as soon as there is complete information, the permitting authority can establish any additional requirements that are necessary. In this situation EPA recommends that the permitting authority encourage the permittee to develop and implement an MMP for the reasons discussed in section 7.5.1.2.2.1.

# 7.5.1.2.2 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury but the fish tissue concentrations of methylmercury in the receiving waterbody do not exceed and are not close to the criterion?

Once the permitting authority has determined that a facility discharges quantifiable amounts of mercury and that the concentration of methylmercury in fish tissue in the receiving waterbody does not exceed and is not close to the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion.

To assist in preventing future impairments, in some situations as outlined below, EPA recommends that states and authorized tribes also consider other factors or conditions such as a trend of rising fish tissue concentrations or the relative contribution of mercury or methylmercury from the source when determining whether a facility has reasonable potential in waters that are not yet impaired.

EPA notes that, unlike typical water quality criteria that are expressed as water column values, the fish tissue water quality criterion integrates spatial and temporal complexity as well as the cumulative effects of variable mercury loading from point and nonpoint sources that affect methylmercury bioaccumulation in aquatic systems. EPA believes that comparing the fish tissue concentration in steady state systems 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 value. Existing tissue-based data are indicators of accumulation that has already occurred. Thus, where fish tissue concentrations in a watershed are expected to be constant (i.e., steady state conditions) or decreasing over time, data that indicate that the fish tissue criterion is

currently being attained may be effective indicators of current and potential continued future attainment.

However, in dynamic systems where the levels in tissue in a watershed may be expected to increase, EPA recommends that the permitting authority account for this as part of the reasonable potential determination that is designed to prevent potential future impairments.

Another factor that permitting authorities may consider is the impact of permitted discharges to downstream waters (e.g., a discharge to a river that flows into a lake where mercury is a concern). In such a circumstance, it may be appropriate to conclude that the discharge has reasonable potential on the grounds that its discharge causes or contributes to the excursion of the fish tissue criterion in the downstream water.

The presence of these other factors or conditions such as the relative contribution of mercury or methylmercury from the source, rising fish tissue concentrations, or potential excursion of the criterion downstream, could constitute a basis for concluding that an effluent limit is necessary depending on the particular facts.

As discussed in section 7.5.1.2.2.2, for discharges to waters that are not impaired, EPA recommends that states and tribes regard any activity that could result in an increase in receiving water or fish tissue mercury concentration as a significant lowering of water quality for the purposes of triggering an antidegradation review.

#### Implementing tier 2 antidegradation

If the facility undertakes any activity that could increase mercury loading to the receiving waterbody, an antidegradation review may be necessary. Such increases 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, and federal regulations at 40 CFR 131.12 identify the elements of an acceptable antidegradation policy. Section 303(d)(4)(B) requires that applicable antidegradation requirements be satisfied prior to modifying NPDES permits (for example, prior to removing a WQBEL or including less stringent effluent limitations).

The federal antidegradation policy is composed of three levels of protection commonly referred to as tiers. The first tier, 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 tier prohibits lowering water quality to the point where existing uses are impaired. The second tier, found at 40 CFR 131.12(a)(2), protects water quality where water quality is better than that needed to support "fishable/swimmable" uses of the water. Where these conditions exist, the waterbody is typically 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 tier, at 40 CFR 131.12(a)(3), involves the protection of water quality in waterbodies that are of exceptional ecological, aesthetic, or recreational significance. Water quality in such waterbodies, identified and specifically designated by states or authorized tribes as Outstanding National Resource Waters, must be maintained and protected.

States and authorized tribes should determine whether the discharger will undertake an activity that can result in an increase in mercury loading to the receiving waterbody.

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

- The discharger will not undertake an activity that can increase mercury loading to the waterbody.
- The discharger will undertake an activity that can increase mercury loading to the waterbody.

As part of conducting a tier 2 antidegradation analysis, the permitting authority would evaluate the activity's potential to lower water quality, whether there are alternatives that would avoid lowering water quality, and whether lowering of water quality would be necessary to accommodate important economic or social development in the area of the discharge. EPA considers analyses of potential pollution prevention and enhanced treatment alternatives as an appropriate starting point for the antidegradation review for both industrial and municipal dischargers. See 67 FR 68971, 68979. The results of such an analysis of potential alternatives could provide the basis for developing an MMP.

EPA's recommendations for implementing antidegradation provisions and addressing increases in mercury loads are summarized in figure 8 and explained in sections 7.5.1.2.2.1 and 7.5.1.2.2.2. EPA recognizes, however, that states and tribes have the flexibility to interpret their antidegradation policies differently. For example, some states use limits established at existing effluent quality to implement their antidegradation provisions.

7.5.1.2.2.1 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury into a waterbody in which the fish tissue concentration of methylmercury does not exceed the criterion and the facility will not undertake an activity that could increase mercury loading to the waterbody?

If the facility discharges a quantifiable amount of mercury and the fish tissue concentration of methylmercury in the receiving water does not exceed the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge does not have reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion. In such situations, however, EPA recommends that the permitting authority encourage the facility to develop and implement an MMP.

An MMP helps ensure that the discharge will continue to have no reasonable potential to cause or contribute to an exceedance of applicable water quality standards. The recommendation to develop a voluntary MMP is also based on the extent of potential mercury impairment across the country and the scientific complexities of and uncertainties associated with assessing mercury loadings and evaluating their effects.

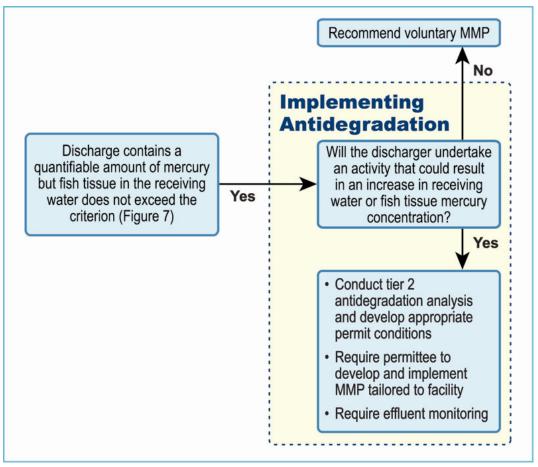


Figure 8. Implementing tier 2 antidegradation.

If future monitoring data demonstrate that a discharge does have reasonable potential, development of a MMP could assist the permit writer in establishing appropriate permit conditions. Furthermore, EPA believes that simply developing an MMP might provide dischargers of mercury with sufficient information to economically reduce the discharge of mercury into our Nation's waters by voluntarily implementing the mercury minimization measures identified in the plan. Section 7.5.2.1 provides additional information on MMPs.

7.5.1.2.2.2 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury into a waterbody in which the fish tissue concentration of methylmercury does not exceed the criterion but the facility will undertake an activity that could result in an increase in receiving water or fish tissue mercury concentration?

In this situation, the receiving water does not currently exceed the fish tissue criterion. EPA believes that increases in mercury loading to a waterbody should be allowed at levels determined appropriate by an antidegradation analysis and that such dischargers should be required to implement MMPs under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4).

EPA recommends the following WQBEL requirements:

- Include permit conditions consistent with antidegradation requirements.
- Require the permittee to implement an MMP tailored to the facility's potential to
  discharge mercury. Depending on the particular facts, the permitting authority may
  include in the MMP a trigger level, reduction goal, or enforceable numeric level to
  further manage mercury discharges.
- Require the permittee to monitor its effluent using a sufficiently sensitive EPA-approved method (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods).

Other considerations and requirements might be necessary in developing permits:

- The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1).
- For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements (see section 7.2.4).

Activities 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. Consistent with EPA's antidegradation regulations for water quality standards, state and tribal antidegradation regulations are to provide that the quality of waters at levels better than the levels necessary to support "fishable/swimmable" uses of the water may 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 recommends that states and authorized tribes regard any activity that could result in an increase in receiving water or fish tissue mercury concentration 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 allowed, the permitting authority would not authorize or allow any such discharge to occur. If 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 require state and tribal antidegradation regulations to protect the minimum level of water quality necessary to support existing uses by prohibiting lowering of water quality to the point where existing uses are impaired (see 40 CFR 131.12(a)(1)). 22 For new and increased discharges, states have the flexibility to interpret their antidegradation policies differently. For example, some states use limits established at existing effluent quality.

<sup>&</sup>lt;sup>22</sup> 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.

EPA expects that fluctuations in mercury loadings arising from normal industrial production fluctuations, or loading fluctuations that are not results of change in existing POTW service areas, would generally not trigger a tier 2 antidegradation analysis. EPA expects that increases in mercury loadings from a POTW arising from adding a new subdivision or an unsewered neighborhood to a sewer service area would generally trigger a tier 2 antidegradation review. If an antidegradation review is triggered, the review should consider the source of the increased mercury loading, the potential for source reduction through either treatment, pretreatment or pollution prevention, and the expected benefits likely to accrue to the affected community as a result of the activities that result in increased mercury loadings. EPA recommends that states and tribes tailor the level of detail and documentation for antidegradation demonstrations to the specific circumstances. For example, in some instances, as with diffuse domestic sources of mercury, available treatment and pollution prevention alternatives may be limited or lacking, leaving only the importance of social and/or economic development as the primary focus of the review.

EPA recognizes that an increase in the discharge of mercury might be due to mercury present in stormwater or input process water that does not originate with and is not under the reasonable control of a facility. While an MMP, to the extent that there are available BMPs to minimize mercury discharges, might still be appropriate in such circumstances, EPA would not generally expect that such discharges would trigger the need for an antidegradation review, or numeric WQBELs.

In addition to permit conditions consistent with antidegradation requirements, EPA recommends that the permit require the dischargers to implement an MMP under the authority of CWA section 402(a)(1)(B) and 40 CFR 122.44(k)(4). The MMP should be tailored to the individual facility's potential to discharge mercury. For more information on MMPs, see section 7.5.2.1.

# 7.5.1.2.3 What are the recommended permit conditions when a facility discharges quantifiable amounts of mercury and the fish tissue concentrations of methylmercury in the receiving waterbody are close to or exceed the criterion?

EPA believes that, depending on the particular facts, a permitting authority may 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 fish tissue concentrations of methylmercury from the receiving waterbody are close to or exceed the fish tissue water quality criterion.

Where fish tissue concentrations are below but close to the criterion, EPA recommends that a finding of reasonable potential be made since the effect of current discharges and other relevant factors may not yet be reflected in fish tissue concentrations. For example, where the tissue data are below the water quality criterion, the permitting authority may consider applying an appropriate confidence interval (e.g., 95 percent upper confidence limit on the mean) to such values and compare that value to the fish tissue criterion to the extent necessary to account for variability in fish tissue data. As an example of an

alternative to this statistical approach, the State of Idaho's implementation guidance<sup>23</sup> for its methylmercury fish tissue criterion of 0.3 mg/kg recommends that where the levels in fish exceed 0.24 mg/kg, the permitting authority should determine that reasonable potential exists. Where methylmercury levels in fish tissue are thought to be relatively sensitive to a water point source load of mercury or methylmercury, the permitting authority may take that into account in the reasonable potential determination.

When reasonable potential exists, it is necessary to establish an appropriately protective WQBEL in the permit. For guidance on recommended WQBELs, see section 7.5.2.1.

### 7.5.1.3 How to consider mercury in intake water with a reasonable potential approach

For some facilities, the only source of mercury in a discharge may be the intake water taken directly from the same body of water to which 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 reasonably conclude, based on the particular facts, that there is no reasonable potential to cause or contribute to an exceedance of 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 fish tissue unless the fish are known to frequently inhabit the water in the area immediately adjacent to the discharge. In making this decision, the permitting authority should consider the monitoring data from both the intake and discharge to verify that there are no known sources of additional contributions of mercury at the facility. EPA also recommends that permitting authorities consider evaluating whether the methylmercury concentration in fish tissue significantly increases for facilities with anaerobic conditions in the discharge. This procedure represents a comprehensive approach for conducting a site-specific analysis of the potential for a discharge to cause or contribute to an excursion above a water quality standard, which can lead to a decision to not require a WQBEL. This approach is consistent with the rationale for the federal regulations pertaining to the Great Lakes Basin, which included consideration of intake pollutants in finding reasonable potential (see 40 CFR part 132, appendix F, procedure 5.D).

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

As discussed in section 3.1.2.2 of this document, EPA recommends that states and authorized tribes adopt a new or revised methylmercury water quality criterion in the form of a fish tissue concentration. When the criterion is adopted into standards as a fish tissue value, some states and authorized tribes may not have sufficient data to translate from a fish tissue value to a traditional water column value using BAFs or translators. When developing WQBELs, the permitting authority must ensure that the level of water quality to be achieved by such limits derives from and complies with water quality

<sup>&</sup>lt;sup>23</sup> Implementation Guidance for the Idaho Mercury Water Quality Criteria is available at <a href="http://www.deq.state.id.us/water/data\_reports/surface-water/monitoring/idaho-mercury-wq-guidance.pdf">http://www.deq.state.id.us/water/data\_reports/surface-water/monitoring/idaho-mercury-wq-guidance.pdf</a>.

standards (see 40 CFR 122.44(d)(1)(vii)). This section provides recommendations on how a permitting authority could derive appropriate WQBELs in the absence of a TMDL and a water column translation of the fish tissue criterion at the time of permit issuance. The information discussed in this section is summarized in figure 9.

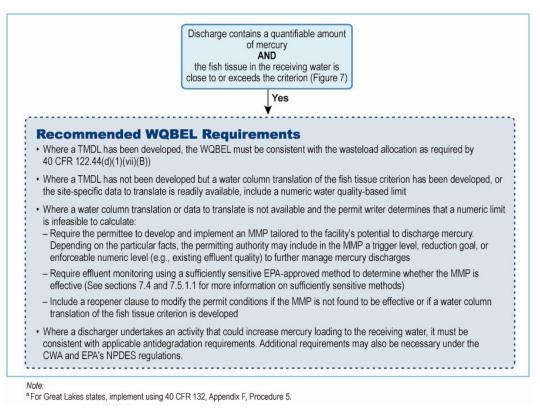


Figure 9. Determining WQBEL requirements.

