Mercury TMDLs – Significance to the Power Industry and Guidance for Individual Power Plants

Technical Report

Mercury TMDLs – Significance to the Power Industry and Guidance for Individual Power Plants

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REPORT SUMMARY

This project was initiated by EPRI to provide guidance for individual power plants faced with mercury total maximum daily loads (TMDLs) and to assess the significance of establishing mercury TMDLs.

Background

Many states have issued advisories restricting fish consumption based on the Environmental Protection Agency's (EPA's) reference dose and levels observed in fish tissue and have placed them on state lists of impaired waters under the Clean Water Act (CWA), Section 303(d). In response to these listings and recent court orders, EPA and the states have developed and continue to develop mercury TMDLs (a calculation of the maximum amount of mercury a waterbody can assimilate without exceeding the applicable water quality standards for its designated use).

Objectives

- To review available data to assess the level of mercury in power plant effluents.
- To review mercury TMDLs nationwide to enable comparison of TMDL water quality targets to plant effluent levels and to assess strengths and weaknesses of TMDL approaches.
- To develop guidance for individual power plants facing mercury TMDLs.

Approach

The project approach consisted of reviewing and analyzing power plant data from EPRI's PISCES database, data provided by EPRI members, data discovered as part of the TMDL review process, TMDL reviews, and reviews of relevant regulatory documents. Seventy-three mercury (73) TMDLs were reviewed nationwide. In addition to establishing ranges of water quality and fish tissue targets, the TMDL reviews evaluated the strengths and weaknesses of various regulatory approaches. Guidelines for addressing TMDLs were built on results of the first two objectives.

Results

Geometric mean total mercury concentrations in power plant discharges range from 0.76 ng L^{-1} to 36 ng L^{-1}. A comparison of these concentrations to the range of typical water quality targets observed in mercury TMDLs across the country (0.52 to >10 ng L^{-1}) indicates a substantial overlap. Methylmercury targets observed in TMDLs across the United States ranged from 0.029 ng L^{-1} to 0.46 ng L^{-1}, and observed methylmercury effluent concentrations were uniformly less than 0.1 ng L^{-1}. Given this overlap, power plants could find themselves in a situation where their effluent might exceed a TMDL target.

Several factors may increase the future impact of mercury TMDLs to the power industry. They include implementing flue gas desulfurization (FGD) systems for sulfur emission control, implementing selective catalytic reduction (SCR) / selective non-catalytic reduction (SNCR) systems for NO_X control, and lowering regulatory compliance levels through consideration of mercury effects on wildlife.

Strengths and weaknesses of TMDL regulatory approaches are summarized in four categories:

- use of a fish tissue criterion as a water quality standard,
- water column targets derived from fish tissue targets,
- approaches for deriving water-column-based criteria, and
- approaches to TMDL allocations and implementation.

Guidelines are given for individual power plants that may be facing mercury TMDLs. Guidance is divided into two major portions, the first dealing with 303(d) listing and delisting issues and the second dealing with mercury TMDLs themselves. The focus of the 303(d) section is collection and analysis of fish and water samples and presentation of resulting data to best influence the listing/delisting process. The focus of the TMDL guidance section is how the TMDL process can be influenced to mitigate the potential regulatory burden.

EPRI Perspective

This report provides information on the TMDL process and, through a data analysis methodology, demonstrates that power plant effluents might exceed TMDL targets. The report also provides guidelines on collecting and analyzing fish and water samples and assists power plant operators in interacting with permitting authorities in the list and delisting process. The better informed operators are of permitting activities, the earlier they can participate in the process. This report is a follow-on to *Implementation of the United States Environmental Protection Agency's Methylmercury Criterion for Fish Tissue* (EPRI report 1005520).

