NORTH SAN MATEO COUNTY SANITATION DISTRICT

a subsidiary of the City of Daly City

OPERATION OFFICES

153 Lake Merced Blvd., Daly City, California 94015

(650) 991-8200

(650) 991-8220 (Fax)

AB 61

679

303 (d) Deadline:1/31/06

January 10, 2006

Ms. Selica Potter, Acting Clerk to the Board
State Water Resources Control Board
Executive Office
1001 I Street, 24th Floor
Sacramento, CA 95814

Subject: Comments on the *Revision to Federal Clean Water Act Section 303(d) List of Water Quality Limited Segments for California*

Dear Ms. Selica:

The North San Mateo County Sanitation District (NSMCSD) appreciates the opportunity to provide comments on the draft *Revision of the Clean Water Act Section 303(d) List of Water Quality Limited Segments,* released in September 2005. NSMCSD has reviewed the state's proposed revisions and has a concern that the proposed mercury listing for the San Mateo Coast is not supported by the data cited by the State Water Resources Control Board (State Board).

The 2006 303(d) list proposes to list the entire San Mateo Coastline for mercury due to exceedances of the Office of Environmental Health Hazard Assessment (OEHHA) Screening Value of 0.3 µg/g in three out of five samples analyzed. All five samples were collected by the Coastal Fish Contaminant Project in May 2000 (Table 1) at one station named "San Mateo Coast" (lat 37º29.42, long 122º30.44, Figure 1). This station is approximately 0.7 miles offshore and 25 miles south of the Golden Gate.

Table 1. Data Considered for Proposed Mercury Listing on San Mateo Coast

Species Common Name	Collection Date	Hg Concentration (µg/g)	Exceeds OEHHA Level?
Black Rockfish	5/9/00	0.0637	No
Rosethorn Rockfish	5/9/00	0.3010	Yes
Spotfin Surfperch	5/22/00	0.0382	No
Brown Rockfish	5/23/00	0.5180	Yes
Lingcod	5/23/00	0.3340	Yes

Figure 1. Location of San Mateo Coast Monitoring Station

Based on our review, it appears that the data used does not meet the Data Quantity Assessment standards contained in Section 6.1.5 of the *Water Quality Control Policy for Developing California's Clean Water Act Section 303(d) List,* adopted September 2004 (Policy). More specifically, Section 6.1.5.3 of the Policy states:

> "Samples should be representative of the critical timing that the pollutant is expected to impact the water body. Samples used in the assessment must be temporally independent. If the majority of samples were collected on a single day or during a single short-term natural event (e.g., a storm, flood, or wildfire), the data shall not be used as the primary data set supporting the listing decision."

In addition, the Policy states, "... samples should be available from two or more seasons or from two or more events when effects or water quality objective exceedances would be expected to be clearly manifested." (Policy, Section 6.1.5.3, page 23.) Finally, the Functional Equivalent

Document[1] for the Policy indicates that small sample populations can be used as long as the samples are spatially and temporally representative. In other words, data that is not temporally representative should not be used as the primary data set to support listing decisions, and when the data set is small it is even more important that the data be temporally representative.

As shown in Table 1, the data used to propose listing of the San Mateo Coast for mercury does not meet the temporal representation guidelines contained in the Policy. The samples used were all collected in May 2000 at one site, all within 2 weeks of one another. This clearly does not follow the temporal representation guidelines discussed above, nor does it appear to be spatially representative of ocean waters along the San Mateo Coast. Furthermore, there are only 5 samples, which is clearly a small sample size and therefore in need of temporal representation.

In addition, there is other evidence that suggests the listing may not be appropriate for the San Mateo Coast. Other studies have shown that surfperch, lingcod and rockfish travel to estuaries in the spring to bear young and again in the summer to feed (adapted from Salmon and Trout in Estuaries: http://www.harborside.com/~ssnerr/EMI%20papers/salmon.htm). This movement could indicate that these species are spending extended periods of time in nearby San Francisco Bay, which is currently listed for mercury. These travel patterns make it difficult to indicate whether it is the influence of San Francisco Bay that is being measured in the five samples, or whether the San Mateo Coast is indeed impaired.

S/B RESPONDE TO. done by

Based on the lack of temporal representation and the lack of any additional evidence that there is impairment, we respectfully request that the San Mateo Coast not be listed at this time for mercury, as there is not adequate information to assess whether water quality standards are being met or beneficial uses are impaired.

Sincerely,

Cynthia J. Royer
Manager of Technical Services

L06-005 A

cc: Dyan White, Region 2 Water Board, San Francisco Bay

[1] Final Functional Equivalent Document: Water Quality Control Policy for Developing California Clean Water Act Section 303(d) List. July 2004.

http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#der
Last updated on Thursday, August 3rd, 2006.

Water Quality Criteria

Fish tissue criterion for methylmercury to protect human health

Fact Sheet; January 2001

This water quality criterion describes the maximum advisable concentration of methylmercury in freshwater and estuarine fish and shellfish tissue to protect consumers of fish and shellfish among the general population. EPA expects the criterion recommendation to be used as guidance by States, authorized Tribes, and EPA in establishing or updating water quality standards for waters of the United States. Because consumption of contaminated fish and shellfish is the primary route of human exposure to methylmercury, EPA is expressing this water quality criterion as a fish and shellfish tissue value rather than as a water column value. EPA is providing suggested approaches for relating this criterion to water column concentrations and also plans to develop more detailed guidance to help water quality managers implement the methylmercury criterion in water pollution control programs.

What are human health water quality criteria?

Human health water quality criteria are numeric values we believe will protect human health for pollutant concentrations in aquatic media, such as ambient waters and edible tissue. EPA publishes water quality criteria under the authority of Section 304(a) of the Clean Water Act (CWA) based solely on data and scientific judgments about the relationship between pollutant concentrations and environmental and human health effects. CWA Section 303(c) and its implementing regulations require states and authorized tribes to adopt water quality criteria to protect designated uses in their water quality standards. EPA's recommended section 304 (a) water quality criteria may guide States and authorized Tribes in establishing water quality

standards. The resulting standards may serve as a basis for controlling discharges or releases of pollutants. EPA's recommended human health water quality criteria are not regulations themselves, and do not impose legally binding requirements. EPA may change the section 304(a) water quality criteria in the future.

How does mercury accumulate in fish and shellfish?

Mercury is found in the environment as a result of natural and human activities. The amount of mercury that cycles in the environment has increased since the industrial age. The main source of mercury is air emissions from power generation and other industrial and waste disposal activities. During its movement among the atmosphere, land, and water, mercury undergoes a series of complex chemical transformations. One of the products of these transformations is an organic form called methylmercury. Methylmercury is easily absorbed into the living tissue of aquatic organisms and is not easily eliminated. Therefore, it accumulates in predators. The degree to which mercury is transformed into methylmercury and transferred up the food chain through bioaccumulation depends on many site-specific factors (such as water chemistry and the complexity of the food web) through processes that are not completely understood.

What adverse effects on human health are related to mercury?

Methylmercury is highly toxic to mammals, including people, and causes a number of adverse effects. Health studies and information showing neurotoxicity, particularly in developing organisms, are most abundant. The brain is the most sensitive organ for which suitable data are available to quantify a dose-response relationship. A recent study by the National Academy of Science concluded that the population at highest risk is the children of women who consume large amounts of fish and seafood during pregnancy, and that the risk to that population is likely to be sufficient to result in an increase in the number of children who have to struggle to keep up in school and who might require remedial classes or special education.