#### 7.5.2.1 What are the recommended WQBELs?

If the facility has a quantifiable amount of mercury in its discharge and the concentration of methylmercury in fish tissue in the receiving water is close to or exceeds the criterion, depending on the particular facts, the permitting authority may reasonably conclude that the discharge has reasonable potential to cause or contribute to an exceedance of the applicable fish tissue water quality criterion. In this situation, in the absence of a TMDL and a water column translation of the fish tissue criterion, it may be appropriate to conclude that it is infeasible to calculate a numeric WQBEL at the time of permit issuance and to instead express the WQBEL as narrative BMPs, as provided in 122.44(k)(3).

Where a TMDL containing wasteload allocations for the discharge of mercury (and methylmercury where appropriate) has been developed, the WQBEL for that discharge must be consistent with the wasteload allocation (see 40 CFR 122.44(d)(1)(vii)(B)). Where a TMDL is not available at the time of permit issuance, to satisfy 122.44(d)(1)(vii)(A), EPA recommends that the WQBEL consist of the following elements:

- Where a water column translation of the fish tissue criterion has been developed, or site-specific data to do so are readily available, include a numeric water qualitybased limit
- Where a water column translation or site-specific data are not available and the permit writer determines that a numeric limit is infeasible to calculate:
  - Require the permittee to implement an MMP tailored to the facility's potential to discharge mercury. Depending on the particular facts, the permitting authority may include in the MMP a trigger level, reduction goal, or enforceable numeric level to further manage mercury discharges.
  - Require effluent monitoring using a sufficiently sensitive EPA-approved method to enable evaluation of the effectiveness and implementation of the MMP. (See sections 7.4 and 7.5.1.1 for more information on sufficiently sensitive methods.)
  - Include a reopener clause to modify the permit conditions if the MMP is not found to be effective or if a water column translation of the fish tissue criterion is developed.

Other considerations and requirements may be necessary in developing permits:

- Where a discharger undertakes an activity that could increase mercury loading to the receiving water, it must be consistent with applicable antidegradation requirements. Additional requirements may also be necessary under the CWA and EPA's NPDES regulations.
- The permitting authority would need to include appropriate technology-based limits pursuant to CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1).
- For modified or reissued permits with existing effluent limits for mercury, any less stringent effluent limit must be consistent with anti-backsliding requirements (see section 7.2.4).

### 7.5.2.2 What does EPA recommend where direct water inputs are relatively high?

This section describes EPA's recommendations where direct water inputs of mercury are relatively high. In this section, EPA discusses the recently developed "5m" listing approach for waters impaired by mercury from primarily atmospheric sources, as well as approaches for developing TMDLs, analyses of sources and loading capacity similar to what would be provided in a TMDL, or water column translations of the fish tissue criterion, to serve as the basis for permit limits.

As described in section 6.2, EPA recently developed an optional voluntary approach for deferring TMDL development for waters impaired by mercury predominantly from atmospheric sources pursuant to CWA section 303(d). Under this approach, states with comprehensive mercury reduction programs may consider waters appropriate for inclusion in a subcategory of their impaired waters lists (category 5m under the Integrated Report Guidance) and defer the development of TMDLs for those waters. EPA's 5m guidance states that in deciding on the scope of waterbodies proposed for

subcategory 5m, a contribution for states to consider would be approximately 90 to 95 percent of the loadings or higher from air deposition to the waterbody; the specific percent may vary, however. A full description of the 5m approach is at http://www.epa.gov/owow/tmdl/mercury5m/.

In watersheds where direct water inputs (mercury from point sources and nonpoint sources other than air deposition) represent a relatively high contribution of mercury, EPA recommends that states and authorized tribes specifically consider developing numeric permit limits for mercury dischargers to these waterbodies. States and authorized tribes may develop TMDLs for these waterbodies in the short term to provide important information for developing appropriate permit limits. Where a state or authorized tribe chooses not to develop a TMDL in the short term for such a waterbody, EPA recommends that the state or tribe develop an analysis of sources and loading capacity similar to what would be provided in a TMDL or a water column translation of the fish tissue criterion using the methods outlined in 3.1.3.1. Consistent with the 5m approach for establishing priorities for mercury TMDL development, in deciding whether there is a relatively high contribution from direct water inputs, a contribution for states to consider would be approximately 5 to 10 percent or more of mercury loadings from direct water inputs, taking into account that the specific percent may vary by state. At the same time, states may consider other factors, such as the complexity of the TMDL, in determining schedules for developing TMDLs.

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 mercury impairment. These situations are more complicated because the specific location and magnitude of each source could significantly affect fish tissue concentrations. In these situations, a TMDL provides the best basis for developing the appropriate permit limits.

Once EPA has approved or established a TMDL containing a wasteload allocation for the discharge of mercury (and methylmercury where appropriate), 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)). In addition to developing a WQBEL, the permitting authority 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 a sufficiently sensitive EPA-approved method for monitoring purposes.

In such watersheds where direct water inputs represent a relatively high mercury loading, EPA recommends that the permitting authority and the mercury dischargers in the watershed work together to collect the data necessary to develop a TMDL, an analysis of sources and loading capacity similar to what would be provided in a TMDL, or a water column translation of the fish tissue criterion. One approach for collecting information for a source analysis described above or a water column translation of the fish tissue criterion 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 the absence of a final TMDL, EPA recommends that a permitting authority conduct an analysis of sources and loading capacity similar to what would be provided in a TMDL.

Such an analysis that applied factors similar to those considered 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. The permitting authority may also use a water column translation of the fish tissue criterion to derive numeric permit limits if such a translation or site-specific data to translate are available.

A water column translation of the fish tissue criterion may not always be necessary in developing a TMDL or an analysis of sources and loading capacity similar to what a TMDL would provide. For example, section 6.2.2.2.1 of this guidance provides descriptions of TMDLs that have been developed using steady state models and the proportionality approach.

Since permitting authorities need to establish and maintain WQBELs as stringent as necessary to meet water quality standards, if a state or tribe has yet to complete the transition from an existing water column criterion to a fish tissue-based criterion, states may consider retaining their existing water column criteria until translators are developed. Alternatively, until a translator is available, EPA recommends that one of the approaches outlined in this document for relating a concentration of methylmercury in fish tissue to a concentration of methylmercury in ambient water be considered (see section 3.1.3.1.)

#### 7.5.2.3 What additional requirements may apply?

Activities that could increase mercury loadings to a receiving waterbody

Permits for sources that are seeking authorization to increase their discharge of mercury (or commence the discharge of mercury) must be consistent with applicable antidegradation requirements. See discussions of antidegradation elsewhere in this chapter, including sections 7.2.3 and 7.5.1.2.2.

The permitting authority may consider whether an offset of such discharges by other pollutant source reductions would support the development of a WQBEL that would ensure that the level of water quality to be achieved by such effluent limitation is derived from and complies with the water quality standards, as required by 40 CFR 122.44(d)(1)(vii)(A) and any other applicable NPDES regulations.

#### Pretreatment

A POTW is 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)). A POTW that accepts mercury in its collection systems may need to ensure that its pretreatment program prevents its effluent from contributing to exceedance of the fish tissue criterion. The general pretreatment regulations (at 40 CFR part 403) require that each POTW, or combination of POTWs operated by the same water authority, with a design flow of 5.0 million gallons per day (MGD) or more develop an approved pretreatment program that protects 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. The POTW is 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. The categorical standards, however, do not address POTW-specific problems that 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 to protect the treatment facilities, receiving water quality, and worker health and safety and to allow for the beneficial use of sludge.

#### Technology-based limits

When developing effluent limits for an NPDES permit, a permit writer must impose limits based on the technology available to treat mercury (technology-based limits) as a minimum level of control, as required by CWA section 301(b) and 40 CFR sections 125.3 and 122.44(a)(1). There are two general approaches for developing technology-based effluent limits for industrial facilities: national effluent limitation guidelines (ELGs) and best professional judgment (BPJ) on a case-by-case basis (in the absence of ELGs). Technology-based effluent limits for municipal facilities (POTWs) are derived from secondary treatment standards.

#### Anti-backsliding

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 1996b).

#### Permit documentation

Documentation is an important part of the permit development process. The NPDES permit fact sheet should provide an explanation of how the limit proposed in the associated draft permit is as stringent as necessary to achieve water quality standards (40 CFR 124.8 and 124.56). 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.

#### 7.5.2.4 Mercury minimization plans

EPA recommends that the permit contain a special condition requiring the permittee to implement an MMP that includes effluent monitoring using a sufficiently sensitive EPA-approved method (see sections 7.4 and 7.5.1.1 for information on sufficiently sensitive methods), with the expectation that effluent monitoring will allow for evaluation of the effectiveness and implementation of the plan. The MMP would be included in the permit in addition to a numeric WQBEL in cases where a TMDL, a water column translation of the fish tissue criterion, or other water concentration criterion is available at the time of issuance. If neither a TMDL nor a water column translation (or other water criterion) is available at the time of permit issuance, however, the MMP would be included in the permit as part of a narrative WQBEL in lieu of a numeric WQBEL. EPA believes that,

depending on the particular facts, a permit writer may reasonably conclude that such MMPs are as stringent as necessary to achieve water quality standards, for the reasons discussed below.

EPA believes that mercury reductions achieved through implementing MMPs tailored to the facility's potential to discharge mercury could result in important reductions in mercury loadings. EPA's basis for this conclusion is its study of pollutant minimization programs and their success in reducing mercury loadings to the environment. The reports *Mercury Study Report to Congress* (USEPA 1997c) and draft *Overview of P2 Approaches at POTWs* (USEPA 1999b) 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, not on 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 for those products 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 those from medical and dental facilities.

Using pollutant minimization or prevention programs can also reduce the transfer from wastewater to other media through disposal of mercury-containing sludge from which mercury may subsequently reenter the environment. For example, mercury removed at a POTW through treatment is likely to reenter the environment through POTW sludges that are then 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 removing and recycling mercury at the source (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 reduce the amount of mercury entering the environment through other media or sources. (For example, 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 approach, see the draft Overview of P2 Approaches at POTWs (USEPA 1999a). For an example of guidance on developing an MMP, see the EPA Region 5 final document Mercury Pollutant 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 state permitting authorities in EPA's Regional Office in Chicago. See also the City of Superior's document, Mercury Pollutant Minimization Program Guidance Manual for Municipalities, at http://www.ci.superior.wi.us/

<u>index.asp?NID=129</u>, and EPA's *Local Limits Development Guidance* (USEPA 2004) at http://www.epa.gov/npdes/pubs/final local limits guidance.pdf.

Finally, as explained in section 2.1.1, mercury is a bioaccumulative, persistent pollutant that can cause adverse health effects. Given this fact, EPA believes that point sources that can cost-effectively reduce their mercury discharges should do so. The fact that air sources or historical contamination are likely dominant causes of impairment does not mean that point sources should not implement cost-effective, feasible pollution prevention measures to reduce their contribution of mercury to the environment, however small those contributions may be. In short, EPA believes that it is reasonable to expect NPDES permittees to 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 writers may reasonably conclude that permit limits that require such measures derive from and comply with water quality standards as required by EPA regulations at 40 CFR 122.44(d)(1)(vii)(A).

In cases where a permittee believes it may have reasonable potential, EPA recommends that the permittee provide information that the permitting authority can use in developing appropriate permit conditions and would encourage the permittee to provide a draft MMP. Alternatively, where a draft MMP is not initially submitted by the permittee, the permitting authority may request that the permittee provide a draft MMP. The permitting authority retains the final responsibility for determining reasonable potential, and for incorporating the appropriate permit conditions, including an effective MMP and its implementation, in the permit.

Developing an MMP need not be an intensive or burdensome activity. The content of an MMP should be determined on a case-by-case basis and tailored to the individual facility's potential to discharge mercury and implement reasonable controls. The MMP could be as little as one or two pages or as much as a major engineering study. Table 6 contains suggestions for the content of an MMP based on the type of facility. Of course, MMPs should vary in their level of detail and degree of stringency on the basis of site-specific factors and the degree to which the facility has the ability to reduce environmental releases of mercury. For example, if the mercury analysis performed for the permit application shows a much higher concentration than would be expected for the type of facility, further investigation would be appropriate and could lead to increased requirements. On the other hand, EPA recognizes that MMPs may not be effective in certain cases such as when 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.

If a permittee has several of the types of sources listed in table 6, each of these sources should be considered in developing an appropriate MMP. For example, if the service area of a POTW contains dental offices and medical facilities, the MMP should contain appropriate measures for both. The mercury minimization measures suggested in table 6 are expected to reduce mercury levels in the wastewater discharge as well as other waste streams and media. Most of the mercury discharged to POTWs, for example, ends up in biosolids that may be incinerated or disposed on the land, thus contributing to the overall mercury burden in the environment. In addition, any measures that reduce releases to the atmosphere should be encouraged.

Table 6. Suggested content for MMPs based on the type of facility

Type of facility	Suggested content		
Publicly (or privately) owned treatment works serving a purely residential area. No dental or medical offices or hospitals. No industrial users.	Recommended distribution of outreach materials on fish-consumption advisories and properly disposing of mercury-containing products.		
POTW whose service area contains dental offices.	Recommend or require that dental offices follow American Dental Association BMPs. Collect any bulk mercury in the offices. Develop an approach for using amalgam separators.		
POTW whose service area contains one or more hospitals.	Recommend or require that hospitals follow the practices recommended by the American Hospital Association. <sup>b</sup>		
POTW whose service area contains schools or medical offices.	Recommend or require that schools and medical offices properly dispose of bulk mercury in their possession (including, for example, mercury-containing sphygmomanometers).		
Industrial direct or indirect dischargers that use mercury as an intentional component of their process or recover mercury as a by-product of their process.	Generally, such a case would involve a thorough analysis of opportunities to reduce their releases of mercury.		
Industrial direct or indirect dischargers that do not use mercury as an intentional component of their process and do not recover mercury as a by-product of their process.	Such facilities should investigate opportunities to reduce their incidental releases of mercury such as recycling fluorescent lamps, switches, thermostats, etc. and replacing them with low-mercury or non-mercury products.		