Keywords

Criteria and standards
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INTRODUCTION AND BACKGROUND

Environmental concerns for mercury have grown increasingly over the last decade. In 1997, as result of the 1990 Amendments to the Clean Air Act (CAA), the United States Environmental Protection Agency (EPA) prepared its Mercury Study Report to Congress (U.S. EPA 1997). The Utility Air Toxics Report to Congress, published in 1998, identified mercury as the utility air toxic of greatest concern. In December, 2000, the EPA issued a regulatory determination under the Clean Air Act that regulation of mercury is appropriate and necessary for coal- and oil-fired power plants. On March 15, 2005, EPA issued the final Clean Air Mercury Rule (CAMR) for coal-fired power plants. The CAMR utilizes a market-based cap-and-trade approach that requires emission reductions in two phases: a cap of 38 tons in 2010, and 15 tons after 2018, for a total reduction of 70 percent from current levels. Thus, the utility industry will be continuing its efforts to reduce atmospheric emissions of mercury from combustion of coal and other fossil fuels.

The chief concern of the EPA and the electric utility industry for mercury under the Clean Water Act (CWA) is emission of mercury, in either particulate or gaseous forms, and its subsequent deposition to landscapes and water bodies. In rivers, lakes and estuaries, atmospherically deposited divalent (inorganic) mercury may become transformed into methylmercury (MeHg), a species more toxic and bioaccumulative than inorganic mercury, enhancing its entry into aquatic food chains. As methyl mercury works its way up the food chain, it becomes present at increasingly higher levels in fish tissue and at increasingly greater percentages of the total mercury present. According to EPA, mercury levels present in fish tissue above 0.3 mg kg^{-1} are of concern to the general population of human consumers. In addition to regulated air emissions, power plants are permitted direct discharge of some mercury in wastewater as regulated by the National Pollutant Discharge Elimination System (NPDES). Mercury loadings to wastewater systems may increase in the future as air emissions are reduced through the use of scrubbers and other devices to remove mercury from stack gases.

Many states have issued fish consumption advisories restricting fish consumption based on EPA's reference dose and levels observed in fish tissue. Many of these same states have adopted the position that restriction of fishing and/or fish consumption in these water bodies constitutes an impairment of the resource and have placed them on the state's list of impaired waters under CWA Section 303(d). Over two thousand water bodies across the United States have been thus classified. In response to these listings and recent court orders, EPA and the states have developed and continue to develop mercury Total Maximum Daily Loads (TMDLs), a calculation of the maximum amount of mercury a waterbody can assimilate without exceeding the applicable water quality standard(s) for its designated use.

The current project was initiated by the Electric Power Research Institute (EPRI) to provide guidance for individual power plants faced with mercury TMDLs and to assess the risk that the establishment of mercury TMDLs poses to the industry. This project builds on a document prepared for EPRI (2003) to provide perspectives to EPA and the states on implementation of the methylmercury fish tissue criterion (U.S. EPA 2001).

This section provides important background information necessary to the understanding of the issues facing regulated facilities resulting from mercury TMDLs. It begins by defining a TMDL and goes on to describe the process by which water bodies are placed on state 303(d) lists. Typical TMDL components are then reviewed and discussed so that the reader may appreciate the technical issues involved in establishing mercury TMDLs and load allocations. Finally, in growing response to the difficulties of applying the TMDL process to regulate mercury in the environment, alternatives to TMDLs are discussed. Because of the general familiarity of environmental managers in the electric utility industry with these introductory topics, they are presented only briefly, and with specific emphasis on issues related to mercury.