What actions reduce health risks?

States, Tribes, and Territories have primary responsibility for protecting their residents from the risks of eating contaminated noncommercially-caught fish and wildlife. They do this by issuing fish consumption advisories for the general population (including recreational and subsistence fishers) and for sensitive subpopulations (such as pregnant women, nursing mothers, and children). These advisories inform the public that unacceptable concentrations of chemical contaminants have been found in local fish and wildlife. They also recommend limiting or avoiding consumption of certain fish and wildlife species from specific waterbodies or, in some cases, from specific waterbody types (e.g., all lakes). Given the ongoing atmospheric sources of mercury and the long-term presence of mercury in the environment, the most effective way to protect public health for the next few decades will be issuing fish consumption advisories to ensure the public knows what level of fish from specific waters is safe to eat.

How is the methylmercury criterion derived?

To assess health risks, EPA developed a reference dose that is a scientifically justifiable maximum level of exposure to protect public health from all toxic effects. EPA based the methylmercury criterion on a new reference dose that protects all exposed populations. EPA also updated the exposure assessment and relative source contribution following the recently published 2000 Human Health Methodology. The resulting criterion of 0.3 mg methylmercury/kg in fish tissue should not be exceeded to protect the health of consumers of noncommercial freshwater/estuarine fish. EPA has taken into account the fact that consumers of freshwater/estuarine fish are also consumers of marine fish.

EPA suggests three approaches that can be used to translate fish tissue methylmercury concentrations into concentrations of methylmercury found in the water column:

- Calculate site-specific bioaccumulation factors based on data collected from a specific waterbody;
- Calculate site-specific bioaccumulation factors based on computer models; and
- Use experimentally-derived bioaccumulation factors that are based on field data published in the criteria.

EPA developed a set of empirically- derived bioaccumulation factors in the initial efforts to derive a revised ambient water quality criteria for methylmercury. EPA has also derived factors to translate methylmercury in water to its total mercury equivalent.

How can this criterion help control mercury pollution?

The United States needs to establish effective source control and management programs in the coming years to begin to recover from the widespread mercury contamination in our aquatic environments. Such actions will hopefully reduce mercury contamination so that fish consumption advisories can be removed. EPA expects the criterion recommendation to be used as a guide by States, authorized Tribes, and EPA in establishing or updating water quality standards that may serve as a basis for pollutant source control and for fish and shellfish consumption advisories.

What future activities are related to this criterion?

EPA recognizes and emphasizes that States and authorized Tribes will need additional specific procedures and water quality program guidance to implement the water quality criteria they adopt based on this guidance. These procedures include, but are not limited to, procedures for translating methylmercury concentrations in fish to total mercury concentrations in ambient surface water or effluent, and procedures for setting permit limits and calculating Total Maximum Daily Loads. EPA is developing these procedures and guidance documents for this water quality criterion.

How do I obtain a copy of the criteria document?

You can get copies of the criterion document titled *Water Quality Criterion for the Protection of Human Health: Methylmercury* from EPA's National Service Center for Environmental

Publications (NSCEP) by calling 1-800-490-9198.

Order from the Water Resource Center[11].

Or you can get the document from EPA's web site[12].

Where can I get more information?

For general questions about the criterion: contact USEPA Health and Ecological Criteria Division, (Mail Code 4304T), Office of Science and Technology, 1200 Pennsylvania Avenue, NW, Washington, DC 20460, (202) 566-1100.

URLs Provided for your Reference

1. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#hh
2. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#acc
3. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#adv
4. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#act
5. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#der
6. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#help
7. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#future
8. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#obtain
9. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#info
10. http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html#content
11. http://www.epa.gov/safewater/resource/
12. http://www.epa.gov/waterscience/criteria/methylmercury/document.html

United States Environmental Protection Agency | Office of Water 4305T | EPA 823-F-06-011 July 2006

EPA Publishes Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

Summary

EPA is publishing for public comment a draft of the *Guidance for Implementing the January 2001 Methylmercury Water Quality Criteria*. You can download the document from EPA's website at http://www.epa.gov/waterscience/criteria/methylmercury. When final, this document will help protect waters by giving state, territory, and authorized tribal water quality programs guidance on how to adopt and implement the fish tissue-based methylmercury water quality criteria.

Background

In January 2001, EPA published a new water quality criterion for mercury that for the first time bases the human health criterion on fish and shellfish tissue rather than on a water column value. This fish and shellfish tissue criterion approach for setting water quality standards creates several challenges, such as translating the fish tissue residue value into a water concentration and ultimately into NPDES permit limits. In a 2001 Federal Register announcement, EPA stated its intent to develop guidance on implementing the criterion to address these issues. Subsequently, EPA formed a workgroup of representatives from state environmental agencies, EPA Regions, and headquarters air and water programs to develop the draft guidance.

About this Draft Guidance Document

The draft guidance, entitled the Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion, helps states implement the 2001 Methylmercury Water Quality Criterion. This guidance generally consolidates existing guidance on water quality standards, TMDLs, and permits where relevant to mercury. The new aspect of the guidance is a suggested approach for implementing the new methylmercury criterion that does not necessarily result in all NPDES discharges reducing the level of mercury in the discharge. Instead, for NPDES discharges that contribute only a very small amount of the mercury to a watershed, the suggested approach consists of holding the discharges at current levels. This suggested approach mirrors current practice where wasteload allocations are developed for TMDLs where point sources are only small contributors to the total loading in a watershed. This approach also does not require a site-specific bioaccumulation factor that can be costly to develop.

How to Get Additional Information

You may download the draft document at www.epa.gov/waterscience/criteria/methylmercury. You can also order a copy of the document from our Water Resource Center at (202) 566-2426; email: center.water-resource@epa.gov. Further information is also available from Jim Pendergast at pendergast.jim@epa.gov.

Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

United States Environmental Protection Agency
Office of Science and Technology (4305T)
1200 Pennsylvania Ave., NW
Washington, DC 20460
EPA-823-B-04-001
www.epa.gov/waterscience
August 2006

4 Monitoring and Assessment

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

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

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

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

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

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

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

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

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

- Methods 1630 and 1631 were developed by EPA to support implementation of water quality criteria for mercury and methylmercury. Both are already in the appropriate EPA format and include all standardized quality control (QC) elements needed to demonstrate that results are reliable enough to support permitting and enforcement programs.

- Appendix A to Method 1631 was developed by EPA to support its National Study of Chemical Residues in Fish Tissue. Appendix A provides information on preparing a fish tissue sample for analysis using Method 1631. The method was validated by Brooks Rand (USEPA 1998b) and is currently being used by Battelle Marine Sciences to analyze more than a thousand tissue samples collected during EPA's National Fish Tissue Survey (USEPA 2000j). Successful use of these techniques also has been widely reported in the literature. This history, combined with the fact that Appendix A supplements the already well-characterized and approved Method 1631, makes this method a good candidate for use with the new fish tissue criterion.

- Method 1630 already has been used in several studies including EPA's Cook Inlet Contaminant Study (USEPA 2001g) and the Savannah River TMDL study (USEPA 2001e). The techniques described in the method and in the recommended method modifications also have been successfully applied in numerous studies described in the published literature. The procedures in Method 1630 also are nearly identical to those given in the USGS method and in the University of Wisconsin SOP, listed in Table D2 (Hurley et al. 1996). The University of Wisconsin SOP was used in EPA's Lake Michigan Mass Balance Study (USEPA 2001f).