#### Notes:

When developing MMPs, EPA recommends beginning with any existing best management plans and spill prevention and containment control plans for that facility. Many of the activities covered by those plans can also reduce mercury sources to wastewater. After reviewing many pollutant minimization programs, EPA recommends that a plan include at least the following elements:

- Identification and evaluation of current and potential mercury sources
- For POTWs, 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
- 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, material recovery, spill control and collection, waste recycling, process modifications, housekeeping and laboratory use and disposal practices, and public education

<sup>&</sup>lt;sup>a</sup> For more information on the American Dental Association BMPs, see Best Management Practices for Amalgam Waste (September 2005) at <a href="http://www.ada.org/prof/resources/topics/">http://www.ada.org/prof/resources/topics/</a> topics amalgamwaste.pdf.

<sup>&</sup>lt;sup>b</sup> For more information on American Hospital Association practices, see Replacing Mercury in Healthcare Facilities—A Step-by-Step Approach at <a href="http://www.h2e-online.org/hazmat/mercquide.html">http://www.h2e-online.org/hazmat/mercquide.html</a>.

- Implementation of appropriate minimization measures identified in the plan
- Effluent monitoring to verify the effectiveness of pollution minimization efforts

EPA believes that these minimum permit conditions may be appropriate because they help to ensure that the discharge does not cause or contribute to an exceedance 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, a permit writer may reasonably conclude that such an MMP is as stringent as necessary to achieve water quality standards.

To further manage mercury discharges, the permitting authority should consider including an effluent trigger level or reduction goal in an MMP. Such a trigger level or goal could be set at a level that would provide a basis for evaluating whether the mercury minimization measures or BMPs specified in the MMP are working as anticipated. The level or goal could be expressed numerically or in narrative form. For example, the MMP might provide a trigger level equal to the existing effluent quality that, if exceeded, would indicate that mercury minimization measures may not be effective. Alternately, the MMP might provide goals for mercury reductions that are expected to occur as a result of the implementation of mercury minimization efforts specified in the MMP. As explained in this section and in section 7.5.2.1, an MMP includes a set of BMPs that would be part of an enforceable special condition of the permit. The MMP might specify that exceeding a trigger level or failing to achieve a mercury reduction goal would prompt actions such as reevaluation of the MMP, additional monitoring, or the implementation of additional BMPs. In this case, the failure of the permittee to undertake the additional actions identified in the MMP would be a violation of the permit special condition.

Even where it is infeasible to calculate a numeric WQBEL (for the reasons discussed in section 7.5.2.1), a permitting authority should consider including in the MMP an enforceable numeric level on the discharge of mercury. In this case, the enforceable numeric level would not constitute a stand-alone water quality-based effluent limit, but rather, a baseline for achieving mercury reductions that, combined with the other measures and practices in the MMP, would together constitute the water quality-based effluent limit. Such an enforceable numeric level could represent either existing effluent quality or a level representing some increment of the mercury reduction determined achievable as a result of the measures and practices specified in the MMP. Depending on the particular facts, the permit writer may reasonably conclude that the enforceable numeric level combined with the other measures and practices in the MMP will result in a level of mercury discharge that is controlled as stringently as necessary to meet water quality standards. Where the MMP contains an enforceable numeric level for mercury and/or methylmercury in the effluent, exceeding that value would be a violation of the permit special condition.

The permitting authorities should consider use of effluent trigger levels, effluent reduction goals, and enforceable numeric levels in any discharge permits that are based on MMPs as water quality-based effluent limits. EPA recommends that permitting authorities include such levels or goals in permits where direct water inputs are relatively high.

#### **8 Related Programs**

# 8.1 What are EPA and others doing as a whole to address mercury?

A wide variety of actions are under way in the United States and internationally to address mercury contamination. EPA's mercury Web site, at <a href="http://www.epa.gov/mercury">http://www.epa.gov/mercury</a>, provides a broad range of information about mercury: actions by EPA and others, including international actions, effects on people and the environment, and how people can protect themselves and their families.

With respect to EPA's actions, on July 5, 2006, EPA issued a report titled *EPA's Roadmap for Mercury* ("*Roadmap*"). It is at <a href="http://www.epa.gov/mercury/roadmap.htm">http://www.epa.gov/mercury/roadmap.htm</a>. EPA's *Roadmap* describes the Agency's progress to date in addressing mercury issues domestically and internationally, and it outlines EPA's major ongoing and planned actions to address risks associated with mercury. The *Roadmap* describes the Agency's most important actions to reduce both mercury releases and human exposure to mercury. Creating the *Roadmap* has enabled EPA to maximize coordination of its many diverse efforts, with the goal of improving its mercury program. In addition to providing a roadmap for EPA, the report provides important information about mercury to other federal agencies; to EPA's partners in state, tribal, and local governments; and to the public.

# 8.2 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)<sup>24</sup> to their collection system and wastewater treatment plant. However, as water quality criteria, sludge standards, and air emissions standards become more restrictive, even low levels of pollutants like mercury might cause noncompliance with these standards. Therefore, POTWs must 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)

<sup>&</sup>lt;sup>24</sup> 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 an 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 403.4(v)).

contribute a major portion of the mercury in its 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's 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 implementing 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 communicate with their permitting authority, as well as 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, the success of a POTW P2 effort depends on 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). A POTW might minimize community resistance and apathy by undertaking the following activities prior to developing its plan:

- Conduct a preliminary investigation of the problem and potential sources. Verify
  that the problem is not a wastewater treatment plant operational issue. 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 familiar with P2 strategies or 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.

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 that most people can understand).
- Identify the goals to determine whether the POTW intends to help minimize mercury introduced to all environmental media (air, water, solid waste), known as "front-end" P2 or merely to 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 or 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 resources necessary to implement the plan such as staffing, equipment, and funding.
- Create contingency plans that describe actions to be taken if the planned efforts do not succeed, such as obtaining the 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 mercury levels in wastewater treatment plant effluent) 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.

# 8.3 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 the Amendments of 1990, compliance by emitting sources and actions taken voluntarily have already begun to reduce mercury emissions to the air across the country. EPA expects that a combination of ongoing activities will continue to reduce such emissions over the next decade.

#### **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.

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; hospital, medical, and infectious waste incinerators; chlor-alkali plants; 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 58 percent reduction in domestic mercury air emissions between 1990 and 2005 (see figure 4 and <a href="http://cfpub.epa.gov/eroe/index.cfm?fuseaction="

The relevant regulations that EPA has issued to date under the CAA are described briefly below. For more information about other CAA actions to control mercury, see <a href="http://www.epa.gov/mercury">http://www.epa.gov/mercury</a> under "What EPA and Others Are Doing."

#### 8.3.1 Municipal waste combustors

In 1995 EPA promulgated new source performance standards (NSPS) that apply to all new municipal waste combustor units (both waste-to-energy plants and incinerators) with the capacity to burn more than 250 tons of municipal solid waste, including garbage, per day and emission guidelines that apply to existing units with the same capacity through either an EPA-approved State plan or a promulgated Federal plan (see 60 FR 65,415 [December 19, 1995], codified at 40 CFR part 60, subparts Eb and Cb). These regulations cover approximately 130 existing waste-to-energy plants and incinerators, as well as 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 emission levels (57 tons per year of mercury emitted from domestic municipal waste combustors in 1990 versus 2.3 tons per year in 2005). In 2000, EPA promulgated NSPS and emission guidelines establishing similar requirements for small municipal waste combustor units (units with a capacity of 35 to 250 tons per day) (see 65 FR 76,355 [December 6, 2000], codified at 40 CFR part 60, subparts AAAA and BBBB).

#### 8.3.2 Hospital, medical, and infectious waste incinerators

Hospital/medical/infectious waste incinerators (HMIWIs) are used by hospitals, health care facilities, research laboratories, universities, and commercial waste disposal companies to dispose of hospital waste and/or medical/infectious waste. EPA adopted regulations controlling mercury and other emissions from HMIWIs on September 15, 1997 (62 FR 48,348, codified at 40 CFR part 60, subparts Ce and Ec). All existing HMIWIs were required to comply with the regulations by September 15, 2002. EPA estimated that the regulations would reduce mercury emissions from HMIWIs at existing facilities by 93–95 percent (from 16.5 to 0.9-1.2 tons per year). In fact, the actual mercury emission reductions achieved as a result of implementing the regulations were approximately 98 percent. At the time the regulations were issued, EPA expected that 50 to 80 percent of the 2,400 then-existing HMIWIs would close in response to the rule. 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 1997 rule, approximately 98 percent of the 2,400 HMIWIs operating at health care facilities in 1997

have shut down or obtained exemptions, and few facilities have installed new HMIWIs (5 new HMIWIs at 4 facilities). Instead, many facilities have switched to other methods of waste treatment and disposal, such as autoclaving and off-site commercial waste disposal. There are currently 57 existing HMIWIs operating at 52 facilities. EPA adopted revised regulations for HMIWIs on October 6, 2009 (74 FR 51,368). The revisions were issued in order to respond to a court remand of the 1997 rule and to satisfy the Clean Air Act section 129(a)(5) requirement to conduct a review of the standards every 5 years. EPA estimates that the revised regulations will reduce mercury emissions at existing HMIWIs by 89 percent (from 0.3 to 0.04 tons per year). The revised mercury standards are estimated to impact 20 HMIWIs, which are expected to employ mercury control technology (e.g., installing activated carbon injection systems or increasing current use of activated carbon). All existing HMIWIs are required to comply with the revised regulations by October 6, 2014.

#### 8.3.3 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 IIIII). These air regulations have reduced mercury air emissions from existing chlor-alkali plants by approximately 50 percent since the compliance date of December 19, 2006. The regulation requires a combination of controls for point sources, such as vents, and BMPs to address fugitive air emissions, that are more stringent work practices than those required by a preexisting regulation that covered this source category. Today, there are four (4) such plants in the United States, compared to 20 when work on the rule began. In addition, EPA completed a study of fugitive mercury emissions at existing chlor-alkali plants and found the levels of elemental mercury emissions much lower than previously thought. Current total emissions from the four plants are estimated to be approximately 0.3 tons per year of mostly (>98%) elemental mercury.

#### 8.3.4 Hazardous waste combustors

In 2005, EPA published standards under Section 112(d) of the CAA for hazardous waste combustors (HWCs)--incinerators, cement kilns, lightweight aggregate kilns, liquid fuel boilers, solid fuel boilers, and hydrochloric acid production furnaces that burn hazardous waste (70 FR 59402 (October 12, 2005)). The mercury standards for existing and new sources, respectively, are under 40 CFR 63.1216(a)(2) and (b)(2) for solid fuel boilers, 40 CFR 63.1217(a)(2) and (b)(2) for liquid fuel boilers, 40 CFR 63.1218(a)(2) and (b)(2) for hydrochloric acid production furnaces, 40 CFR 63.1219(a)(2) and (b)(2) for incinerators, 40 CFR 63.1220(a)(2) and (b)(2) for cement kilns, and 40 CFR 63.1221(a)(2) and (b)(2) for lightweight aggregate kilns. Approximately 200 HWCs are complying with these standards.

EPA will be reviewing these standards as a result of the D.C Circuit Court of Appeals' approval in June 2009 of EPA's motion for voluntary remand of the emission standards. Any revised standards would be no less stringent than the current standards.

#### 8.3.5 Coal-fired power plants

At present, the largest single source of anthropogenic mercury emissions in the country 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 (70 FR 15994; March 29, 2005). EPA has initiated a rulemaking effort to develop emission standards under Clean Air Act section 112(d) for emissions of hazardous air pollutants (including mercury) from coal- and oil-fired electric utility steam generating units. Consistent with a Consent Decree, the Agency intends to issue final emission standards for these units by the end of 2011.

#### 8.3.6 Other

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 to which the American Hospital Association has committed, will contribute to reduced emissions from waste combustion.

# 9 References

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<sup>&</sup>lt;sup>25</sup> On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses in this document.

<sup>&</sup>lt;sup>26</sup> On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses in this document.

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

Source	Ecosystem type	Fish species	MethylHg/ total Hg ratio
Hammerschmidt et al. 1999	Freshwater lakes in Wisconsin, USA	Yellow perch (Perca flavescens)	mean: 0.95 range: 0.84 to 0.97
Becker and 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 dolomieui</i> ) Walleye ( <i>Stizostedion vitreum</i> )	> 0.90 Note: Authors did not provide specific percentages for individual species.
Grieb et al. 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.
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
Lasorsa and 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.
Kannan, et al. 1998	Estuaries in South Florida	Hardhead catfish ( <i>Arius felis</i> ) White grunt ( <i>Haemulon plumieri</i> ) Sand perch ( <i>Diplectrum formosum</i> ), Lane snapper ( <i>Lutjanus synagris</i> ) Gafftopsail catfish ( <i>Bagre marinus</i> ) Pinfish ( <i>Lagodon rhomboides</i> ) Spot ( <i>Leiostomus xanthurus</i> ) Pigfish ( <i>Orthopristis chrysoptera</i> ) Sand seatrout ( <i>Cynoscion arenarius</i> ) Brown shrimp ( <i>Penaeus aztecus</i> )	0.90 0.91 0.91 0.97 0.71 0.78 0.75 0.82 0.85 0.72 Note: Author sampled the 10 fish species at 20 locations.
Jackson 1991	Lakes and reservoirs in northern Manitoba, Canada	Walleye (Stizostedion vitreum) Northern pike (Esox lucius) Lake whitefish (Coregonus clupeaformis)	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.

Source	Ecosystem type		MethylHg/ total Hg ratio
Wagemann et al. 1997	Sampling location not provided; presumed to be from Canadian waters	Walleye (Stizostedion vitreum)	mean 1.00 Note: Authors did not provide more specific information.

For trophic level assignments for specific fish species, refer to tables 6-4 and 6-6 of the 2000 Human Health BAF guidance (USEPA 2003). Additional information on trophic level assignments is in the appendix of that guidance (<a href="http://www.epa.gov/waterscience/criteria/humanhealth/method/tsdvol2.pdf">http://www.epa.gov/waterscience/criteria/humanhealth/method/tsdvol2.pdf</a>).

# Appendix B. Tables from Methylmercury Criteria Document

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

Table B1. Exposure parameters used in derivation of the water quality criterion.

(References cited in this table can be found in the 2001 methylmercury criterion document.)

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

#### Notes:

<sup>&</sup>lt;sup>a</sup> For children and women of childbearing age, intake rates are estimates of "consumers only" data (as described in USEPA 2000a).