1.1 What is a TMDL?

Section 303(d) of the CWA requires that states identify waters that are impaired because they are not attaining ambient water quality standards. For those waters that do not meet these standards, or for which attainment of standards is not reasonably anticipated due to observed water quality trends, or which lack a plan providing reasonable assurance that standards will be met, the establishment of a TMDL is required. The Clean Water Act requires that *"each State shall establish for [impaired] waters […], and in accordance with the priority ranking, the total maximum daily load, for those pollutants which the Administrator identifies […] as suitable for such calculation. Such load shall be established at a level necessary to implement the applicable water quality standards with seasonal variations and a margin of safety [MOS] which takes into account any lack of knowledge concerning the relationship between effluent limitations and water quality."*

Despite several attempts by EPA to revise the TMDL program and the definition and scope of TMDLs themselves, the operational definition remains the same as in EPA's 1991 statements (U.S. EPA 1991):

Total maximum daily load (TMDL) *– "The sum of the individual [Waste Load Allocations] WLAs for point sources and [Load Allocations] LAs for nonpoint sources and natural background. […] TMDLs can be expressed in terms of either mass per time, toxicity, or other appropriate measure that relate to a State's water quality standard. If Best Management Practices (BMPs) or other nonpoint source pollution control actions make more stringent load allocations practicable, then WLAs can be made less stringent. Thus, the TMDL process provides for nonpoint source control tradeoffs." (40 CFR 130.2(i))*

Fundamentally, these definitions lead to the familiar expression:

$$TMDL = \Sigma WLA + \Sigma LA + MOS \quad \textbf{Equation 1-1}$$

With regard to mercury, the simplicity of the above expression is an issue. As will be discussed in later parts of this report, there is considerable uncertainty in the establishment of WLAs due to the paucity of data with detection limits low enough to characterize mercury in wastewaters of contributing point sources.

The lack of data is even more of a problem when it comes to establishing LAs. Nonpoint source loads are ultimately mainly of atmospheric origin. However, current deposition may only account for a fraction of the mercury burden in watershed soils and mercury that is being transported on an annual basis into aquatic systems, and only a fraction of this deposition is due to power plant emissions. A substantial portion of the watershed mercury burden may in fact be attributable to older industrial anthropogenic sources (e.g. smelting, mining, etc.), non-industrial anthropogenic sources (e.g. volcanoes, forest fires), and natural background (e.g. crustal mercury). Although studies are underway to understand the transport of mercury from watersheds to water bodies, there is general lack of scientific understanding of such processes. Fate and transport processes are dependent upon the use and management of land on which mercury is deposited and little has been done to study these effects.

The MOS is the mechanism in the TMDL process by which variability and uncertainty are accounted for. However, the MOS is rarely used in this way due to a lack of appreciation of the uncertainties involved and gaps in the body of knowledge concerning mercury in the environment. The greatest contributor to uncertainty in mercury TMDLs is the methylation process. Where, how, and to what extent mercury is methylated and bioaccumulated is poorly understood. Added to the uncertainties due to lack of knowledge is variability. Variability comes about through natural spatial and temporal interactions of mercury with plants, soils, sediments, and biota and the inability to measure it precisely at the extremely low levels commonly encountered, especially in water.

Seasonal variation, mentioned specifically in the TMDL definition as something to be considered in the TMDL process, is a concern that frequently arises in mercury TMDLs and is usually ineffectively considered. Methylation of mercury is seasonally dependent in that it is a function of (at a minimum) temperature and dissolved oxygen levels in water and sediments. Most supporting studies for TMDL development rarely extend over adequate time periods to account for this variation. Measurements taken during short time intervals can incorrectly characterize water column levels of total and methyl mercury, which can lead to incorrect calculation of bioaccumulation factors (BAFs) and ultimately to incorrect water quality targets (WQTs). Incorrect WQTs may in turn lead to inappropriate discharge limits and ultimately to permit compliance issues.

1.2 Authority of EPA and the States to Perform TMDLs

In those states for which CWA authority has been delegated, the responsibility for TMDLs falls upon the state. However, EPA, the delegating authority, is made responsible if delegated states do not perform and EPA has been frequently sued over the failure of the states to perform TMDLs. Therefore, the states and EPA will typically agree, especially in those cases where lawsuits force immediate establishment of TMDLs, to share responsibility for performing them. Thus, it is not uncommon for some TMDLs to be performed by the state and other to be performed by EPA. The EPA Regions have taken the responsibility for many mercury TMDLs because of the intractability of the technical and policy issues and the lack of resources at the state level to undertake them.