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

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

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

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

4.1.2 What analytical methods are available for determination of methylmercury?

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

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

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

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

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

4.2.1 What fish species should be monitored?

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

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

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

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

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

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

4.2.2 What sample types best represent exposure?

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

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

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

4.2.3 What is the recommended study design for site selection?

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

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

4.2.4 How often should fish samples be collected?

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

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

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

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

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

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

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

4.2.5 How many samples should be collected?

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

4.2.6 What form of mercury should be analyzed?

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

4.3 How should waterbody impairment be assessed for listing decisions?

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

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

4.3.1 How should nondetections be addressed?

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

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

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

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

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

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

4.3.2 How should data be averaged across trophic levels?

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

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

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

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

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

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

Where:

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

This calculation is based on apportioning the 17.5 grams/day national default consumption rate for freshwater and estuarine fish and shellfish by trophic level (5.7 grams/day of trophic level 4 fish, 8.0 grams/day of trophic level 3 fish, and 3.8 grams/day of trophic level 2 fish[16]). However, as noted throughout this document, the consumption pattern of the target population should be used if available

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

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

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

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

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

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

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

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

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

4.3.3 How should older data be assessed?

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

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

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

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

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

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

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

Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

United States Environmental Protection Agency
Office of Science and Technology (4305T)
1200 Pennsylvania Ave., NW
Washington, DC 20460
EPA-823-B-04-001
www.epa.gov/waterscience
August 2006

FOREWORD

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

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

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

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

Benjamin H. Grumbles
Assistant Administrator for Water
U.S. Environmental Protection Agency

CONTENTS

TABLES

FIGURES

From: "Fish tissue criterion for methylmercury to protect human health."

avg. period

6.0 METHYLMERCURY BIOACCUMULATION

6.1 INTRODUCTION

Aquatic organisms can accumulate and retain certain chemicals in their bodies when exposed to these chemicals through water, their diet and other sources. This process is called bioaccumulation. In order to prevent harmful exposures to waterborne pollutants through the consumption of contaminated fish and shellfish, national 304(a) water quality criteria for the protection of human health must address the process of chemical bioaccumulation in aquatic organisms. For deriving national 304(a) ambient water column criteria to protect human health, EPA accounts for potential bioaccumulation of pollutants in fish and shellfish through the use of national bioaccumulation factors (BAFs). A national BAF is a ratio (in L/kg) which relates the concentration of a chemical in water to its expected concentration in commonly consumed aquatic organisms in a specified trophic level. The magnitude of bioaccumulation by aquatic organisms varies widely depending on the chemical but can be extremely high for some highly persistent and hydrophobic chemicals. For such highly bioaccumulative chemicals, concentrations in aquatic organisms may pose unacceptable human health risks from fish and shellfish consumption even when concentrations in water are too low to cause unacceptable health risks from drinking water consumption alone. These chemicals may also biomagnify in aquatic food webs, a process whereby chemical concentrations increase in aquatic organisms of each successive trophic level due to increasing dietary exposures (e.g., increasing concentrations from algae, to zooplankton, to forage fish, to predator fish). Methylmercury is a chemical that bioaccumulates and biomagnifies to a relatively high extent. Methylmercury BAFs for upper trophic level freshwater and estuarine fish and shellfish typically consumed by humans generally range between 500,000 and 10,000,000 (Glass et al., 1999; Lores et al., 1998; Miles and Fink, 1998; Monson and Brezonik, 1998; Watras et al., 1998; Mason and Sullivan, 1997).

6.2 ISSUES IN DEVELOPING METHYLMERCURY BAFS

The fates of mercury and methylmercury in the environment are complex processes affected by numerous biotic and abiotic factors that are subjects of ongoing research by various government, private, and academic groups around the world. Methylation of mercury is a key step in the entrance of mercury into food chains. The biotransformation of inorganic mercury species to methylated organic species in water bodies can occur in the sediment and the water column. Inorganic mercury can be absorbed by aquatic organisms but is generally taken up at a slower rate and with lower efficiency than is

environment. EPA prefers this approach because BAFs derived with field data integrate the chemical, biological, and physical factors that can affect bioaccumulation in fish and shellfish. With this preference in mind, EPA explored the feasibility of developing field-derived national methylmercury BAFs for each trophic level of the aquatic food chain consumed by humans (i.e., trophic levels 2-4). Using Agency guidance on BAFs contained in the 2000 Human Health Methodology and procedures outlined in Volume III, Appendix D of the peer-reviewed MSRC (U.S. EPA, 1997c), EPA empirically derived draft national methylmercury BAFs for each trophic level of the aquatic food chain. The draft national BAFs were single value trophic level-specific BAFs calculated as the geometric mean of field data collected across the United States and reported in the open literature as well as other publically available reports. These draft methylmercury BAFs were compiled in a draft internal report and submitted to a panel of external scientific experts for peer review. The Appendix contains a summary of the internal BAF report and BAF peer review report. The entire internal draft methylmercury BAF report and peer review report can be obtained from the Water Docket W-00-20.

Within any given trophic level, the individual empirically derived draft methylmercury BAFs generally ranged up to two orders of magnitude. This range in BAFs reflects the various biotic factors (such as food chain interactions and fish age/size) and abiotic factors (such as pH and dissolved organic carbon). The large range in the individual empirically derived draft methylmercury BAFs results in uncertainty as to the ability of single trophic level-specific national methylmercury BAFs to accurately predict bioaccumulation of methylmercury in general across the waters of the United States. Presently, it is EPA's understanding that the mechanisms that underlie many of the influencing factors are not well understood and can not be accurately predicted. As the science of methylmercury improves, in the future it may be possible predict or model these processes and use such information to more accurately predict bioaccumulation. Until such time, EPA is unable to improve the predictive power of the methylmercury BAFs by universally accounting for influencing factors. This is not the case for other highly bioaccumulative pollutants; for example polychlorinated biphenyls (PCBs). For such pollutants, EPA has methods that improve the predictive capability of empirically derived or model predicted BAFs (such as normalizing fish tissue concentrations to lipid and normalizing ambient water concentrations to dissolved and particulate organic carbon). EPA is actively involved in, and will continue to support, various types of research aimed at better understanding the fate of mercury in the environment and the processes that underlie methylmercury bioaccumulation. EPA hopes that results of new research will enable better predictions of methylmercury bioaccumulation.

The BAF peer reviewers recognized the need for methylmercury BAFs and were supportive of most aspects of the methodology used to derive the draft national methylmercury BAFs. The peer reviewers did have issues with certain data used to derive the methylmercury BAFs and certain assumptions about food chain relationships. Overall, most of the peer reviewers believed that derivation of single-value trophic level-specific national BAFs for methylmercury that would be generally applicable to all waters of the United States under all conditions is difficult at best, and perhaps impossible. This opinion was based on consideration of the highly site-specific nature of methylmercury bioaccumulation in aquatic environments and the large range in the empirically derived draft methylmercury BAFs. These peer reviewers recommended developing methylmercury BAFs on a more local or regional scale, if not on a site-specific basis. Although EPA generally agrees with this suggestion, the data needed to derive BAFs at more localized scales across the U.S. are not available. See Appendix A for a summary of the internal BAF report and the BAF peer review report.