<sup>&</sup>lt;sup>b</sup> For adults in the general population, intake rates are estimates of all survey respondents to derive an estimate of long-term consumption (USEPA).

<sup>&</sup>lt;sup>c</sup> This is the 90th percentile freshwater and estuarine fish consumption value.

<sup>&</sup>lt;sup>d</sup> Inhalation rates for children and women of childbearing age from USEPA, 1997d. Inhalation rates for adults in the general population from USEPA (1994).

<sup>&</sup>lt;sup>e</sup> Pica child soil ingestion.

Table B2. Average mercury concentrations in marine fish and shellfish<sup>a</sup>

(References cited in this table can be found in the 2001 methylmercury criteria document.)

Species	Concentration <sup>b</sup> (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 <sup>d</sup>
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, Rainbow*	0.1
Herring	0.013	Snapper*	0.25
Kingfish	0.10	Sturgeon	0.235
Mackerel*	0.081	Swordfish*	0.95 <sup>e</sup>
Mullet	0.009	Tuna*	0.206
Ocean Perch*	0.116	Whiting (silver hake)*	0.041
Pollock*	0.15	Whitefish*	0.054 <sup>f</sup>
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 <sup>d</sup>
Molluscan Ceph	alopods		·
Octopus*	0.029	Squid*	0.026

#### Notes

<sup>\*</sup>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 (USEPA 2000a).

<sup>&</sup>lt;sup>a</sup> More current information on commercial fish and shellfish is provided by the Food and Drug Administration at <a href="http://www.cfsan.fda.gov/%7Efrf/sea-mehg.html">http://www.cfsan.fda.gov/%7Efrf/sea-mehg.html</a>.

<sup>&</sup>lt;sup>b</sup> Mercury concentrations are from NOAA (1978) as referenced in the NMFS database, as reported in USEPA (1997c) unless otherwise noted, measured as micrograms (μg) of mercury per gram (g) wet weight of fish tissue.

<sup>&</sup>lt;sup>c</sup> Mercury data for flounder were used to estimate mercury concentration in marine flatfish for intake calculations.

<sup>&</sup>lt;sup>d</sup> Mercury concentration data are from Stern et al. (1996) as cited in USEPA (1997f).

<sup>&</sup>lt;sup>e</sup> Mercury concentration data are from U.S. FDA Compliance Testing as cited in USEPA (1997f).

<sup>&</sup>lt;sup>f</sup> Mercury concentration data are from U.S. FDA (1978) compliance testing as described in the NMFS database, as cited in USEPA (1997f).

Table B3. 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 x 10 <sup>-9</sup>	0.0047	0.004
Drinking water intake <sup>a</sup>	5.6 x 10 <sup>-8</sup>	0.0605	0.006
Nonfish dietary intake	0	0	0
Marine fish intake	2.7 x 10 <sup>-5</sup>	29.33	27
Air intake	4.6 x 10 <sup>-9</sup>	0.005	0.005
Soil intake	1.3 x 10 <sup>-9</sup>	0.0014	0.001

#### Note:

<sup>&</sup>lt;sup>a</sup> 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	Quantitation Level or ML <sup>a</sup>	Technique	Known studies or literature references using the techniques in this method
Method 1630, with draft modifications for tissue (Recommended method – see section 4.1.3)	Methylmercury in tissue	0.001 mg/kg 0.002 mg/kg	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.	<ul> <li>EPA Cook Inlet Contaminant Study</li> <li>Lake Michigan fish and invertebrates, Mason and Sullivan 1997</li> <li>Northeastern Minnesota lake plankton, Monson and Brezonik 1998<sup>b</sup></li> <li>Method performance testing in freshwater and marine fish, Bloom 1989</li> </ul>
Method 1631, draft appendix A (Recommended method – see section 4.1.3)	Total mercury in tissue, sludge, and sediment	0.002 mg/kg	Digest tissue with HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> . Dilute digestate with BrCl solution to destroy remaining organic material. Analyze digestate per method 1631: 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 <sub>2</sub> 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.	<ul> <li>EPA National Fish Tissue Study (&gt;1,000 samples over 4-year period)</li> <li>EPA Cook Inlet Contaminant Study</li> <li>Lake Michigan fish and invertebrates, Mason and Sullivan 1997</li> <li>Northeastern Minnesota lake plankton, Monson and Brezonik 1998<sup>b</sup></li> <li>Method performance testing in freshwater and marine fish, Bloom 1989</li> </ul>
Method 245.6	Total mercury in tissue	0.020 mg/kg	Sulfuric and nitric acid digestion, oxidation with potassium permanganate and potassium persulfate, SnCl <sub>2</sub> reduction, CVAAS detection	Unknown
Draft method 7474 (SW-846)	Total mercury in sediment and tissue	40 mg/kg	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.

#### Notes:

<sup>&</sup>lt;sup>a</sup> Quantitation level or minimum level (ML) is considered the lowest concentration at which a particular contaminant can be quantitatively measured using a specified laboratory procedure for monitoring of the contaminant.

<sup>&</sup>lt;sup>b</sup> Used similar techniques but used a methylene chloride extraction instead of the distillation.

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

Method	Forms/species and applicable matrices	Quantitation Level or ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1630 <sup>a</sup> (Recommended method – see section 4.1.3)	Methylmercury in water	0.06 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 $Hg^0$ followed by CVAFS detection.	<ul> <li>USEPA Cook Inlet Study</li> <li>USEPA Savannah River TMDL study</li> <li>Northern Wisconsin Lakes, Watras et al. 1995</li> <li>Lake Michigan waters, Mason and Sullivan 1997</li> <li>Anacostia River Study, Mason and Sullivan 1998</li> <li>Northeastern Minnesota lakes, Monson and Brezonik 1998<sup>b</sup></li> <li>Poplar Creek, TN CERCLA Remedial Investigation of surface water, sediment, and pore water, Cambell et al. 1998<sup>c</sup></li> <li>Scheldt estuary study of water, polychaetes, and sediments, Baeyens et al. 1998</li> </ul>
UW-Madison SOP for MeHg Analysis <sup>a</sup>	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.	<ul> <li>Lake Michigan tributaries to support GLNPO's LMMB Study</li> <li>Fox River, WI, waters and sediments, Hurley et al. 1998</li> </ul>
USGS Wisconsin - Mercury Lab SOPs 004 <sup>a</sup>	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 <sup>a</sup>	Methylmercury in water	0.04 ng/L	Distillation (heat) and N <sub>2</sub> flow, HCl and copper sulfate. Addition of acetate buffer and ethylation with sodium tetraethyl borate. Purge with N <sub>2</sub> 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 Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by GC Separation with CVAFS Detection.

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

Method	Forms/species and applicable matrices	Quantitation Level or ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 1631, revision E <sup>d</sup> (CVAFS) (Recommended method – see section 4.1.3)	Total or dissolved mercury in water	ML = 0.5 ng/L (MDL = 0.2 ng/L)	Oxidize all Hg compounds to Hg(II) with BrCI. Sequentially pre-reduce with hydroxylamine hydrochloride to destroy the free halogens and reduce with SnCl <sub>2</sub> to convert Hg(II) to Hg(0). Hg(0) is purged from solution with N <sub>2</sub> 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 <sup>d</sup> (CVAAS)	Total or dissolved mercury in wastewater	200 ng/L	$H_2SO_4$ and $HNO_3$ digestion, $KMnO_4$ , $K_2S_2O_8$ oxidation + heat, cool +NaCl- $(NH_2OH)_2 \cdot H_2SO_4$ , $SnSO_4$ , aeration. Detection by CVAAS.	Effluent guideline development studies for the Meat Products Industry, Metal Products and Machinery Industry, and Waste Incinerators
EPA 245.2 <sup>d</sup> (CVAAS)	Total or dissolved mercury in wastewater and sewage	200 ng/L	$\mbox{H}_2SO_4$ and $\mbox{HNO}_3$ added, $\mbox{SnSO}_4,$ $\mbox{NaCl-}(\mbox{NH}_2\mbox{OH}_2\cdot\mbox{H}_2\mbox{SO}_4,$ $\mbox{KMnO}_4$ , $\mbox{K}_2\mbox{S}_2\mbox{O}_8$ , 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 <sub>4</sub> added, cool +NaCl-(NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnSO <sub>4</sub> , aeration. Detection by CVAAS.	Pharmaceutical industry effluent guideline development study
EPA 245.7 <sup>d</sup> (CVAFS) (Recommended method – see section 4.1.3)	Total or dissolved mercury in water	ML = 5 ng/L; (MDL = 1.8 ng/L) <sup>e</sup>	HCI, KBrO <sub>3</sub> /KBr, NH <sub>2</sub> OH·HCI, SnCl <sub>2</sub> , 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 <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> added, KMnO <sub>4</sub> added, K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> added + heat, cool +NaCl-(NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnSO <sub>4</sub> , aeration of sample. CVAAS detection.	Method is similar to and cites performance data given in EPA 245.5.

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

Method	Forms/species and applicable matrices	Quantitation Level of ML	Sample preparation	Known studies or literature references using the techniques in this method
EPA 7471B (CVAAS)	Total or dissolved mercury in solid wastes and semisolid wastes	200 ng/L (IDL)	$H_2SO_4$ and $HNO_3$ added, $KMnO_4$ added, $K_2S_2O_8$ added + heat, cool +NaCl-(NH $_2$ OH) $_2$ ·H $_2SO_4$ , 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 750°C in oxygen atmosphere. Decomposition products carried into catalytical furnace for completed oxidations, then to algamated trap. Mercury is thermally desorbed and determined by CVAA.	Unknown
Draft Method 7474 (SW-846) <sup>f</sup>	Total mercury in sediment and tissue	20 ng/g	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.
EPA 1620 (CVAAS)	Mercury in water, sludge, and soil	200 ng/L	$\rm H_2SO_4$ and $\rm HNO_3$ added, $\rm KMnO_4$ , $\rm K_2S_2O_8$ + heat, cool +NaCl- (NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnSO <sub>4</sub> , aeration. CVAAS detection.	Industry effluent guideline development studies
SM 3112B (CVAAS)	Total or dissolved mercury in water	500 ng/L	H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> added, KMnO <sub>4</sub> added, K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> added + heat, cool +NaCl (NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnCl <sub>2</sub> or SnSO <sub>4</sub> , aeration. CVAAS determination.	Unknown
ASTM D3223- 97, 02 (CVAAS)	Total or dissolved mercury in water	500 ng/L	H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> added, KMnO <sub>4</sub> added, K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> added + heat, cool +NaCl (NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnSO <sub>4</sub> , aeration. CVAAS determination.	Unknown
AOAC 977.22 (Atomic absorption spectrometry)	Total or dissolved mercury in water	200 ng/L	H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> added, KMnO <sub>4</sub> added, K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> added + heat, cool +NaCl (NH <sub>2</sub> OH) <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub> , SnSO <sub>4</sub> , aeration. Determine mercury by CVAA.	Unknown

*Notes:* (1) CVAAS = cold vapor atomic absorption spectrometry.

<sup>(2)</sup> CVAFS = cold-vapor atomic fluorescence spectrometry.

<sup>(3)</sup> ASTM and AOAC analytical methods are available from the respective organization.

<sup>&</sup>lt;sup>a</sup> All four methylmercury methods above are based on the work of Bloom 1989, as modified by Horvat et al. 1993, and are virtually identical as a result.

<sup>&</sup>lt;sup>b</sup> Used similar techniques but used a methylene chloride extraction instead of the distillation.

<sup>&</sup>lt;sup>c</sup> Used similar techniques but omitted the distillation procedure.

<sup>&</sup>lt;sup>d</sup> Promulgated and approved under 40 CFR part 136, Table 1B.

<sup>&</sup>lt;sup>e</sup> The method detection level (MDL) is the minimum concentration of an analyte (substance) that can be measured and reported with a 99 percent confidence that the analyte concentration is greater than zero as determined by the procedure set forth in appendix B of 40 CFR part 136.

<sup>&</sup>lt;sup>f</sup> Provided for reference purposes only. EPA recommends using method 1631 for analyzing mercury for water and fish tissue.

# Appendix D. Synopsized Mercury TMDLs Developed or Approved by EPA

- I. Ochlockonee Watershed, Georgia
- II. Arivaca Lake, Arizona
- III. McPhee and Narraguinnep Reservoirs, Colorado
- IV. Clear Lake, California
- V. Cache Creek, California
- VI. Minnesota Statewide Mercury Total Maximum Daily Load

# 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, Georgia has used a numeric "interpretation" of its narrative water quality standard for toxic substances to ensure that a TMDL will protect human health. The numeric interpretation of its narrative water quality standard is a 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 g/day or less of freshwater fish.

This approach is consistent with EPA's recommended water quality criterion for the protection of human health from methylmercury, described in the document *Water Quality Criterion for the Protection of Human Health: Methylmercury* (USEPA 2001a). The methodology uses a "weighted consumption" approach. When only trophic level 3 and 4 fish have been collected, the methodology assumes that 8 g/day (58.4 percent) of the total fish consumption is trophic level 3 fish (e.g., catfish and sunfish) and 5.7 g/day (41.6 percent) is 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

```
Weighted fish tissue concentration = (avg. trophic 4 conc. x.416) + (avg. trophic 3 conc. x.584)
```

where:

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average trophic level 3 concentration = 0.2 mg/kg
average 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, 0.3 mg/kg. To determine this concentration, EPA used the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000b). EPA also used the recommended national values from the *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 g/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 2000 and March and April 2001. From this site-specific data, EPA determined a representative weighted BAF. The BAF was calculated

by taking the average calculated BAF from each of the two trophic levels. The BAF calculation also used 0.17 as the measured fraction of the total mercury as methylmercury. 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 concentration was calculated as

 $WQS = \underline{((reference\ dose - RSC)\ x\ body\ weight\ x\ units\ conversion)}$ (consumption rate x weighted BAF x 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. Sixteen water point sources in the Ochlockonee River watershed could have mercury in their discharges.

According to a review of the *Mercury Study Report to Congress* (USEPA 1997c), significant potential air emission sources include coal-fired power plants, waste incinerators, cement and lime kilns, smelters, 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 wet and dry deposition of mercury as a function of air emissions and global sources, and it was used to calculate wet and dry deposition rates for south Georgia.