1.3 When are TMDLs Required?

TMDLs are required whenever a water body is place on the state's 303(d) list of impaired waters. Once a waterbody is placed on the 303(d) list, it cannot be removed until a TMDL is done and/or water quality standards are met. State 303(d) lists are normally revised every two years. Water bodies can be delisted if new information becomes available showing that water quality standards are being met. This is an important point and will be discussed further in Section 4.

1.4 303(d) Lists

According to EPA's latest guidance (U.S. EPA 2005), the states' lists of waters should consist of the following five categories:

- Category 1: All designated uses supported, no use threatened;
- Category 2: Some, not all, designated uses supported;
- Category 3: Insufficient data to make use support determination;
- Category 4: At least one use not supported or threatened, TMDL not needed; and
- Category 5: At least one use not supported or threatened, TMDL needed.

Category 4 has three subcategories, as follows:

- Category 4a: TMDL has been completed but standards are not yet met;
- Category 4b: Other (alternative) regulatory programs will lead to attainment of standards; and
- Category 4c: Standards violations are caused by "pollution" rather than a specific "pollutant".

To this researcher's knowledge, the existence of regulations to be implemented under the CAA to control emission sources of mercury has not been tested as a reason for placing waterbodies in Category 4b. Variances, however (see section 1.6.8.4) might result in the waterbody being placed in section 4b, obviating the need for a TMDL[1]. In Michigan, which has such a variance program, waterbodies impaired for mercury have been placed in Category 5 but the TMDLs have been postponed until 2011. In Ohio, another state with a variance program, water bodies deemed to be impaired are also listed in Category 5, with the TMDLs assigned priority per Ohio's ranking methodology.

[1] The variance program requires that participating facilities develop and implement a pollution minimization plan, which might be considered an alternative regulatory approach.

Water bodies on the 303(d) list impaired for fishing use due to the presence of a fish consumption advisory will likely be placed in category 5 and will require a TMDL. An exception to this is possible, when the fish consumption advisory is based on more stringent health risk criteria than those used to derive the water quality standard (WQS). In such a case, the waterbody need not be listed and a TMDL is not required. This was the case for the Savannah River in Georgia, where the threshold for the State's fish consumption guideline for mercury was 0.23 mg kg^{-1} (based on a consumption rate of 30 g day^{-1}), and the adopted 0.3 mg kg^{-1} methyl mercury criterion was derived based on a consumption rate of 17.4 g day^{-1}. In this case, trophic-level averaging produced a weighted-average tissue concentration less than 0.3 mg kg^{-1} but above the 0.23 mg kg^{-1} state threshold for fish consumption guidelines. Therefore, affected river segments were removed from the 303(d) list but the fish consumption guidelines were retained. Similarly in Michigan, a water body can have a fish consumption advisory but not be placed on the 303(d) list according to differences in the advisory posting thresholds and 303(d) listing criteria.

1.4.1 Prioritization of TMDLs

Section 303(d) requires that states establish a priority ranking of the waterbody segments identified on the list, taking into account the severity of pollution and the beneficial uses of those waters, and update this prioritization every two years. TMDLs proposed to be established in the next two year period are to be clearly identified with a completion date or a high, medium, low ranking. States have considerable flexibility in this regard. For instance, some water quality problems may be given a lower priority to allow time to collect necessary information to complete the analysis. This seems to often be the case with mercury, where many states have opted to delay these TMDLs for a variety of reasons including data limitations, resource limitations at the state level, and lack of clear and consistent guidance for conducting mercury TMDLs. EPA approves or disapproves of a state's ranking.