6.3 CONSIDERATION OF A FISH TISSUE RESIDUE CRITERION

After considering the various issues about mercury fate in the environment, the recent report by the National Research Council (NRC, 2000) on the toxicological effects of mercury, and the methylmercury BAF peer review comments, EPA concluded that it is more appropriate at this time to derive a fish tissue (including shellfish) residue water quality criterion for methylmercury rather than a water column-based water quality criterion. EPA believes a fish tissue residue water quality criterion for methylmercury is appropriate for many reasons. A fish tissue residue water quality criterion integrates spatial and temporal complexity that occurs in aquatic systems and that affect methylmercury bioaccumulation. A fish tissue residue water quality criterion in this instance is more closely tied to the CWA goal of protecting the public health because it is based directly on the dominant human exposure route for methylmercury. The concentration of methylmercury is also generally easier to quantify in fish tissue than in water and is less variable in fish and shellfish tissue over the time periods in which water quality standards are typically implemented in water quality-based controls, such as NPDES permits. Thus, the data used in permitting activities can be based on a more consistent and measurable endpoint. Finally, this approach is consistent with the way in which fish advisories are issued. Fish advisories for mercury are also based on the amount of methylmercury in fish tissue that is considered acceptable, although such advisories are usually issued for a certain fish or shellfish species in terms of a meal size. A fish tissue residue water quality criterion should enhance harmonization between these two approaches for protecting the public health.

Because EPA did not use national, empirically derived methylmercury BAFs to establish today's section 304(a) recommended methylmercury water quality criterion, EPA has deferred further efforts to derive national BAFs for methylmercury at this time. EPA notes, however, that there may be adequate field data for some waterbodies or geographical regions on which to base accurate predictive, site-specific methylmercury BAFs. EPA may reconsider developing national methylmercury BAFs in the future once more field data is available for a broader range of species and aquatic ecosystems, or once more information is available describing the mechanisms that affect bioaccumulation. Such information could enable EPA to more accurately predict methylmercury bioaccumulation on a broader scale given a certain total mercury concentration in water.

7.0 WATER QUALITY CRITERION CALCULATION

7.1 EQUATION FOR TISSUE RESIDUE CONCENTRATION AND PARAMETERS USED

The equation for calculating the methylmercury fish tissue residue criterion is:

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

Where:

TRC	=	Fish tissue residue criterion (mg methylmercury/kg fish) for freshwater and estuarine fish
RfD	=	Reference dose (based on noncancer human health effects) of 0.0001 mg methylmercury/kg body weight-day
RSC	=	Relative source contribution (subtracted from the RfD to account for marine fish consumption) estimated to be 2.7×10^{-5} mg methylmercury/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 is 0.0175 kg fish/day for general adult population. Trophic level breakouts for the general population are: TL2 = 0.0038 kg fish/day; TL3 = 0.0080 kg fish/day; and TL4 = 0.0057 kg fish/day.

This yields a methylmercury TRC value of 0.3 mg methylmercury/kg fish (rounded to one significant digit from 0.288 mg methylmercury/kg fish).

This equation is essentially the same equation used in the 2000 Human Health Methodology to calculate a water quality criterion, but 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 (as discussed above, exposure from drinking water is negligible). The TRC of 0.3 mg methylmercury/kg fish is the concentration in fish tissue that should not be exceeded based on a total consumption of 0.0175 kg fish/day.

7.2 SITE-SPECIFIC OR REGIONAL ADJUSTMENTS TO CRITERIA

Several parameters in the Water Quality Criterion equation can be adjusted on a site-specific or regional basis to reflect regional or local conditions and/or specific populations of concern. These include the fish consumption rates and the RSC estimate. States and authorized Tribes can also choose to apportion an intake rate to the highest trophic level consumed for their population or modify EPA's default intake rate based on local or regional consumption patterns. EPA strongly encourages States and authorized Tribes to consider developing a criterion using local or regional data over the default values if they believe that they would be more appropriate for their target population. States and authorized Tribes are encouraged to make such adjustments using the guidance provided in the 2000 Human Health Methodology (U.S. EPA, 2000a).

8.0 REFERENCES

Aaseth J., A. Wannag, and T. Norseth. 1976. The effect of N-acetylated DL-penicillamine and DL-homocysteine thiolactone on the mercury distribution in adult rats, rat foetuses and Macaca monkeys after exposure to methyl mercuric chloride. Acta Pharmacol. Toxicol. 39:302-311 (as cited in Luecke et al., 1997).

Aberg, B., L. Ekman, R. Falk, U. Greitz, G. Persson, and J. Snihs. 1969. Metabolism of methyl mercury (Hg) compounds in man: excretion and distribution. Arch. Environ. Health 19:478-484.

Akagi, H., O. Malm, Y. Kinjo, M. Harada, F.J.P. Branches, W.C. Pfeiffer, and H. Kato. 1995. Methylmercury pollution in the Amazon, Brazil. Sci. Total Environ. 175:85-95.

Akagi-H, I. Kanoka, and K. Kaneko. 1997. J. Jpn. Soc. Obstet. Gynecol. Neonat. Hematol. 7(2):S112-S113.

Al-Shahristani, H., and K.M. Shihab. 1974. Variation of biological half-life of methyl mercury in man. Arch. Environ. Health 28:342-344.

Allen, B.C., R.J. Kavlock, C.A. Kimmel, and E.M. Faustman. 1994. Dose-response assessment for developmental toxicity. II. Comparison of generic benchmark dose estimates with no observed adverse effect levels. Fundam. Appl. Toxicol. 23(4):487-495.

Altmann, L., K. Sveinsson, U. Kramer, et al. 1998. Visual functions in 6-year-old children in relation to lead and mercury levels. Neurotoxicol. Teratol. 20(1):9-17.

Amin-Zaki, L., S. Elhassani, M.A. Majeed, T.W. Clarkson, R.A. Doherty, and M. Greenwood. 1974. Intra-uterine methylmercury poisoning in Iraq. Pediatrics 54:587-595.

Amin-Zaki, L., S. Elhassani, M. Majeed, T. Clarkson, R. Doherty, and M. Greenwood. 1976. Perinatal methylmercury poisoning in Iraq. Am. J. Dis. Child 130:1070-1076.

Amin-Zaki, L., M. Majeed, S. Elhassani, T. Clarkson, M. Greenwood, and R. Doherty. 1979. Prenatal methylmercury poisoning. Am. J. Dis. Child 133:172-177.

Amin-Zaki, L., M. Majeed, M. Greendow, et al. 1981. Methylmercury poisoning in the Iraqi suckling infant: A longitudinal study over five years. J. Appl. Toxicol. 1:210-214.

Andersen, M.E., H.J. Clewell, and K. Krishnan. 1995. Tissue dosimetry, pharmacokinetic modeling, and interspecies scaling factors. Risk Anal. 15:533-537.

Arito, H., and M. Takahashi. 1991. Effect of methyl mercury on sleep patterns in the rat. In: Suzuki, T., N. Imura, and T.W. Clarkson, eds. Advances in mercury toxicology. New York: Plenum Press, 381-394.

Aschner, M., and J.L. Aschner. 1990. Mercury neurotoxicity: mechanisms of blood-brain barrier transport. Neurosci. Biobehav. Rev. 14(2):169-176.