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. The MDN data were compared with the RELMAP deposition predictions and the MDN data were found to be substantially higher. Using the MDN data, the average annual wet deposition rate was determined to be  $12.75~\mu g/square$  meter. The dry deposition rate was determined to be  $6.375~\mu g/square$  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. The linkage analysis helped estimate the 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 approach 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 it 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, 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 D1.

Table D1. Annual average mercury load from each subbasin

Watershed	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 Ochlocklonee	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, as well as particulate material. Local equilibrium is assumed so that the distribution of the chemical among the species and phases is defined by distribution or partition coefficients. The predicted mercury concentrations are shown in table D2.

Table D2. 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 enter the Ochlockonee River, the current loading conditions were evaluated and the instream concentration was determined using the modeling approach described above. This allowed 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 gave a TMDL load of 1.22 kg/yr mercury, which 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 kg/yr. Because EPA's assessment indicates that over 99 percent of the current loading of mercury is from atmospheric sources, 99 percent of the allowable load is assigned to the load allocation and 1 percent of the allowable load is assigned to 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 kg/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, a number of activities to address remaining sources of mercury are planned or under way, and EPA expects that further reductions in mercury loadings will occur over time as a result of those activities. EPA is not able to estimate the reductions in mercury deposition to the Ochlockonee River watershed that will be achieved from future activities. As contemplated by CWA section 303(d)(1)(C), however, 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 (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 on human fetuses even at minute quantities and that it 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-permitted 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 by discharging mercury only at concentrations below the applicable water quality standard, 1.6 ng/L, or by implementing a pollutant minimization program.

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 lower 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. EPA also recognizes, however, 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' waste load allocation 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 dischargers

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 standards 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  $\mu$ g/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  $\mu$ g/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 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 for developing a model and analyzing 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 the mercury load to the lake include natural background load from the watershed, atmospheric deposition, and possible nonpoint load 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 is also present within the parent rock formations of the Arivaca watershed, although no concentrated ore deposits are known.

The net contributions of 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. These data show that 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.

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 like bottles and plates. Samples were taken at three different locations of the Ruby Dump: the 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 the 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. A review of Mercury Study Report to Congress (USEPA 1997c) and a search of EPA's AIRS database of permitted point sources found 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 that 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  $5.3 \,\mu g/m^2/yr$  by wet deposition and  $7.1 \,\mu g/m^2/yr$  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 more wet deposition and less dry deposition than Caballo because more of the particulate mercury and reactive gaseous mercury that contribute to dry deposition are scavenged at a site with higher rainfall.

### Loading Capacity—Linking Water Quality and Pollutant Sources

The linkage analysis in a TMDL defines the connection between numeric targets and identified sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, the associated numeric targets, and the identified sources. This linkage analysis provides the basis for estimating total assimilative capacity and any needed load reductions. Specifically, for the linkage analysis in the Arivaca TMDL, models of watershed loading of mercury were used together with a model of mercury cycling and bioaccumulation in the lake. This approach 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 through 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 it 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 D3. A background loading estimate was first calculated and then combined with estimates of loads from individual hot spots. Most 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.

Table D3. Annual total mercury load to Arivaca Lake

	Mercury loading to lake (g/year)			
Watershed 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

Loading from the Ruby Dump was calculated separately, but it 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.

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 data for 1980 through 1995 were 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 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.

The results of the model calibration are shown in table D4. The model calculations are the predicted annual ranges after the model has reached steady state. The observed concentrations are from July 1997.

Table D4. 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 a portion of the loading capacity in reserve to provide a margin of safety (MOS), as provided for in the TMDL regulation. The allocations and MOS are shown in table D5. 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 D5. 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
Load allocations			
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 most 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 g/year of mercury.

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 no reliable estimates are available, 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 might be suitable for further investigation include the following:

- Hypolimnion aeration or mixing
- Sulfur chemistry modification
- Alum treatment
- Reduction of DOC and nutrient levels
- Dredging of 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 four meals per month for nonpregnant adults and one meal per month for women who are pregnant, nursing, or planning to become pregnant and children nine years of age or younger. The criterion is applied to an average-age top predator. In 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 onto the watershed, including deposition and storage in snowpack. A summary of the mercury load estimates for McPhee Reservoir is presented in table D6.

Reservoir	Water- shed runoff (g/yr)	Water- shed sediment (g/yr)	Inter- basin transfer (g/yr)	Atmos. deposition (g/yr)	Total (g/yr)	Load per volume (mg/ac-ft)	Load per surface area (mg/m²)
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. There are large mining districts 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 the two reservoirs. Because no direct measurements of atmospheric deposition of mercury are available, 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 2,592 g/year of mercury. Narraguinnep Reservoir's loading capacity was estimated at 39.1 g/year of mercury. This is the maximum rate of loading consistent with meeting the numeric target of 0.5 mg/kg in fish tissue. Because of 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 g/yr), while that for 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). Summaries of the TMDL allocations and needed load reductions for the McPhee and Narraguinnep Reservoirs are presented in tables D7 and D8, respectively.

Table D7. 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	2,592		

Note: Measurements in g/year of mercury.

Table D8. 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		

Note: Measurements in g/year of mercury.

### IV. Clear Lake, California

### Description of the Applicable Water Quality Standards

EPA promulgated the California Toxics Rule (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 through 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 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 composed 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 consists 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 American Indian tribes use the 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

present 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 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 the 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 those in other parts of Clear Lake. In contrast to the mercury in SBMM ground water, the 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 on flow rates. Loads in average water years are 18 kg/year, approximately 3 percent of the 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, approximately 0.3 percent of the 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, such as sulfide and sulfate concentrations, temperature, and organic carbon, affect methylation or concentrations of methylmercury. 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 demonstrating that 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 the 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, the Regional Board staff was unable to refine these relationships to incorporate the 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 reducing 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 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 D9 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 D10. 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 D9. Summary of mercury load allocations

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

Table D10. Sediment goals for mercury in Clear Lake

Site designation	Location	Sediment mercury goal (mg/kg dry weight) <sup>a</sup>
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 <sup>b</sup> OA-02 <sup>b</sup> OA-03 <sup>b</sup> OA-04 <sup>b</sup> Narrows O1	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 <sup>c</sup> 16 <sup>c</sup> 16 10 3

#### Notes:

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 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 D10.

EPA anticipates implementing additional actions to address the ongoing surface and ground water releases from 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

<sup>&</sup>lt;sup>a</sup>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).

<sup>&</sup>lt;sup>b</sup>Sediment goal is part of the load allocation for SBMM.

<sup>&</sup>lt;sup>c</sup>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.

site. EPA also plans to investigate what steps are appropriate under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to address the existing contamination in the lakebed sediments from past releases from 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 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 of 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 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 on 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 five years after the effective date of this amendment and implement load reduction plans within five years thereafter. The goal is to complete the load reductions within 10 years of implementation plan approval.

The Regional Board will work with the American Indian tribes in the Clear Lake watershed on mercury reduction programs for the tributaries and surface water runoff. It will solicit the tribes' participation in developing 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 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 the Clear Lake watershed and depositing from air onto the lake surface are established at the existing input rate, estimated to be 1 to 2 kg/year.

### V. Cache Creek, California

### Description of the Applicable Water Quality Standards

EPA promulgated the California Toxics Rule (CTR) in May 2000 (65 FR 31682). The CTR contains a water quality criterion of 50 ng/L total recoverable mercury for waters designated for water and organism consumption, and it was intended to protect humans from exposure to mercury in drinking water and through fish and shellfish consumption. This criterion is enforceable in California for all waters with a municipal or domestic water supply designated use, and it is applicable to all waters in the Cache Creek watershed. The State of California, however, does not consider this criterion sufficiently protective of human and wildlife consumers of fish in the watershed.

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 Cache Creek, Bear Creek, and Harley Gulch at the same time it adopted mercury TMDLs for those waterbodies. The state's water quality criteria are expressed as concentrations in fish tissue and are intended to protect designated uses, which include human and wildlife fish consumption. The applicable criteria are as follows: for Cache Creek and Bear Creek, the average methylmercury concentration shall not exceed 0.23 mg methylmercury/kg wet weight of muscle tissue in trophic level 4 fish 250–350 mm (piscivorous species, including bass and catfish), and 0.12 mg methylmercury/kg wet weight of muscle tissue in trophic level 3 fish 250–350 mm, or if not available, a minimum of 125 mm (bluegill, sunfish, and sucker); for Harley Gulch, the average methylmercury concentration shall not exceed 0.05 mg methylmercury/kg wet weight in whole, trophic level 2 and 3 fish 75–100 mm total length (hardhead, California roach, or other small resident species). Because Harley Gulch does not support larger, trophic level 3 and 4 fish, no water quality criteria for these larger fish were proposed in that waterbody.

These water quality standards permit safe consumption of about 22–40 g/day of Cache or Bear Creek fish (3 to 5.4 meals/month). In Cache and Bear creeks, the standards protect wildlife species, including bald eagle, peregrine falcon (state endangered), river otter, American mink, mergansers, grebes, and kingfishers. In Harley Gulch, the standards protect wildlife species, including small mammals, herons, and kingfishers.

#### Source Assessment

The Cache Creek watershed is impaired due to elevated levels of mercury in the water and in fish tissue. Because Cache Creek is a primary source of mercury to the Sacramento-San Joaquin Delta Estuary, lowering mercury levels in the Cache Creek watershed will assist in protecting human and wildlife health in the delta. The TMDL

encompasses the 81-mile reach of Cache Creek between Clear Lake Dam and the outflow of the Cache Creek Settling Basin, Bear Creek from its headwaters to its confluence with Cache Creek, and the 8-mile length of Harley Gulch.

Sources of mercury entering the watershed include waste rock and tailings from historical mercury mines, erosion of naturally mercury-enriched soils, geothermal springs, and atmospheric deposition. There are multiple inactive mercury mines in the Cache Creek watershed. The Sulphur Bank Mercury Mine contributes mercury to Cache Creek at the Clear Lake outflow. The Sulphur Creek mining district includes eight mines that drain predominately to Bear Creek via Sulphur Creek and four mines in the Bear Creek Basin. Harley Gulch receives inputs from the Turkey Run and Abbott mines. The Reed Mine drains to Davis Creek, a tributary to Cache Creek.

Historical mining activities in the Cache Creek watershed discharged and continue to discharge large volumes of inorganic mercury (termed total mercury) to creeks in the watershed. Much of the mercury discharged from the mines is now distributed in the creek channels and floodplain downstream from the mines. Natural erosion processes can be expected to slowly move the mercury downstream out of the watershed over the next several hundred years. However, current and proposed activities in and around the creek channel can enhance mobilization of this mercury. Activities in upland areas, such as road maintenance and grazing and timber activities, can add to the mercury loads reaching Cache Creek, particularly when the activities take place in areas that have elevated mercury levels. Mercury can be transformed to methylmercury in sediment by sulfate-reducing bacteria.

Cache Creek. In Cache Creek the watershed above Rumsey is the major source of methylmercury. The highest concentrations and production rates were observed below the mercury mines in Harley Gulch, in Sulphur and Bear creeks, and in the canyon above Rumsey. Lower methylmercury concentrations in water were measured in the North Fork and Cache Creek below Clear Lake Dam, which have lower inorganic mercury concentrations in sediment.

The sources of total mercury in Cache Creek largely parallel the sources of methylmercury. Most mercury derives from the watershed upstream of Rumsey. On a five-year average, mercury loads from the mine-related tributaries (Bear Creek, Harley Gulch, and Davis Creek), North Fork Cache Creek and Clear Lake contributed about 15 percent of the mercury loads measured in Cache Creek at Rumsey. In years with high degrees of runoff or extreme erosional events, inputs from the inactive mines would be much greater. The majority of the inorganic mercury loads were from unnamed sources, which include smaller, unmeasured tributaries and mercury in the Cache Creek bed and banks. Clean sediment entering the watershed below Rumsey diluted sediment mercury concentrations.

Bear Creek. The Bear Creek watershed upstream of all mine inputs contributes less than 10 percent to each of the loads of methylmercury and total mercury in Bear Creek. Sulphur Creek contributes about half of each of the methylmercury and total mercury loads in Bear Creek. The remainder of the Bear Creek methylmercury likely comes from production within the channel and seepage of underground springs. The rest of the mercury load in Bear Creek likely derives from the remobilization of mine waste deposited in the floodplain.

Harley Gulch. Much of the methylmercury in Harley Gulch is likely produced in a wetland area in the West Branch Harley Gulch, downstream of the inactive mercury mines. Over 90 percent the total mercury load in Harley Gulch is estimated to come from the West Branch, where the mines are. Total mercury loads from the mines may be underestimated due to a lack of data collected during heavy rainfall events. An alluvial fan, likely containing mine waste, at the confluence of Harley Gulch and Cache Creek, might contribute to the unknown source of mercury in the Cache Creek canyon.

### Loading Capacity—Linking Water Quality Pollutant Sources

Total mercury in the creeks is converted to methylmercury by bacteria in the sediment. The concentration of methylmercury in fish tissue is directly related to the concentration of methylmercury in the water. The concentration of methylmercury in the water column is controlled in part by the concentration of total mercury in the sediment and the rate at which the total mercury is converted to methylmercury. The rate at which total mercury is converted to methylmercury varies from site to site; some sites (wetlands and marshes) having greatly enhanced methylation rates.

The linkage analysis describes the relationship between methylmercury concentrations in water and in large fish. Data collected in 2000 and 2001 show statistically significant relationships between concentrations of aqueous unfiltered methylmercury in water and large trophic level 3 and 4 fish. In Cache Creek, large trophic level 3 fish tissue concentrations (Sacramento sucker), normalized to 290 mm (from Slotten et al. 2004), were regressed against aqueous unfiltered methylmercury concentrations (Y= 584.8X + 30.2; P < 0.001, R2 = 0.98). In Cache Creek, large trophic level 4 fish tissue concentrations (largemouth bass, small mouth bass, and pikeminnow, depending on site), normalized to 305 mm (from Slotton et al. 2004), were regressed against aqueous unfiltered methylmercury concentrations (Y = 2970.8X - 180.6; P < 0.01, R2 = 0.9). Using these relationships, staff determined concentrations of unfiltered methylmercury in water that correspond to the proposed criteria for trophic levels 3 and 4 fish (0.12 mg/kg and 0.23 mg/kg, respectively). These concentrations are 0.15 ng/l for trophic level 3 fish and 0.14 ng/L for trophic level 4 fish. To ensure meeting both fish tissue criteria, staff selected 0.14 ng/L as the aqueous unfiltered methylmercury goal for Cache Creek.