Many factors contribute to a state's prioritization decisions including rotating basin approaches to establishing TMDLs and the existence of court-ordered schedules where law suits have been settled. In any case, electric utility environmental managers should obtain TMDL schedules for the states that overlap with their operations. The 303(d) can normally be downloaded from the website of the state environmental regulatory agency. If not available there, it can be obtained by request to the regulatory agency's Freedom of Information Act (FOIA) coordinator.

1.4.2 Law Suits

Law suits have been settled in a number of states resulting in court-ordered schedules for completion of TMDLs. Where this has occurred, TMDLs normally are required to be established on an accelerated schedule. In the past, this has been a formula for aggressive schedules which have neglected the difficulties of dealing with mercury issues and have resulted in poorly executed and/or overly conservative TMDLs. Utility environmental managers should be particularly concerned where court settlements have forced these situations on EPA and the states.

There are 23 states and the District of Columbia in which EPA is under court order or has agreed in consent decree to establish TMDLs if states do not establish TMDLs, as follows[2]:

Alabama (1998; 5 yr schedule)	Mississippi (1998; 10 yr schedule)
Alaska (1992; no schedule)	Missouri (2001; 10 yr schedule
Arkansas (2000; 10 yr schedule)	Montana (2000; 7 yr schedule)
Calif. (LA) (1999; 13 yr schedule)	Nevada (2002; one TMDL by 2005)
Calif. (North Coast) (1997; 11 yr schedule)	New Mexico (1997; 20 yr schedule)
Delaware (1997; 10 yr schedule)	Ohio (2004; 4 yr schedule)
District of Columbia (2000; 7 yr schedule)	Oregon (2000; 10 yr schedule)
Florida (1999; 13 yr schedule)	Pennsylvania (1997; 12 yr schedule)
Georgia (1997; 7½ yr schedule)	Tennessee (2001; 10 yr schedule)
Iowa (2001; 9 yr schedule)	Virginia (1999; 12 yr schedule)
Kansas (1998; 10 yr schedule)	Washington (1998; 15 yr schedule)
Louisiana (2002; 10 yr schedule)	West Virginia (1997; 10 yr schedule)

In the following states, suits were dismissed without orders that EPA establish TMDLs (cases were either resolved with settlement agreements or EPA completed all court-ordered obligations and the case was dismissed):

- Arizona (EPA completed all consent decree obligations; decree terminated July 17, 2000);
- California (9th Circuit affirmed dismissal, 2002);
- California (Newport Bay) (EPA completed consent decree obligations; decree terminated 2003);
- Colorado (Joint Motion for Administrative Closure filed August 24, 1999; parties signed settlement agreement in which EPA agreed to establish TMDLs if Colorado did not);
- Hawaii (EPA completed all consent decree obligations; decree terminated December 9, 2002)
- Idaho (EPA Motion to Dismiss granted 1997; settlement agreement signed 2002);
- Lake Michigan (WI, IL, IN, MI) (Scott case – final order 1984; related NWF case challenging EPA actions in response to Scott order – case dismissed 1991);
- Minnesota (Dismissed 1993);
- Maryland (Dismissed 2001);
- New Jersey (Dismissed 2002);
- New York (EPA Motion to Dismiss granted on all but one claim May 2, 2000);

[2] Information on litigation status was taken from EPA's website.

- North Carolina (Joint Stipulation of Dismissal filed June 1998; EPA agreed by letter to ensure development of a TMDL for the Neuse River by date certain);
- Oklahoma (Tenth Circuit upheld dismissal of case on August 29, 2001);
- South Dakota (Dismissed without prejudice on August 27, 1999); and
- Wyoming (Dismissed 2003).

There are no states with pending cases in which plaintiffs have filed litigation seeking to compel EPA to establish TMDLs.

1.5 How Waterbodies are Listed for Mercury

Waterbodies are placed on the 303(d) list when the state makes the determination that the beneficial use of the waterbody of concern is not being met. Normally, this determination makes use of the state's water quality standard for mercury and compares the standard to some relevant measure of compliance. In the case of mercury, this comparison is often fraught with uncertainty.