ATSDR (Agency for Toxic Substances Disease Registry). 1999. Toxicological profile for mercury. Update. Atlanta, GA: ATSDR.

EPA-823-R-01-001
January 2001

Water Quality Criterion for the Protection of Human Health: Methylmercury

Final

Office of Science and Technology
Office of Water
U.S. Environmental Protection Agency Washington, DC 20460

ACKNOWLEDGMENTS

Authors

Denis Borum	U.S. EPA Office of Science and Technology, Office of Water
Mary Ko Manibusan, M.P.H.	U.S. EPA Office of Science and Technology, Office of Water
Rita Schoeny, Ph.D.	U.S. EPA Office of Science and Technology, Office of Water
Erik L. Winchester, M.S.	U.S. EPA Office of Science and Technology, Office of Water

Contributors

Helen Jacobs, M.S.	U.S. EPA Office of Science and Technology, Office of Water
Kate Mahaffey, Ph.D.	U.S. EPA Office of Science Co-ordination and Policy, Office of Prevention, Pesticides and Toxic Substancest
Debra Rice, Ph.D.	U.S. EPA National Center for Environmental Assessment, Office of Research and Development
Keith Sappington, M.S.	U.S. EPA National Center for Environmental Assessment, Office of Research and Development

EPA Reviewers

Larry Hall, Ph.D.	U.S. EPA National Health and Environmental Effects Research Laboratory, Office of Research and Development
John Nichols, Ph.D.	U.S. EPA National Health and Environmental Effects Research Laboratory, Office of Research and Development
Glen Rice, M.S.	U.S. EPA National Center for Environmental Assessment, Office of Research and Development
Jeff Swartout, M.S.	U.S. EPA National Center for Environmental Assessment, Office of Research and Development

Portions of this document were developed under contract with Great Lakes Environmental Center (GLEC), Information Systems Solutions International (ISSI), Inc., and ICF Consulting, Inc.

EXTERNAL PEER REVIEWERS

The following individuals provided technical and scientific reviews of the content and scientific information in the criterion document as part of a formal peer review process.

Methylmercury Reference Dose

Kim N. Dietrich, Ph.D., University of Cincinnati

Bruce A. Fowler, Ph.D., University of Maryland

Gary Ginsberg, Ph.D. (workshop chair), Connecticut Department of Public Health

Martha Keating, M.S., Keating Environmental

Chris Newland, Ph.D., Auburn University

Pam Shubat, Ph.D., Minnesota Department of Health

Andrew Smith, S.M., Sc.D., Maine Department of Human Services

Bioaccumulation of Methylmercury

Nicolas S. Bloom, M.S., Frontier Geosciences Inc.

James P. Hurley, Ph.D., University of Wisconsin Water Resources Institute

David P. Krabbenhoft, Ph.D., U.S. Geological Survey

David Maschwitz, Ph.D., Minnesota Pollution Control Agency

Darell G. Slotton, Ph.D., University of California

Edward Swain, Ph.D., Minnesota Pollution Control Agency

Potential areas for conflict of interest were investigated via direct inquiry with the peer reviewers and review of their current affiliations. No conflicts of interest were identified.

CONTENTS

EXECUTIVE SUMMARY

About This Document

This document is the basis for a human health Ambient Water Quality Criterion (AWQC) for methylmercury. This AWQC replaces the AWQC for total mercury in published in 1980 and partially updated in 1997. Under Section 304(a) of the Clean Water Act, EPA must periodically revise criteria for water quality to accurately reflect the latest scientific knowledge on the kind and extent of all identifiable effects of pollutants on human health.

This document uses new methods and information described in the Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000) (2000 Human Health Methodology) (U.S. EPA, 2000a,b). These new methods include updated approaches to determine toxicity dose-response relationships for both carcinogenic and noncarcinogenic effects, updated information for determining exposure factors, and new procedures to determine bioaccumulation factors.

The Mercury Study Report to Congress (MSRC) (U.S. EPA, 1997), an eight-volume report prepared by the U.S. Environmental Protection Agency (EPA) and submitted to Congress in 1997, serves as a primary information source on methylmercury. However, as the state of the science for methylmercury is continuously and rapidly evolving, the information from the MSRC has been supplemented by inclusion of published information since 1997.

Exposure to Methylmercury

The major pathway for human exposure to methylmercury is consumption of contaminated fish. Dietary methylmercury is almost completely absorbed into the blood and is distributed to all tissues including the brain; it also readily passes through the placenta to the fetus and fetal brain.

Major Health Effects of Methylmercury

Methylmercury is a highly toxic substance with a number of adverse health effects associated with its exposure in humans and animals. Epidemics of mercury poisoning following high-dose exposures to methylmercury in Japan and Iraq demonstrated that neurotoxicity is the health effect of greatest concern. These epidemics led to observation of methylmercury effects on the fetal nervous system. High-dose

human exposure results in mental retardation, cerebral palsy, deafness, blindness, and dysarthria in utero and in sensory and motor impairment in adults. Although developmental neurotoxicity is currently considered the most sensitive health endpoint, data on cardiovascular and immunological effects are beginning to be reported and provide more evidence for toxicity from low-dose methylmercury exposure.

Three large prospective epidemiology studies in the Seychelles Islands, New Zealand, and the Faroe Islands were designed to evaluate childhood development and neurotoxicity in relation to fetal exposures to methylmercury in fish-consuming populations. Prenatal methylmercury exposures in these three populations were within the range of some U.S. population exposures. No adverse effects were reported from the Seychelles Islands study, but children in the Faroe Islands exhibited subtle developmental dose-related deficits at 7 years of age. These effects include abnormalities in memory, attention, and language. In the New Zealand prospective study, children at 4 and 6 years of age exhibited deficiencies in a number of neuropsychological tests.

In addition to the three large epidemiological studies, studies on both adults and children were conducted in the Amazon; Ecuador; French Guiana; Madeira; Mancora, Peru; northern Quebec; and Germany. Effects of methylmercury on the nervous system were reported in all but the Peruvian population.

Other Health Effects of Methylmercury

Methylmercury causes chromosomal effects but does not induce point mutations. The MSRC concluded that because there are data for mammalian germ-cell chromosome aberration and limited data from a heritable mutation study, methylmercury is placed in a group of high concern for potential human germ-cell mutagenicity. There is no two-generation study of reproductive effects, but shorter term studies in rodents, guinea pigs and monkeys have reported observations consistent with reproductive deficits. There are no data to indicate that methylmercury is carcinogenic in humans, and it induces tumors in animals only at highly toxic doses. Application of the proposed revisions to the Guidelines for Cancer Risk Assessment (EPA 1999)leads to a judgment that methylmercury is not likely to be carcinogenic for humans under conditions of exposure generally encountered in the environment.

Quantitative Risk Estimate for Methylmercury

The quantitative health risk assessment for a noncarcinogen relies on a reference dose (RfD). This is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious health effects during a lifetime. To derive an RfD, one first establishes a no adverse effect level (NOAEL) for a particular endpoint. This can be done by inspection of the available data or by using a mathematical modeling procedure to estimate the NOAEL; the latter approach was used for methylmercury. Next the NOAEL is divided by a numerical uncertainty factor to account for areas of variability and uncertainty in the risk estimate.