For Bear Creek, the methylmercury goal of 0.06 ng/L represents the best estimate of the annual, median aqueous (unfiltered) concentration of methylmercury needed to attain the target of 0.23 mg/kg wet weight in trophic level 4 fish. Harley Gulch has no trophic level 4 fish, so the above relationships could not be used. Based on bioaccumulation factors specific to Harley Gulch, the aqueous methylmercury goal for Harley Gulch is 0.09 ng/L.

### **Allocations**

The TMDL presents a plan to reduce mercury and methylmercury loads. Reducing the methylmercury loads will require a multi-faceted approach that includes controlling inorganic mercury loads and limiting the entry of inorganic mercury into sites with high rates of methylmercury production. Inorganic mercury loads may be controlled through remediation of mercury mines, erosion control, removal of highly contaminated sediment, and other activities. In addition to addressing inorganic mercury loads, the TMDL discusses limits to the production of methylmercury in constructed

impoundments, such as gravel pits and water storage facilities. Identification and evaluation of the unknown mercury source(s) in the upper basin are essential to attain the Cache Creek methylmercury targets in fish tissue and to help reduce mercury in sediment of the Sacramento-San Joaquin Delta Estuary.

Since methylmercury in the water column is directly related to mercury levels in fish, the following methylmercury load allocations are assigned to tributaries and the main stem of Cache Creek.

Methylmercury Load Allocations. Tables D11 and D12 provide methylmercury load allocations for Cache Creek, its tributaries, and instream methylmercury production. Allocations are expressed as a percent of existing methylmercury loads. The methylmercury allocations will be achieved by reducing the annual average methylmercury (unfiltered) concentrations to site- specific, aqueous methylmercury goals, which are 0.14 ng/L in Cache Creek, 0.06 ng/L in Bear Creek, and 0.09 ng/L in Harley Gulch. The allocations in tables D11 and D12 apply to sources of methylmercury entering each tributary or stream segment. In aggregate, the sources to each tributary or stream segment must have reductions of methylmercury loads as shown below.

Table D12 provides the load allocation within Bear Creek and its tributaries to attain the allocation for Bear Creek described in table D11. The inactive mines listed in the implementation summary are assigned a 95 percent total mercury load reduction. These mines include mines in the Harley Gulch Sulphur Creek and Bear Creek watersheds. Reductions in mercury loads from mines, erosion, and other sources in the Sulphur Creek watershed are expected to reduce in-channel production of methylmercury to meet the Sulphur Creek methylmercury allocation.

Table D11. Cache Creek methylmercury allocations

Source	Existing annual load (g/yr)	Acceptable annual load (g/yr)	Allocation (% of existing load)
Cache Creek (Clear Lake to North Fork confluence)	36.8	11	30%
North Fork Cache Creek	12.4	12.4	100%
Harley Gulch	1.0	0.04	4%
Davis Creek	1.3	0.7	50%
Bear Creek at Highway 20	21.1	3	15%
Within-channel production and ungauged tributaries	49.5	32	65%
		7 <sup>a</sup>	10% <sup>a</sup>
Total of loads	122	66	54%
Cache Creek at Yolo <sup>b</sup>	72.5	39	54%
Cache Creek Settling Basin Outflow <sup>c</sup>	87	12	14%

Notes:

<sup>&</sup>lt;sup>a</sup>The allocation includes a margin of safety, which is set to 10% of the acceptable loads. In terms of acceptable annual load estimates, the margin of safety is 7 g/yr.

<sup>&</sup>lt;sup>b</sup>Cache Creek at Yolo is the compliance point for the tributaries and Cache Creek channel for meeting the allocations and aqueous goals. Agricultural water diversions upstream of Yolo remove methylmercury (50 g/yr existing load).

<sup>&</sup>lt;sup>c</sup>The Settling Basin Outflow is the compliance point for methylmercury produced in the Settling Basin.

Table D12. Bear Creek methylmercury allocations

Source	Existing Annual Load (g/yr)	Acceptable Annual Load (g/yr)	Allocation (% of existing load)
Bear Creek at Bear Valley Road	1.7	0.9	50%
Sulphur Creek	8	0.8	10%
In-channel production and ungauged tributaries	11.4	1	10%
		0.3 <sup>a</sup>	10% <sup>a</sup>
Total of loads	21.1	3	15%
Bear Creek at Highway 20 <sup>b</sup>	21.1	3	15%

#### Notes:

To achieve the water quality objectives and the methylmercury allocations listed in tables D11 and D12, the following actions are needed: (1) reduce loads of total mercury from inactive mines; (2) where feasible, implement projects to reduce total mercury inputs from existing mercury-containing sediment deposits in creek channels and creek banks downstream from historical mine discharges; (3) reduce erosion of soils with enriched total mercury concentrations; (4) limit activities in the watershed that will increase methylmercury discharges to the creeks and, where feasible, reduce discharges of methylmercury from existing sources; and (5) evaluate other remediation actions that are not directly linked to activities of a discharger. Because methylmercury is a function of total mercury, reductions in total mercury loads are needed to achieve the methylmercury load allocations. Methylmercury allocations will be achieved in part by natural erosion processes that remove mercury that has deposited in creek beds and banks since the start of mining.

The proposed Basin Plan Amendment for mercury in San Francisco Bay assigns a reduction in total mercury loads from the Sacramento–San Joaquin River Delta of 110 kg/yr. Cache Creek is a major source of mercury to the Delta. To attain the San Francisco Bay reduction, loads of total mercury exiting Cache Creek should be reduced. Reductions in total mercury loads to the inactive mines in Harley Gulch and the Bear Creek watershed assigned by this TMDL and proposed changes to the Cache Creek Settling Basin, which would increase the mass of mercury retained in the basin, would create significant reductions in loads from Cache Creek.

<sup>&</sup>lt;sup>a</sup>The allocation includes a margin of safety, which is set to 10% of the acceptable loads. In terms of acceptable annual load estimates, the margin of safety is 0.3 g/yr.

<sup>&</sup>lt;sup>b</sup>Bear Creek at Highway 20 is the compliance point for Bear Creek and its tributaries.

# VI. Minnesota Statewide<sup>27</sup> Mercury Total Maximum Daily Load

### Description of the Applicable Water Quality Standards and TMDL Target

Minnesota Rules Chapters 7050.0222 and 7052.0100 set forth chronic numeric water quality standards based on total mercury concentrations in the water column. The wildlife-based standard applicable to only the waters of the Lake Superior Basin is 1.3 ng/L, while the human health-based standard applicable to waters outside the Lake Superior Basin is 6.9 ng/L. In addition to these numeric standards, Chapter 7050.0150, subpart 7, provides a narrative standard for assessing the contaminants in fish tissue. The narrative standard states that a waterbody is impaired when the Minnesota Department of Health recommends a consumption frequency of less than one meal per week for any member of the population.

To establish the two regional TMDLs, Minnesota selected a target of 0.2 mg/kg fish tissue mercury concentration. Fish tissue mercury concentration was selected as the water quality target for the TMDLs because it was consistent with EPA's 2001 methylmercury fish tissue criterion. In the 2001 guidance, EPA chose to express the water quality criterion as a fish tissue concentration rather than as a water column value because fish consumption is the primary route of human exposure. Two aspects of EPA's criterion are toxicity and exposure. Minnesota relied on EPA's assessments of toxicity to humans but selected a more state-specific exposure rate. For purposes of calculating its recommended human health-based fish tissue criterion, EPA assumes that people consume 17.5 g/day of fish. Minnesota selected a higher consumption rate, 30 g/day of fish, based on several surveys of the fish-eating habits of upper-Midwest recreational fishers.

Since Minnesota's water quality standards are water column chronic standards for total mercury, not fish tissue concentration standards, Minnesota demonstrated a link from the fish tissue mercury concentration TMDL target to the numeric water column water quality standards. Bioaccumulation factors for 14 lakes representing agricultural areas, urban areas, and forested areas were used to calculate the water column concentration that would be equivalent to the 0.2 mg/kg fish tissue mercury concentration target.

### Source Assessment

Sources that Minnesota considered in developing the two regional TMDLs included atmospheric deposition, wastewater treatment plants, non-municipal waste discharges, and stormwater. Atmospheric deposition was the only significant nonpoint source of mercury identified by Minnesota. The state identified 99 percent of the total mercury load to the state as coming from atmospheric deposition. Both natural and anthropogenic

<sup>&</sup>lt;sup>27</sup> As described in Section 6 of this guidance, Minnesota divided the state into two regions, a northeast region and a southwest region, and developed a TMDL for each region. Although Minnesota's report is called a "statewide TMDL," the two regional TMDLs do not address all the mercury impairments in the state. The TMDLs address 511 of the lake and river reach impairments in Category 5 of Minnesota's 2006 Integrated Report.

sources contribute to the atmospheric deposition mercury load. Minnesota identified natural sources as contributing 30 percent to the atmospheric deposition mercury load, while the remaining 70 percent is from worldwide anthropogenic sources. Point sources that Minnesota considered included wastewater treatment plants, pulp and paper mills, taconite mines, coal-fired power plants, and one refinery. The state recognized that stormwater is considered a point source and therefore subject to wasteload allocations; however, for purposes of estimating a baseline mercury load (referred to in the TMDL report as the total source load), the mercury loadings from stormwater were included in the estimate of loadings from atmospheric deposition. Using data from two studies in Minnesota, the state concluded that the primary source of mercury to stormwater is atmospheric deposition rather than specific anthropogenic sources.

### **Loading Capacity**

Minnesota established a loading capacity for each of the two regional TMDLs. Each loading capacity was calculated by multiplying a regional reduction factor<sup>28</sup> needed to achieve the fish tissue mercury concentration target by the total source load<sup>29</sup> for each region, thus calculating a regional load reduction goal.<sup>30</sup> The load reduction goal was subtracted from the total source load to arrive at the loading capacities.

The total source load was considered the baseline condition from which reductions would be needed to achieve water quality standards. Minnesota selected the year 1990 as the baseline to which reductions would be applied. Minnesota selected 1990 as the baseline for three reasons. First, the total source load is the sum of the point source load and the nonpoint source load. The nonpoint source load is represented by total (wet and dry) mercury deposition. Minnesota's estimate of both wet and dry deposition is from lake sediment cores collected in a study conducted from 1988 to 1990. The second reason for selecting 1990 was to remain consistent with other mercury reduction baselines. The state uses 1990 as its mercury emission inventory baseline, and other state and federal plans, such as the Great Lakes Binational Toxics Strategy and the Lake Superior Lakewide Management Plan, use 1990 as a baseline for assessing mercury reductions. Minnesota selected a baseline year that was consistent with other reduction goals and targets. Last, Minnesota selected 1990 because prior to 1990 mercury use was relatively high, and then beginning in around 1990, mercury use dropped precipitously as mercury was removed from many products. For this reason Minnesota concluded that 1990 represents the end of a period when mercury emissions and fish tissue concentrations were in a steady state.

The sum of the point source load and nonpoint source load are the total source load for each region. The total source load for each region simply defines the 1990 baseline condition for the region to which the applicable reduction factor is applied.

The existing point source contribution to the total source load was calculated based on the sum of design flows for point sources within each region and mean effluent mercury concentrations. The design flows were current-day design flows, while the mean effluent

<sup>&</sup>lt;sup>28</sup> The northeast regional reduction factor is 65 percent, and the southwest regional reduction factor is 51 percent.

<sup>&</sup>lt;sup>29</sup> The baseline load for the northeast region is 1153 kg/yr, and the baseline load for the southwest region is 1628 kg/yr.

<sup>&</sup>lt;sup>30</sup> The load reduction goal for the northeast region is 749 kg/yr, and the load reduction goal for the southwest region is 830 kg/yr.

mercury concentrations were "typical" mercury concentrations unless actual facility effluent concentrations were available. Actual facility effluent concentrations were used for the coal-fired power plants, the one refinery, and the Metro and Western Lake Superior Sanitary District wastewater treatment plants. For all other point sources, typical mercury concentrations were used. A typical effluent concentration of 5 ng/L was used for wastewater treatment plants. It was based on a study by the Association of Metropolitan Sewerage Agencies, a state study of 37 NPDES facilities, and the Mercury Maps report. Minnesota relied on the Mercury Maps report in support of the mean effluent mercury concentration of 13 ng/L for pulp and paper mills, although effluent reports from one Wisconsin and one Minnesota facility show effluent concentrations in the range of 1.6 ng/L to 2 ng/L. Minnesota used its discharge monitoring database to calculate 1.5 ng/L as the mean mercury effluent concentration for taconite mines.

The existing nonpoint source contribution to the total source load was based on total mercury deposition to the state. Minnesota used sediment cores from Minnesota lakes to estimate total statewide mercury deposition as 12.5 g km<sup>-2</sup> yr<sup>-1</sup>. Minnesota used the regional surface areas for each of the two regions, along with the total mercury deposition, to estimate the nonpoint source contribution to the total source load.

The reduction factor for each region is the percent reduction in total mercury load needed to achieve the fish tissue target of 0.2 mg/kg for the 90th percentile of the standard-length fish. Fish tissue data were reviewed for the standard-size top predator fish in each region. The 90th percentile fish tissue mercury concentration and median concentrations were calculated for each region for top predator fish (walleye and northern pike). Minnesota used the difference between the 90th percentile mercury concentration in top predator fish within each region and the 0.2 mg/kg target to calculate the reduction factors. Minnesota used fish tissue data from 1988 to 1992 to establish the reduction factors. The state looked at fish tissue data from 1970 to 2002; however, to be consistent with the baseline year of 1990, fish tissue data from 1988 to 1992 were selected. Multiyear data better represent real conditions over time because they account for year-to-year variability in weather, fish populations, and sampling locations. Data for the standard-size top predator fish were used to calculate the reduction factor. Mercury bioaccumulates in fish; therefore, mercury concentrations are typically highest in the top predator fish. To account for temporal and spatial comparisons of mercury concentrations in these top predator fish, Minnesota used the standard-size top predator fish. <sup>31</sup> Top predator fish that are collected for fish tissue analysis vary in size and age. Because mercury concentrations vary with the size of fish and age of fish, it is difficult to make comparisons regarding mercury concentrations in fish without establishing a standard of comparison. Use of the standard-size fish accounted for differences in mercury concentrations due to age and size and allowed Minnesota to compare mercury concentrations across waterbodies.