There may be a number of beneficial uses designated by states for a water body and each may have its own unique set of standards. In addition, separate standards may be set to protect both human health and the environment. Attainment of uses typically is judged by comparing ambient water quality data to the numerical water quality standard for a given water body. Where there is no numerical standard and EPA and the states have relied on narrative standards to judge attainment or nonattainment. As mentioned above, EPA and the states have used the existence of fish consumption advisories as an interpretation of narrative standards prohibiting discharges of pollutants to water in quantities that might cause deleterious effect to human health or the environment. In the case of mercury, where states may have adopted EPA's recommended fish tissue based standard, there may actually be dual water quality standards. For instance, the State of Georgia adopted EPA's fish tissue standard of 0.3 mg kg^{-1} but still has the 12 ng L^{-1} standard in its regulations, and may list waters on exceedance of either.

1.5.1 Exceedance of Water Quality Standards

Violations of water quality standards are the least ambiguous of the listing criteria. However, there are numerous issues. Historically, ambient measurements made for mercury in the water column have been compared to the water quality standard, which may typically be 12 ng L^{-1} for fresh waters and 25 ng L^{-1} for marine waters (EPA's 1984 criterion) or 50 ng L^{-1} (EPA's 1998 criterion for consumption of water and organisms)[3]. Issues to consider with regard to such listings are the following:

- Prior to 1995 (when EPA first published its low level analytical Method 1631 for mercury in water), the detection limit for mercury in water was 200 ng L^{-1} (EPA Method 245.1) and detections were rare. However, with the advent of better analytical methods (EPA Method 1631 has a method detection limit of 0.5 ng L^{-1}), detections became more common and contamination of samples due to improper sample collection was rampant. As awareness of this issue has grown, sample collection techniques have improved. Utility managers should be suspicious of ambient water quality data;

[3] The reader is referred to EPRI 2003 for a detailed review of the history of water quality standards for mercury.

- indicating exceedance of the 12 ng L^{-1} standard as ambient levels typically are lower;
- If multiple laboratories have been used to collect environmental samples, interlaboratory differences in results can be an issue, especially when using low-level methods; and
- An adequate number of samples for proper comparison to standards is almost never available, given the variability of mercury measurements in the water column. In some cases, single samples have been used to list waterbodies.

1.5.2 Posting of Fish Consumption Advisories

Fish consumption advisories have been commonly used as a tool for interpreting states' narrative standards for mercury, resulting in thousands of listings of waters as impaired by mercury, even though no exceedance of water column-based water quality standards have been observed. These listings have been made both for specific waterbodies and entire regions, even though no data may have been available in some cases to assess contravention of standards.

1.5.2.1 Waterbody-Specific Advisories

Waterbody-specific advisories usually result from routine monitoring performed by the states. Programs are instituted to ensure that citizens can utilize the waters of the state for fishing uses and to assess trends in fish tissue and water quality. Programs to evaluate fishery uses usually involve the collection of popularly harvested sport fishes. Other programs may use bottom feeding fish as indicative of sediment quality issues. It is undeniable that these programs, and the guidance that exists for targeting species and specimen sizes, were *not* developed with the objective of assessing fish tissue concentrations vis-à-vis a tissue-based water quality standard.

As a rule, such programs usually target predatory fish in the upper food chain, as bioaccumulative contaminants are more likely to be found in these specimens (U.S. EPA 2000). Within this subpopulation, the guidance recommends targeting older, larger fish for the same reasons. As a result, observations of average fish tissue body burdens may be biased toward higher values. EPA's methylmercury criterion, however, is based on the fish tissue concentrations across trophic levels, from piscivorous trophic level 4 fish down to and including herbivorous trophic level 2 fish. EPA's methylmercury criterion is formulated by using average tissue concentrations in each trophic level and weighting those values by the overall percentage of that trophic level in the diet of the consuming population. Thus, comparison of fish tissue data to the methylmercury criterion may produce a biased assessment of risk to consumers in a given water body. It follows that the use of fish consumption advisories to list water bodies impaired for fishing use may overestimate the risk to consumers for a given water body.