There has been considerable discussion within the scientific community regarding the level of exposure to methylmercury that is likely to be without an appreciable risk of deleterious health effects during a lifetime. In 1999, the Congress directed EPA to contract with the National Research Council (NRC) of the National Academy of Sciences to evaluate the body of data on the health effects of methylmercury. NRC was to concentrate on new data since the 1997 MSRC, and to provide recommendations regarding issues relevant to the derivation of an appropriate RfD for methylmercury. NRC published their report, *Toxicological Effects of Methylmercury*, in 2000. EPA generally concurred with the NRC findings and recommendations. The NRC document was used as a resource in determining the EPA RfD for methylmercury documented here.

Choice of Study

The adverse effect of methylmercury observed at lowest dose is neurotoxicity, particularly in developing organisms. The brain is considered the most sensitive target organ for which there are data suitable for derivation of an RfD. There is an extensive array of peer-reviewed, well-analyzed data from human studies of low-dose exposure to methylmercury. NRC and EPA considered three epidemiologic longitudinal developmental studies suitable for quantitative risk assessment: the Seychelles Child Development Study (SCDS); the ongoing studies of children in the Faroe Islands; and the study of children in New Zealand. All cohorts consisted of children exposed in utero through maternal consumption of mercury-contaminated fish or marine mammals. In all studies there were biomarkers of maternal exposure (hair), and in the Faroes study cord blood was also used as an additional measure of fetal exposure. The SCDS yielded no evidence of impairment related to methylmercury exposure, but the two other studies have found dose-related adverse effects on a number of

neuropsychological endpoints. EPA chose to base the RfD on data from the Faroes study. The SCDS has no findings of effects associated with methylmercury exposure, and thus is not the best choice for a public health protective risk estimate. While the New Zealand study does show mercury-related effects it relatively small by comparison to the other two. Advantages of the Faroes study include these:

- Large sample size ($n > 900$ for some measures)
- Good statistical power as calculated by conventional means
- Use of two different biomarkers of exposure
- Comprehensive and focused neuropsychological assessment
- Assessment at an age and state of development when effects on complex neuropsychological functions are most likely to be detectable
- Statistically significant observations which remain after adjusting for potential PCB effects
- Extensive scrutiny in the epidemiological literature

The Faroe Islands study was used for derivation of the RfD.

Estimation of the No Adverse Effect Level

A benchmark dose analysis was chosen as the most appropriate method of quantifying the dose-effect relationship. The level chosen was a Benchmark Dose Lower Limit (BMDL); this was the lower 95% limit on a 5% effect level obtained by applying a K power model ($K \geq 1$) to dose-response data based on mercury in cord blood. The BMDL was chosen as the functional equivalent of a no-adverse-effect level for calculation of the RfD.

Choice of Endpoint

Several endpoints are sensitive measures of methylmercury effects in the Faroese children. EPA considered the recommendations of the NRC and EPA's external scientific peer review panel in coming to a decision as to the appropriate endpoint. The NRC recommended the use of a BMDL of 58 ppb mercury in cord blood from the Boston Naming Test (BNT). The external peer panel felt that the BNT scores showed an effect of concomitant PCB exposure in some analyses. They preferred a PCB-adjusted BMDL of 71 ppb mercury in cord blood for the BNT. A difficulty with this choice is that this BMDL is based on scores from only about one-half of the total cohort. The peer panel further suggested using a composite index across several measures in the Faroes data set. EPA prepared a comparison of the

endpoints recommended by NRC and peer reviewers; this also included the BMDLs from the NRC integrative analysis and geometric means of four scores from the Faroes. These BMDLs and corresponding estimates of ingested methylmercury are within a very small range. Rather than choosing a single measure for the RfD critical endpoint, EPA considers that this RfD is based on several scores. These test scores are all indications of neuropsychological processes related to the ability of a child to learn and process information.

Calculation of Ingested Methylmercury Dose

In the risk assessment discussion EPA uses the NRC-recommended BMDL of 58 ppb mercury in cord blood as an example in the dose conversion and RfD calculation. The BMDL in terms of mercury in cord blood was converted to an estimate of ingested methylmercury. This was done by use of a one-compartment model similar to that used in the MSRC. Single-parameter estimates were used rather than a distributional approach. It was assumed that the cord blood methylmercury level was equal to maternal blood level. The ingested dose of methylmercury that corresponds to a cord blood level of 58 ppb is 1.081 μg/kg bw/day.

Uncertainty Factor

Several sources of variability and uncertainty were considered in the application of a composite uncertainty factor of 10. This included a factor of 3 for pharmacokinetic variability and uncertainty; one area of pharmacokinetic uncertainty was introduced with the assumption of equivalent cord blood and maternal blood mercury levels. An additional factor of 3 addressed pharmacokinetic variability and uncertainty. Other areas of concern include inability to quantify possible long-term sequelae for neurotoxic effects, questions as to the possibility of observing adverse impacts (such as cardiovascular effects) below the BMDL, and lack of a two-generation reproductive effects assay.

Methylmercury Reference Dose

The RfD derived in this assessment is 0.1 μg/kg bw/day or $1x10^{-4}$ mg/kg bw/day. The RfD for methylmercury was not calculated to be a developmental RfD only. It is intended to serve as a level of exposure without expectation of adverse effects when that exposure is encountered on a daily basis for a lifetime. In the studies so far published on subtle neuropsychological effects in children, there has been no definitive separation of prenatal and postnatal exposure that would permit dose-response modeling.

That is, there are currently no data that would support the derivation of a child (vs. general population) RfD.

Relative Source Contribution

The assessment of methylmercury exposure from common media sources (e.g., diet, air) and relative source contribution (RSC) estimates follows the 2000 Human Health Methodology. The RSC is used to adjust the RfD to ensure that the water quality criterion is protective, given other anticipated sources of exposure. The exposure assessment characterizes the sources of methylmercury exposure in environmental media, providing estimates of intake from the relevant sources for children, women of childbearing age, and adults in the general population. Based on available data, human exposures to methylmercury from all media sources except freshwater/estuarine and marine fish are negligible, both in comparison with exposures from fish and compared with the RfD. Estimated exposure from ambient water, drinking water, nonfish dietary foods, air, and soil are all, on average, at least several orders of magnitude less than those from freshwater/estuarine fish intakes. Therefore, these exposures were not factored into the RSC. However, ingestion of marine fish is a significant contributor to total methylmercury exposure. For the methylmercury criterion, the RSC is the estimated exposure from marine fish intake. This is subtracted from the RfD when calculating the water quality criterion. One hundred percent of the mercury in marine fish was assumed to be present as methylmercury. The estimated average exposure to methylmercury from marine fish is 2.7 x 10-5 mg/kg-day. This exposure represents almost 30% of the RfD.

Methylmercury Bioaccumulation

Methylmercury is a chemical that bioaccumulates and biomagnifies in aquatic food webs. The fates of mercury and methylmercury in the environment are complex processes affected by numerous biotic and abiotic factors that are subjects of ongoing research. Methylation of mercury is a key step in the entrance of mercury into food chains. The biotransformation of inorganic mercury forms to methylated organic forms in water bodies can occur in the sediment and the water column. Inorganic mercury can be absorbed by aquatic organisms but is generally taken up at a slower rate and with lower efficiency than is methylmercury. Methylmercury continues to accumulate in fish as they age. Predatory organisms at the top of aquatic and terrestrial food webs generally have higher methylmercury concentrations because methylmercury is typically not completely eliminated by organisms and is

transferred up the food chain. Nearly 100% of the mercury that bioaccumulates in upper-trophic-level fish (predator) tissue is methylmercury.