<sup>&</sup>lt;sup>31</sup> Minnesota uses a standard size of 40 cm (approximately 22 inches) for walleye and 55 cm (approximately 16 inches) for northern pike.

### **Allocations**

Consistent with the regional approach used to establish the loading capacities, Minnesota did not assign waterbody-specific allocations; rather, the state established gross allocations for each region.

Minnesota assigned 1 percent of the loading capacity to point sources as the wasteload allocation for each regional TMDL. Minnesota chose 1 percent of the loading capacity based on an approach used in the Mercury Maps report to screen watersheds for significant point source impacts to identify waterbodies impaired primarily by atmospheric mercury (see appendix E on Mercury Maps). The northeast region wasteload allocation was set at 1 percent of the loading capacity, while the southwest region's wasteload allocation was set equal to the point source load portion of the total source load because it was slightly less than 1 percent of the southwest region's loading capacity and the state chose the more restrictive allocation.

Load allocations for each region were established by subtracting the wasteload allocation and any explicit margin of safety from the established loading capacity. The remaining load within each region was assigned to the load allocation. The approved loading capacity and allocations for both regional TMDLs are shown in table D13.

Table D13. Approved northeast and southwest mercury TMDLs

Region	Loading capacity	Load allocation	Wasteload allocation	Margin of safety
Northeast	1.10 kg/day	1.09 kg/day	0.01 kg/day	Implicit
Southwest	2.18 kg/day	1.55 kg/day	0.02 kg/day	0.61 kg/day

### **Appendix E. Model Descriptions**

This appendix describes currently available models discussed in this guidance. These models aid in developing bioaccumulation factors and modifying fish tissue criteria (see chapter 3), making assessments (see chapter 4), developing total maximum daily loads (TMDLs) (see chapter 6), and in carrying out related programs such as 319 Nonpoint Source Program activities, watershed management, stormwater permits, and National Pollutant Discharge Elimination System (NPDES) discharge evaluations. This appendix provides a description of each model, some examples of how or where it has been used, and a Web site for further information about each model.

### BASS (Bioaccumulation and Aquatic System Simulator)

The Bioaccumulation and Aquatic System Simulator (BASS) is a model that simulates the population and bioaccumulation dynamics of age-structured fish communities. Although BASS was specifically developed to investigate the bioaccumulation of chemical pollutants within a community or ecosystem context, it can also be used to explore population and community dynamics of fish assemblages that are exposed to a variety of non-chemical stressors such as altered thermal regimes associated with hydrological alterations or industrial activities, commercial or sports fisheries, and introductions of non native or exotic fish species.

BASS is being used to investigate methylmercury bioaccumulation in the Florida Everglades and to predict population and community dimensions of "fish health" for a regional analysis of the ecological sustainability of the Albemarle Pamlico drainage basin in North Carolina and Virginia.

Information on BASS can be found at: <a href="http://www.epa.gov/athens/research/modeling/bass.html">http://www.epa.gov/athens/research/modeling/bass.html</a>.

### Community Multi-Scale Air Quality (CMAQ) Model

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 (Byun and Ching 1999; Byun and Schere 2006; Dennis et al. 1996). 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 (Bullock and Brehme 2002; Byun and Schere 2006) 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 in version 4.3 from that described in Bullock and Brehme (2002) are as follows:

- 1. The elemental mercury (Hg<sup>0</sup>) reaction with H<sub>2</sub>O<sub>2</sub> assumes the formation of 100 percent reactive gaseous mercury (RGM) rather than 100 percent particulate mercury (Hg<sub>P</sub>).
- 2. The Hg<sup>0</sup> reaction with ozone assumes the formation of 50 percent RGM and 50 percent Hg<sub>P</sub> rather than 100 percent Hg<sub>P</sub>.

- 3. The Hg<sup>0</sup> reaction with OH assumes the formation of 50 percent RGM and 50 percent Hg<sub>P</sub> rather than 100 percent Hg<sub>P</sub>.
- 4. The rate constant for the  $Hg^0$  + OH reaction was lowered from 8.7 to 7.7 x  $10^{-14}$  cm<sup>3</sup> molecules<sup>-1</sup>s<sup>-1</sup>.

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 content 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 recent CMAQ modeling, meteorological input files were derived from a simulation of the 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 provided by McNally (2003).

These initial and boundary concentrations were obtained from the 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 NASA's Goddard Earth Observing System (GEOS). This model was run for 2001 with a grid resolution of 2 degrees x 2.5 degrees (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 grid cell. 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.

A CMAQ modeling run was performed to estimate the impact of global sources on U.S. deposition estimates. For this analysis, all non-U.S. mercury input species to the model were set to zero. By comparing the results of this analysis with the 2001 Clean Air Mercury Rule (CAMR) base case run, which included all U.S. and global mercury species, the percent of total mercury deposition attributable to global sources can be

estimated.<sup>32</sup> The model estimated that over 80 percent on average of total mercury deposition in the United States is attributable to global sources.

Due to the evolving nature of mercury modeling science, such deposition estimates have associated uncertainties. For example, it remains difficult to distinguish between the natural emissions of mercury and the re-emission of previously deposited anthropogenic mercury and there remains uncertainty in the scientific community concerning the atmospheric processes that control the oxidation state of atmospheric mercury. Thus, further advances in the current understanding of mercury chemistry could potentially lead to changes in the modeling parameters and assumptions governing the mercury chemistry in the models and therefore, changes in the estimate of the fraction deposited in the U.S. attributable to global sources.

For more information on CMAQ, see <a href="http://www.epa.gov/asmdnerl/CMAQ">http://www.epa.gov/asmdnerl/CMAQ</a>.

### **D-MCM (Dynamic Mercury Cycling Model)**

D-MCM is a food web simulation of mercury accumulation in lakes. It predicts the cycling and fate of major forms of mercury in lakes, including methylmercury, Hg (II), elemental mercury, and total mercury. It is a time-dependent mechanistic model which considers the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. D-MCM is meant for lotic (lake) systems, and is not meant to be used for lentic (streams, rivers, etc.) systems.

D-MCM can be used to develop and test hypotheses, scope field studies, improve understanding of cause and effect relationships, predict responses to changes in loading, and support design and evaluation of mitigation options. It was used in the development of mercury TMDLs for McPhee and Narraguinnep Reservoirs in Colorado and for the TMDLs for Arivaca and Pena Blanca Lakes in Arizona. The Everglades Mercury Cycling Model (E-MCM) was developed off of D-MCM and added vegetation processes and the ability to simulate multiple sediment layers for wetlands.

Information on D-MCM can be found at: <a href="http://rd.tetratech.com/DraftHgBrochurev2.pdf">http://rd.tetratech.com/DraftHgBrochurev2.pdf</a>.

### EXAMS2 (Exposure Analysis Modeling System)

EXAMS2 is a model for creating aquatic ecosystem models which can evaluate the fate, transport, and exposure concentrations of chemicals. Chemicals include synthetic organic chemicals like pesticides, industrial materials, and leachates from disposal sites. EXAMS2 core is a set of modules that link chemical properties to limnological characteristics that control the fate and transport of chemicals in aquatic systems. This model allows for both long-term analysis of chronic chemical discharges at constant release and varying release over time, and short-term analysis of chemical releases.

EXAMS2 has commonly been used to predict pesticide fate in water and soil. This model has been used to evaluate the role of hydroxyl radicals in degrading pesticides by

<sup>&</sup>lt;sup>32</sup> On February 8, 2008, the D.C. Circuit Court of Appeals vacated the Clean Air Mercury Rule and remanded portions of it to EPA, for reasons unrelated to the technical analyses cited in this guidance.

researchers at the University of Georgia. EXAMS2 was also used to simulate mercury fate in the Withlacoochee River watershed and the Ohoopee River watershed in Georgia.

Information on EXAMS2 can be found at: <a href="http://www.epa.gov/ceampubl/swater/exams/">http://www.epa.gov/ceampubl/swater/exams/</a>.

### GBMM (Grid Based Watershed Mercury Model)

EPA's Grid Based Watershed Mercury Model (GBMM) is a continuous grid-based watershed mercury loading model using the latest ArcGIS platform. It simulates the spatial and temporal dynamics of mercury from both point and non-point sources on a daily basis. The model calculates the water balance, sediment generation and transport, and mercury dynamics within a watershed. The mercury transport and transformation module simulates the following key processes:

- Mercury input from atmospheric deposition.
- Mercury assimilation and accumulation in forest canopy and release from forest litter.
- Mercury input from bedrock weathering.
- Mercury transformation in soils.
- Mercury transformation in lakes and wetlands including reduction and net methylation.
- Mercury transport through sediment and runoff.
- Mercury transport in stream channels.

GBMM accepts input data from atmospheric deposition, point sources, and natural background in time series or in digital spatial maps. By using the grid-based technology, flow and mercury dynamics can be examined at any of several points in the watershed.

The software has been peer reviewed and tested on two watersheds in Georgia, where it was used to calculate mercury TMDLs. GBMM has been used to investigate the mercury fate and transport in Brier Creek watershed located in the coastal plain of Georgia. GBMM was used to investigate detailed watershed mercury processes. The findings of this study were presented in Eighth International Conference on Mercury as a Global Pollutant (August 2006), Madison, Wisconsin, USA.

For more information on GBMM please visit: <a href="http://www.epa.gov/athens/research/modeling/mercury/gbmm.html">http://www.epa.gov/athens/research/modeling/mercury/gbmm.html</a>.

### **GEOS-CHEM Model**

The Global GEOS-CHEM model simulates physical and chemical atmospheric processes driven by observations by NASA's Goddard Earth Observing System (GEOS). This model is managed and supported by the atmospheric chemistry modeling group at Harvard University. This model is used as a tool for atmospheric composition problems.

This model was run for the 2001 CMAQ model with a grid resolution of 2 degree x 2.5 degree (latitude-longitude) and 20 vertical layers. GEOS—Chem is a major contributor to

the NASA Global Model Initiative (GMI). GEOS—Chem has been interfaced with the NASA/GISS general circulation model to investigate the effects of climate change. This work contributes to the multi-institutional Global Change and Air Pollution (GCAP) project. GEOS—Chem provides chemical modules for data assimilation of tropospheric composition at the NASA GMAO.

For more information on GEOS-CHEM please visit: <a href="http://www-as.harvard.edu/chemistry/trop/geos/geos">http://www-as.harvard.edu/chemistry/trop/geos/geos</a> overview.html.

### **GWLF** (Generalized Watershed Loading Function)

GWLF simulates mixed land use watersheds to evaluate the effect of land use practices on downstream loads of sediment and nutrients (N, P). As a loading function model, it simulates runoff and sediment transport using the curve number (CN) and Universal Soil Loss Equation (USLE), combined with average nutrient concentration, based on land use. Recently, a GIS-interface has been integrated which can use national land use and soil GIS data. Also GWLF models in-stream routing using the Muskingum-Cunge method and simulates three particle classes of sediment transport.

GWLF has been used in studies and TMDL development nationally. It is suitable for application to generalized watershed loading, source assessment, and seasonal and interannual variability. It has been extensively used in northeast and mid-Atlantic regions. It has been adopted by Pennsylvania as state system for TMDL development and agricultural land management. GWLF was used to calculate mercury load from the watershed to a lake in several TMDLs in Arizona (e.g., TMDL for Pena Blanca Lake, Arizona). GWLF is also applied in West Virginia TMDL projects by Tetra Tech, Inc.

Information on GWLF can be found at: <a href="http://www.epa.gov/nrmrl/pubs/">http://www.epa.gov/nrmrl/pubs/</a> 600r05149/600r05149gwlf.pdf and <a href="http://www.vims.edu/bio/models/basinsim.html">http://www.vims.edu/bio/models/basinsim.html</a>.

### Mercury Maps screening analysis

A simple screening-level analysis of the mercury sources affecting a waterbody or waterbodies can assist in determining what type of approach to TMDLs is most appropriate. EPA's Mercury Maps (USEPA 2001b) is a geographic information system (GIS)-based analysis using 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 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.

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 tribe-defined watershed boundaries. The state might have its own data on point source effluent loads and more detailed information on other significant sources of mercury in the state, e.g., erosion of mine tailings or natural geology.

Because Mercury Maps is a simplified approach, it has several limitations.

- The Mercury Maps approach is based on the assumption of a linear, steady state
  relationship between concentrations of methylmercury in fish and present-day air
  deposition mercury input. This condition might 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, and international emissions have increased.
- 2. Environmental conditions might not remain constant over the time required to reach steady state inherent in the Mercury Maps methodology, particularly in systems that respond slowly to changes in mercury inputs.
- 3. Many waterbodies, particularly in areas of historical gold and mercury mining in western states, contain significant non-air sources of mercury. Mercury Maps' methodology should not be applied to such waterbodies.
- 4. Finally, 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, for those watersheds where mercury comes almost exclusively from air deposition, Mercury Maps can be used as a simple screening tool to show the watersheds across a region where the current fish tissue concentration on average exceeds the new methylmercury fish tissue criterion and, thus, to estimate the atmospheric load reductions needed to meet the new criterion. Further information on Mercury Maps is at <a href="http://www.epa.gov/waterscience/maps">http://www.epa.gov/waterscience/maps</a> and from the Office of Air Quality Planning and Standards at <a href="http://www.epa.gov/ttn/atw/utility/ria\_final.pdf">http://www.epa.gov/ttn/atw/utility/ria\_final.pdf</a>.

#### MOBILE

MOBILE is an EPA model for estimating air pollution from highway vehicles. MOBILE predicts emissions (grams/mile) of air pollutants from cars, trucks, and motorcycles under various conditions. MOBILE models emissions of several air toxics, hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), carbon dioxide (CO<sub>2</sub>), and particulate matter (PM). MOBILE is based on emissions testing of tens of thousands of vehicles. The model accounts for the impact on emissions of factors such as legislative changes in vehicle emission standards, variation in local conditions such as temperature, humidity, and fuel quality, and changes in the types and use of the vehicles being driven.