1.5.2.2 Statewide and/or Regional Advisories

Statewide or regional advisories have been made by comparing waters where fish consumption advisories have been posted, to waterbodies where such data is unavailable, on the basis of similarity of the waterbodies involved. Such listings may provide a case-by-case opportunity for utilities to collect fish tissue data and demonstrate that the standard is not being exceeded in the receiving waters to which they discharge.

1.5.3 Exceedance of Tissue-Based Standards

Where states have adopted EPA's methylmercury or similarly derived criterion, fish tissue results may be compared directly to the criterion to assess whether or not the water body should be placed on the 303(d) list. As alluded to above, caution should be exercised to assure that the tissue residues are representative of fish caught and consumed by the population for which the standard has been established. EPA's methylmercury criterion was developed for the general population nationwide and as such encompasses a wide variety of fish species and consumption patterns. To the extent that a state's standard is targeted at a specific consumer group, fish tissue residues used for comparison to the standard should align as closely as possible to the size and species typically consumed for such a comparison to be valid. In addition, the number of fish tissue values should be sufficient in a given water body to make valid statistical comparisons to the standard.

1.6 Typical Components of a TMDL

This section familiarizes the reader with the typical components of a TMDL, both to let the TMDL reviewer know what to expect and to highlight issues and potential shortcomings in each section.

1.6.1 Problem Statement

The problem statement section of the TMDL specifies why it is being performed. It typically identifies the waterbody or waterbody segments the TMDL addresses, often by the Hydrologic Unit Code (HUC) employed by the United States Geological Survey (USGS) to uniquely identify waterbodies of the United States. Some states use their own identification systems.

This section gives the rationale for the 303(d) listing. The TMDL sometimes identifies the data used to place the water body on the 303(d) list and may provide a data summary, although it is rare that the actual data is included in the TMDL document. It is important to obtain and review this data, as flawed information may have been used for listing purposes.

1.6.2 Applicable Standards

Applicable standards are those on which the listing is based. Numerical standards should be identified and/or the basis for interpreting a narrative standard (e.g. a fish consumption advisory) should be provided.

1.6.2.1 Water Quality Standards

As discussed earlier, the water quality standard will normally be water column based. All applicable standards in the state's regulation will normally be listed and the most restrictive will be identified as the basis for the TMDL target (see the discussion below).

1.6.2.2 Narrative Standards

The narrative standard, citing the appropriate section of the state's administrative code, should be stated.

1.6.2.3 Fish Consumption Guidelines

In this section, the state's procedures and policies for posting of fish consumption advisories should be provided, assuming this is the basis for interpretation of the narrative standard.
It is important to know how the advisories (guidelines, in some states) are developed. If the guidelines that set listing thresholds are more stringent than the tissue-based standard (e.g. if the threshold for restricting consumption to one meal per week is 0.24 mg kg^{-1}, and the adopted fish tissues standard is 0.3 mg kg^{-1}), then it may be possible to delist the waterbody even though a fish consumption advisory is, and might remain, in effect. Key factors that may make the threshold listing levels different from EPA's methylmercury criterion include the fish tissue levels used and fish consumption rates.

1.6.3 TMDL Target

Ideally, the TMDL target should be equivalent to the water quality standard. However, in many TMDLs the agency takes license with this target, making it lower than the standard by adding a "margin of safety' that is seldom quantified. This is done in one of several ways if the target is tissue-based. At times agencies will apply the standard (derived from concentrations over all fish consumed) to only trophic level 4 fish. At other times, the agencies will specify the target as the listing threshold for the fish consumption advisory.