Numerous factors can influence the bioaccumulation of mercury in aquatic biota. These include, but are not limited to, the acidity (pH) of the water, length of the aquatic food chain, temperature, and dissolved organic material. Physical and chemical characteristics of a watershed, such as soil type and erosion or proportion of area that is wetlands, can affect the amount of mercury that is transported from soils to water bodies. Interrelationships among these factors are poorly understood and are likely to be site-specific. No single factor (including pH) has been correlated with extent of mercury bioaccumulation in all cases examined. Two lakes that are similar biologically, physically, and chemically can have different methylmercury concentrations in water, fish, and other aquatic organisms.

The Methylmercury Criterion is a Fish Tissue Residue Criterion

EPA concluded that it is more appropriate at this time to derive a fish tissue (including shellfish) residue water quality criterion for methylmercury rather than a water column-based water quality criterion. This decision considered issues of mercury fate in the environment, the NRC report on the toxicological effects of mercury, and in particular the methylmercury peer review comments. EPA believes a fish tissue residue water quality criterion is appropriate for many reasons. Such a criterion integrates spatial and temporal complexity that occurs in aquatic systems and that affects methylmercury bioaccumulation. A fish tissue residue water quality criterion is more closely tied to the CWA goal of protecting the public health because it is based directly on the dominant human exposure route for methylmercury. The concentration of methylmercury is also generally easier to quantify in fish tissue than in water and is less variable over the time periods in which water quality standards are typically implemented in water quality-based. Thus, the data used in permitting activities can be based on a more consistent and measurable endpoint. A fish tissue residue criterion is also consistent with how fish advisories are issued. Fish advisories for mercury are based on the amount of methylmercury in fish tissue that is considered acceptable, although they are usually issued for a certain fish or shellfish species in terms of a meal size. A fish tissue residue water quality criterion should enhance harmonization between these two approaches for protecting the public health.

The methylmercury water quality criterion is, thus, a concentration in fish tissue. It was calculated using the criterion equation in the 2000 Human Health Methodology rearranged to solve for a protective concentration in fish tissue rather than in water.

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

Where:

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

RfD = Reference dose (based on noncancer human health effects) of 0.0001 mg methylmercury/kg body weight-day

RSC = Relative source contribution (subtracted from the RfD to account for marine fish consumption) estimated to be 2.7×10^{-5} mg methylmercury/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 is 0.0175 kg fish/day for general adult population. Trophic level breakouts for the general population are: TL2 = 0.0038 kg fish/day; TL3 = 0.0080 kg fish/day; and TL4 = 0.0057 kg fish/day.

The resulting Tissue Residue Criterion is 0.3 mg methylmercury/kg fish. This is the concentration in fish tissue that should not be exceeded based on a total fish and shellfish consumption-weighted rate of 0.0175 kg fish/day. EPA strongly encourages States and authorized Tribes to develop a water quality criterion for methylmercury using local or regional data rather than the default values if they believe that such a water quality criterion would be more appropriate for their target population.

Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

United States Environmental Protection Agency
Office of Science and Technology (4305T)
1200 Pennsylvania Ave., NW
Washington, DC 20460
EPA-823-B-04-001
www.epa.gov/waterscience
August 2006

1 Executive Summary

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

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

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

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

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

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

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

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

2 Introduction

2.1 What is the interest in mercury?

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

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

2.1.1 What are the health effects of mercury?

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

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

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

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

2.1.2 How frequent are the environmental problems?

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

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

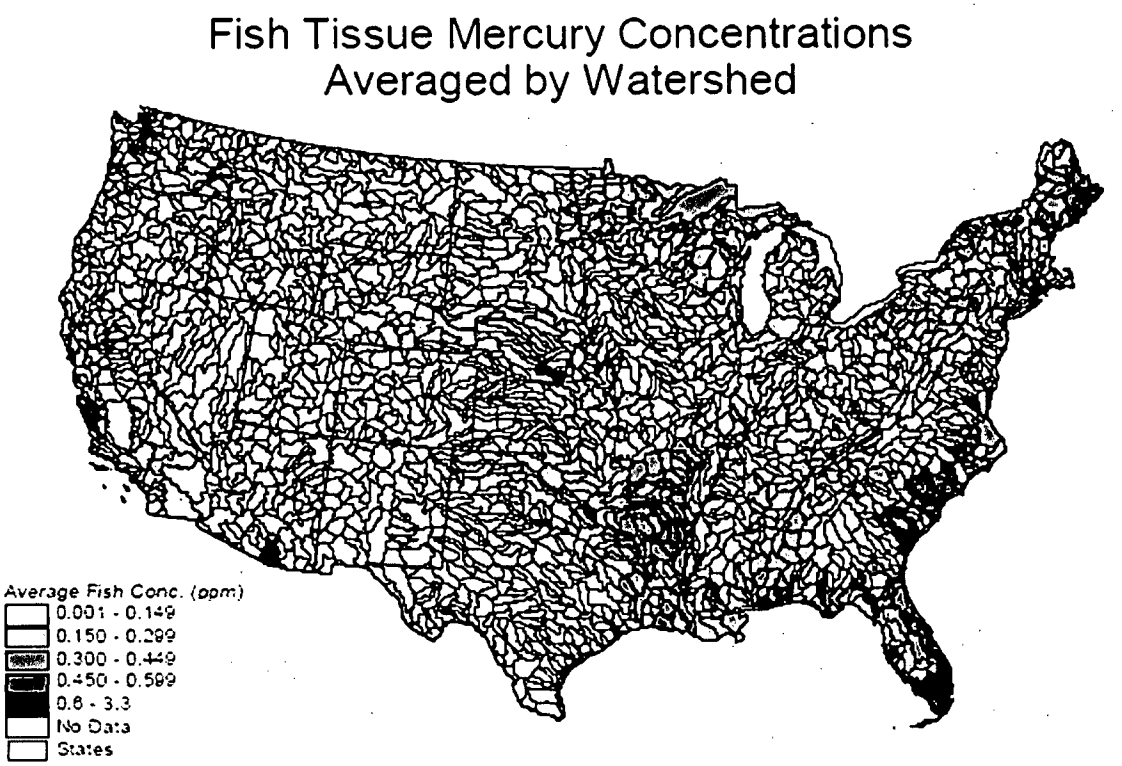


Figure 1. Fish Tissue Mercury Concentrations Averaged by Watershed (USEPA 2001d)

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

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

2.2 What are the sources of mercury in fish?

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

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

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

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

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

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

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

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

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

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

2.3 How does methylmercury get into fish and shellfish?

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

Mercury occurs naturally in the environment as several different chemical species. The majority of mercury in the atmosphere (95–97 percent) is present in a neutral, elemental state (Hg^0) (Lin and Pehkonen 1999), while in water, sediments, and soils, the majority of mercury is found in the oxidized, divalent state (Hg(II)) (Morel et al. 1998). A small fraction of this pool of divalent mercury is transformed by microbes into methylmercury ($CH_3Hg(II)$) (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 emissions sources. Elemental mercury is oxidized in the atmosphere to form the more soluble mercuric ion (Hg(II)) (Schroeder et al. 1989). Particulate and reactive gaseous phases of Hg(II) are the principle forms of mercury deposited onto terrestrial and aquatic systems because they are more efficiently scavenged from the atmosphere through wet and dry deposition than Hg^0 (Lindberg and Stratton 1998). Because Hg(II) species or reactive gaseous mercury (RGM) and particulate mercury (Hg(p)) in the atmosphere tend to be deposited more locally than Hg^0, differences in the species of mercury emitted affect whether it is deposited locally or travels longer distances in the atmosphere (Landis et al. 2004).