MOBILE has been used to calculate national and local inventories of current and future levels of highway vehicle emissions. The inventories are used to inform decision-making

about air pollution policy and programs at the national, state and local level. Inventories based on MOBILE are also used to meet requirement of federal statutes like the Clean Air Act (CAA) and the National Environmental Protection Act (NEPA). MOBILE contributed to the creation of the National Emissions Inventory (NEI).

Information on MOBILE can be found at: http://www.epa.gov/otaq/mobile.htm.

### NDMMF (National Descriptive Model of Mercury in Fish Tissue)

NDMMF is a statistical model which simulates mercury accumulation in varying species of fish. It simulates factors representing differences in species, size, and sampling method. This model has the ability to control for site factors specific to a location that influence mercury concentrations in fish tissue. For example, all fish tissue samples can be scaled to a standardized 14" bass for a specific location. The model works in association with a national dataset of over 30,000 samples of fish tissue for calibration.

NDMMF could be useful for evaluating spatial and temporal trends in fish mercury concentrations and developing fish-consumption advisories. The U.S. Geological Survey recently applied this model to study spatial variation in fish-tissue mercury concentrations in the St. Croix River Basin, Minnesota and Wisconsin.

Information on NDMMF can be found at: <a href="http://emmma.usgs.gov/fishHgAbout.aspx">http://emmma.usgs.gov/fishHgAbout.aspx</a>.

### **NONROAD**

NONROAD is an EPA model for estimating air pollution from all engines, equipment, and vehicles that is considered "nonroad". This includes recreational vehicles, agricultural equipment, industrial equipment, residential equipment, and construction equipment. The NONROAD model is used to predict past, present, and future emissions of air pollutants like hydrocarbons (HC), oxides of nitrogen (NO $_x$ ), carbon monoxide (CO), carbon dioxide (CO $_z$ ), sulfur oxides (SO $_x$ ), and particulate matter (PM). It has been shown that "nonroad" sources contribute a significant amount of air pollutants to the environment.

Used in complement to MOBILE, NONROAD has been used to calculate national and local inventories of current and future levels of "nonroad" emissions. This model has become critical over the past several years in providing state and local pollution control agencies the ability to create accurate and consistent inventories of "nonroad" emissions to satisfy the requirements of the Clean Air Act Amendments of 1990. NONROAD contributed to the creation of the National Emissions Inventory (NEI). The Lake Michigan Air Directors Consortium (LADCO) used NONROAD to forecast emissions in their region and make appropriate policy recommendations.

Information on NONROAD can be found at: <a href="http://www.epa.gov/otaq/nonrdmdl.htm">http://www.epa.gov/otaq/nonrdmdl.htm</a>.

### QEAFDCHN (Quantitative Environmental Analysis Food Chain) Model

The QEAFDCHN model is a tool for predicting chemical residues in aquatic organisms given the concentrations of chemicals in water and sediment. To predict chemical residues, the model requires information on the individual species (bioenergetic and physiological) and their diets. The model is designed to determine chemical residue in

aquatic organisms given varying chemical concentrations in both water and sediment over time.

The QEAFDCHN model can be used in a steady-state or dynamic application. The model allows the specification of complex food webs, e.g., fish preying on multiple species including smaller fish, and even age classes of fishes. The model treats individual segments of the greater ecosystem as individual ecosystems and the model has an aquatic organism migration feature. QEAFDCHN has been applied to the Lavaca Bay, Texas, chlor-alkali facility mercury contamination study by Quantitative Analysis, LLC.

Information on QEADFCHN can be found at: <a href="http://www.epa.gov/superfund//health/conmedia/sediment/pdfs/bsafissue.pdf">http://www.epa.gov/superfund//health/conmedia/sediment/pdfs/bsafissue.pdf</a>.

### Regional Modeling System for Aerosols and Deposition (REMSAD)

REMSAD is a three-dimensional grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations (ICF International 2006). REMSAD has been peer-reviewed and is designed to support an understanding of the distributions, sources, and removal processes relevant to fine particles and other airborne pollutants, including soluble acidic components and several toxic species (mercury, cadmium, dioxin, polycyclic organic matter [POM], atrazine, and lead).

Mercury can be present in the atmosphere in both the gas and particulate phases. The mercury species included in REMSAD are  $\mathrm{Hg}^0$  (elemental mercury vapor),  $\mathrm{Hg}^{2^+}$  (divalent mercury compounds in gas phase), and  $\mathrm{Hg}_P$  (divalent mercury compounds in particulate phase). These species represent the oxidation state of mercury, and the gas and particulate phases. The reactions in REMSAD, which are based on the studies of Lin and Pehkonen (1999) and other recently published studies, simulate the transfer of mercury mass from one of these states to another. REMSAD Version 8 uses the full Carbon Bond-V mechanism to simulate gas-phase photochemical processes in the atmosphere (micro-CB is still available as an option), and it also includes a chemical mechanism to calculate the transformations of mercury.

REMSAD simulates both wet and dry deposition of mercury. Wet deposition occurs as a result of precipitation scavenging. Dry deposition is calculated for each species based on land-use characteristics and meteorological parameters. REMSAD also includes algorithms for the reemission of previously deposited mercury (originating from anthropogenic and natural sources) into the atmosphere from land and water surfaces due to naturally occurring (e.g., microbial) processes.

REMSAD provides estimates of the concentrations and deposition of mercury and all other simulated pollutants at each grid location in the modeling domain. Post-processing can provide concentration averages and deposition totals for any subset of the time span of the simulation for any location within the domain.

The mercury treatment in REMSAD can be expanded to include additional, tagged mercury species. The Particle and Precursor Tagging Methodology (PPTM) feature allows the user to tag or track emissions from selected sources or groups of sources and

to quantify their contribution to mercury deposition throughout the modeling domain and simulation period.

The REMSAD model is capable of "nesting" one or more finer-scale subgrids within a coarser overall grid. This feature uses a fully interactive two-way nesting capability that permits high resolution over selected source and/or receptor regions of interest. The modeling system can be applied at scales ranging from a single metropolitan area to a continent containing multiple urban areas.

REMSAD has been used in identifying the sources contributing mercury deposition to a waterbody. In an EPA Wisconsin pilot project, REMSAD was used to input the air pollutant deposition results to aquatic models like the Mercury Cycling Model, to examine how mercury levels in fish might respond to potential changes in deposition. REMSAD has been used to develop TMDLs and determine strategies for addressing mercury and other air pollutant deposition. REMSAD was used in developing the mercury TMDL for the Coastal Bays and Gulf Waters of Louisiana (approved in 2005) and the mercury TMDLs for middle and south Georgia (approved in 2002).

Information on REMSAD can be found at: <a href="http://remsad.saintl.com/">http://remsad.saintl.com/</a>.

## SERAFM (Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury)

The SERAFM model is a spreadsheet-based risk assessment tool specifically designed for mercury contaminated ecosystems. SERAFM uses a steady-state simplifying assumption and includes a series of sequentially linked modules presented on separate spreadsheets. These modules include:

- Atmospheric deposition
- Watershed soil erosion
- Watershed mercury loading
- Waterbody solids balance
- Equilibrium partitioning (DOC complexation, solids partitioning)
- Mercury speciation
- Waterbody mercury calculations (historic sediment contamination, background, and remedial goal)
- Fish tissue concentrations
- Wildlife hazard quotients

The SERAFM model incorporates more recent advances in scientific understanding 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 1997c).

For more information on SERAFM please visit: <a href="http://www.epa.gov/athens/research/modeling/mercury/serafm.html">http://www.epa.gov/athens/research/modeling/mercury/serafm.html</a> and <a href="http://www.epa.gov/nerl/news/forum2005/knightes.pdf">http://www.epa.gov/nerl/news/forum2005/knightes.pdf</a>.

### TOXI5

TOXI5 is one of two submodels of WASP (Water Quality Analysis Simulation Model), the other being EUTRO5, which deals with eutrophication. TOXI5 is a sediment transport model which can also simulate the transport and transformation of chemicals. The transport of up to three types of sediment and up to three chemicals can be simulated. The chemicals may react independently or they may be linked with reaction yields which predict the fate of the interaction. Dissolved and sorbed chemical concentrations in the waterbody bed and overlying waters can be predicted using TOXI5.

TOXI5 was used to simulate the fate of mercury in the Ochlockonee Watershed in Georgia, to help develop mercury TMDLs for the Southeast U.S., and to evaluate the feasibility of dam release of water on the Nakdong River in Korea to mitigate frequent accidental spills of toxic chemicals.

For more information on TOXI5 please visit: <a href="http://smig.usgs.gov/cgi-bin/SMIC/model">http://smig.usgs.gov/cgi-bin/SMIC/model</a> home pages/model home?selection=wasp.

### WASP (Water Quality Analysis Simulation Program)

The Water Quality Analysis Simulation Program (WASP) is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. It has detailed mercury transformation processes for the water column and benthic sediments. The mercury module simulates the following key processes:

- Volatilization of  $Hg^0$  (aq) to  $Hg^0$  (air)
- Oxidation of  $Hg^0 \rightarrow Hg^{II}$
- Reduction of  $Hg^{II} \rightarrow Hg^0$
- Methylation of HgII → MeHg
- Demethylation of MeHg  $\rightarrow$  Hg<sup>II</sup>
- Photoreduction of MeHg → Hg<sup>0</sup>

WASP has been used to examine eutrophication of Tampa Bay, Florida; phosphorus loading to Lake Okeechobee, Florida; eutrophication of the Neuse River Estuary, North Carolina; eutrophication of the Coosa River and Reservoirs, Alabama; PCB pollution of the Great Lakes; eutrophication of the Potomac Estuary; kepone pollution of the James River Estuary; volatile organic pollution of the Delaware Estuary; heavy metal pollution of the Deep River, North Carolina; and mercury in the Savannah River, Georgia.

Information on WASP can be found at: <a href="http://www.epa.gov/athens/research/modeling/wasp.html">http://www.epa.gov/athens/research/modeling/wasp.html</a>.

### WCS (Watershed Characterization System) Mercury Loading Model

The WCS Mercury Loading model is a GIS-based (ArcView 3.x) extension of the WCS model based on a soil-mercury mass balance model (IEM v 2.05). The soil-mercury mass balance model calculates surface soil concentrations in dissolved, sorbed, and gas phases.

The model accounts for three routes of contaminant entry into the soil:

- Deposition of particle-bound contaminant through dry fall
- Deposition through wet fall
- Diffusion of gas phase contaminant into the soil surface

The model also accounts for four dissipation processes that remove mercury from the surface soils:

- Volatilization (movement of gas phase out of the soil surface)
- Runoff of dissolved phase from the soil surface
- Leaching of dissolved phase through the soil horizon
- Erosion of particulate phase from the soil surface

The model assumes that the diffusion and volatilization processes are roughly balanced on an annual basis. The WCS Mercury Loading model was used to develop many TMDLs in EPA Region 4 including a mercury TMDL for the Middle and Lower Savannah River.

Information on the WCS model can be found at: <a href="http://www.epa.gov/athens/wwqtsc/WCS-toolbox.pdf">http://www.epa.gov/athens/wwqtsc/WCS-toolbox.pdf</a>.

### **Example of Linking Models**

Since there is no single model that can simulate all processes involved in TMDLs, some TMDLs for mercury have linked together models of atmospheric deposition, watershed loading, and mercury cycling with bioaccumulation. For example, a watershed mercury model such as GBMM, or the watershed module within SERAFM could be linked to a receiving water mercury model such as WASP, and a bioaccumulation model such as BASS.

GBMM is a spatially discrete, dynamic watershed mercury loading model which was designed for direct linkage to the EPA receiving waterbody model, WASP. GBMM can simulate mercury fate and transport within the watershed landscape and transport mercury and soils to the receiving waters through the tributaries. WASP can in turn simulate mercury dynamics in the receiving water. To predict bioaccumulation of the resulting mercury concentrations into fish tissues, WASP can then be linked to BASS. SERAFM is a more simplified approach and captures the processes from watershed to waterbody to fish bioaccumulation; however, it makes simplifying assumptions such as the waterbodies are steady state and it uses the national BAFs presented by EPA for trophic level fish.

Linkage of such models may be a workable solution in some situations. One of the limitations of the GBMM-WASP-BASS approach is that it is not an "off-the-shelf" model and a high level of expertise might be required to link the models together.

# Appendix F. Examples of National Deposition Monitoring Networks

A number of national deposition monitoring networks might be useful for developing TMDLs. The networks include the National Atmospheric Deposition Program–National Trends Network (NADP/NTN) and the Mercury Deposition Network (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 geographic 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 and Canada. NADP/NTN results for 2003 are shown in figure F-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, as well as 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 <a href="http://www.epa.gov/castnet">http://www.epa.gov/castnet</a> and <a href="http://nadp.sws.uiuc.edu">http://nadp.sws.uiuc.edu</a>.

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 2000h) (<a href="http://www.epa.gov/oar/oaqps/gr8water/3rdrpt">http://www.epa.gov/ttn/oaa/oaqps/gr8water/3rdrpt</a>) and the Air-Water Interface Plan (<a href="http://www.epa.gov/ttn/caaa/t3/reports/combined.pdf">http://www.epa.gov/ttn/caaa/t3/reports/combined.pdf</a>).

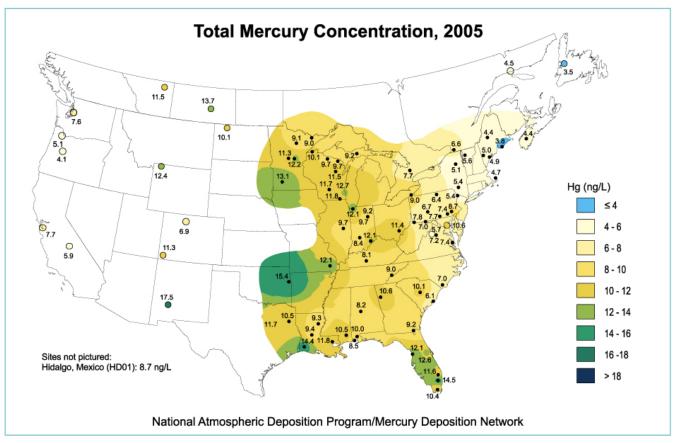


Figure F-1. MDN data for 2005.

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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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