A portion of the mercury deposited in terrestrial systems is re-emitted to the atmosphere. On soil surfaces, sunlight might reduce deposited Hg(II) to Hg^0, which might then evade back to the atmosphere (Carpi and Lindberg 1997, Frescholtz and Gustin 2004, Scholtz et al. 2003). Significant amounts of mercury can be codeposited to soil surfaces in throughfall and litterfall of forested ecosystems (St. Louis et al. 2001), and exchange of gaseous Hg^0 by vegetation has been observed (e.g., Gustin et al. 2004). Hg(II) has a strong affinity for organic compounds such that inorganic mercury in soils and wetlands is predominantly bound to dissolved organic matter (Mierle and Ingram 1991). Concentrations of methylmercury in soils are generally very low. In contrast, wetlands are areas of enhanced methylmercury production and account for a significant fraction of the external methylmercury inputs to surface waters that have watersheds with a large portion of wetland coverage (e.g., St. Louis et al. 2001).

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

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

2.4 Why is EPA publishing this document?

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

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

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

2.5 What is the effect of this document?

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

N. San Mateo County Sanitation District

Where samples were taken:

lat 37° 29.42
long 122° 30.44

} 1 LOCATION APROX .7 MILES off coast

What were the samples.

5 different Species

When samples taken

2 on 5/9/00
1 on 5/22/00
2 on 5/23/00

* This listing represents a small section of the coastline

✓ One location
✓ 5 different species

FROM: "San Francisco Bay Fish Index - Indicator Analysis and Evaluation"

Results of the Bay Study were compared to those of the FMWT and found to be highly correlated (correlation coefficient: 0.88; $p<0.001$) (Figure 2).

For quantitative comparison of fish abundance between the two surveys, a correction factor for the differential in catch effort was generated by comparing catch per unit effort results from the two surveys for the 1980-1990 period.[9] Bay fish abundance for the 1967-1971 period (mean±1 standard error, SE), expressed in terms of Bay Study Midwater Trawl Survey catch per unit effort, was then estimated using FMWT results.

Diversity – This indicator was calculated as the number of Bay-dependent species (listed in Table 1) collected each year using data from both the Midwater Trawl and Otter Trawl surveys. A total of 33 Bay-dependent fish species were identified: 20 resident species that live in the Bay or require the Bay for nursery habitat, and 13 seasonal species with substantial connected populations outside the Bay but that use the Bay for part of their life cycle.

Table 1. San Francisco Bay-dependent fish species collected in the CDFG Bay Study Midwater Trawl and Otter Trawl surveys.

Bay-dependent fish species (common names)	
Bay resident species Species with resident populations in the Bay and/or Bay-obligate species that use the Bay as nursery habitat.	**Seasonal species** Species regularly use the Bay for part of their life cycle but also have substantial connected populations outside the Bay.
Arrow goby Bat ray Bay goby Bay pipefish Brown rockfish Brown smoothhound Cheekspot goby Delta smelt Dwarf surfperch Jack smelt Leopard shark Longfin smelt Pacific herring Pacific staghorn sculpin Pile perch Shiner perch Threespine stickleback Topsmelt, Tule perch White croaker	Barred surfperch California tonguefish Diamond turbot English sole Pacific tomcod Plainfin midshipman Sand sole Speckled sanddab Spiny dogfish Splittail Starry flounder Surfsmelt Walleye surfperch * Northern anchovy were not included in the Diversity calculation.

BLK ROCKFISH
BROWN "
ROSETHORNE "
LINGCOD
SPOTFIN SURF-PERCH

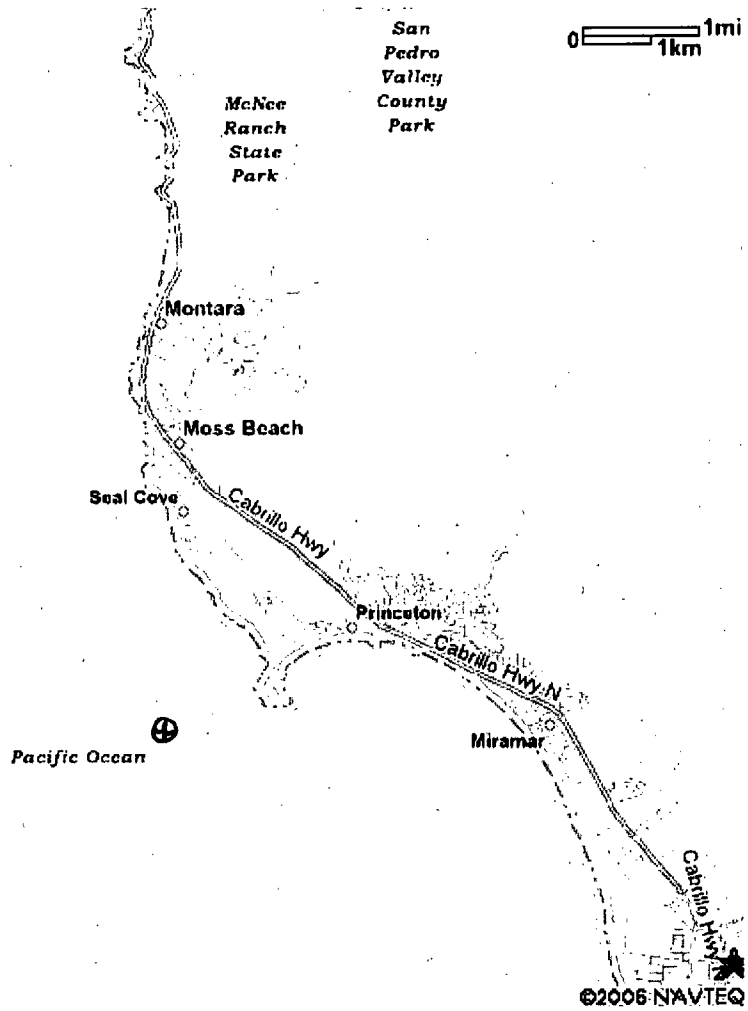
[9] In most years after 1980, the FMWT sampled the Bay only during the fall (September-December). Therefore, for quantitative comparison between the two surveys and development of the correction factors, only data from the September-December surveys were used.

MAPQUEST

Half Moon Bay CA
US

Notes:

MAPQUEST



00-0659t	2300	San Mateo Coast	Year2	BLR	Black Rockfish	N	37 29.42	122 30.44	9-May-00
00-0713-t	2300	San Mateo Coast	Year2	BRR	Brown Rockfish	N	37 29.42	122 30.44	23-May-00
00-0714-t	2300	San Mateo Coast	Year2	OLC	Lingcod	N	37 29.42	122 30.44	23-May-00
00-0660-t	2300	San Mateo Coast	Year2	RTR	Rosethorn Rockfish	N	37 29.42	122 30.44	9-May-00
00-0711-t	2300	San Mateo Coast	Year2	SFS	Spotfin Surfperch	N	37 29.42	122 30.44	22-May-00