In many cases, the TMDL derives a WQT, which is intended to supersede the existing water quality standard. The rationale for this is if fish tissue exceeds the desired target, but the water column-based standard is not exceeded, then the water column-based standard must be inadequate to protect human health; therefore a lower water-column based target is needed. This is one of the most controversial elements of a mercury TMDL. The water column based target is usually calculated using a bioaccumulation factor (BAF). Even though the calculation is simple (the fish tissue concentration divided by the methylmercury concentration in water), there are a number of issues, most of which surround the measurement of methylmercury in the water column and the representativeness (i.e. number, location, time of collection) of these measurements. This will be dealt with in detail in Section 4.

It is important to note that in some cases, the TMDL target is based on the protection of wildlife and is more stringent than that required for the protection of human health. An example is the Great Lakes WQS of 1.8 ng L^{-1}. Having noted this, it is worth mentioning that in other TMDLs where protection of wildlife has been considered, levels to protect human health from fish consumption have been found also to be protective of wildlife.

1.6.4 Source Assessment

The source assessment is the identification of all sources contributing mercury to the water body. This assessment will typically categorize these into point and nonpoint sources, with special consideration paid to atmospheric deposition. Discussion of how load estimates are made for each category is provided in Section 4.

1.6.4.1 Point Sources

Point sources are usually identified in this section by name and by permit number. The narrative will typically identify those facilities having mercury in their permits. The reviewer of the TMDL should check to make sure the facility of his/her concern is properly identified. There have certainly been instances where point sources have been identified as discharging to a particular waterbody, when in fact they discharge to another.

The most significant issue with the development of point source estimates is the paucity or complete lack of data to characterize discharges. In the best of cases, there are typically only a handful of data points. In many cases, there may be only a single data point. This number of data is inadequate to characterize low concentration discharges of mercury. This issue will be dealt with in detail in Section 4.

1.6.4.2 Nonpoint Sources

In the majority of TMDLs, descriptions of the watersheds are provided including topography, soils, land use and hydrology that provide the basis for estimation of nonpoint source pollutant loads. However, most of the models being used to estimate loadings of mercury from the watershed to water bodies are inadequate for this purpose. Many of the physical, chemical, and biological processes important to this estimation are poorly understood or simply overlooked. This will be discussed in detail in Section 4.

The greatest single issue concerning nonpoint sources is the failure of most TMDLs to recognize that much of the mercury in the terrestrial system is there as a result of natural or older anthropogenic sources. In fact, many TMDLs force current emissions to account for all of the mercury observed in watershed soils. In order to do so, buildup of mercury in watershed soils and losses from terrestrial to aquatic systems is overestimated. This creates the illusion that control of current atmospheric emissions and subsequent deposition will result in commensurate reductions in aqueous and biotic mercury and underestimates the time required to achieve compliance.

1.6.4.3 Atmospheric Deposition

Atmospheric deposition usually receives special attention in mercury TMDLs as it is often identified as the principal source of pollutant loading to the watershed and waterbody. This section will typically identify local and regional emission sources, especially electric power plants, chlor-alkali facilities, medical waste incinerators and others suspected of contributing an elevated pollutant load relative to other emission sources.

1.6.5 Linkage Analysis

Linkage analysis is the means by which the TMDL develops the relationship between mercury load estimates and concentrations in the water column or in fish tissue and estimates the magnitude of the load causing exceedance of the water quality standard. This will typically involve the estimation of point, nonpoint, and atmospheric loads. In some cases, estimates of certain nonpoint loads (e.g. mining sources, legacy sediments) are given special consideration. The following sections provide an overview of the issues associated with the steps involved.

1.6.5.1 Loading Scenarios/Models

In this section of the TMDL, loads are developed for known point and nonpoint sources. Point source loads are estimated by multiplying measured or estimated discharge concentrations, usually by the actual, design, or permitted flow rate for the facility or facilities, either individually or as a group.

Nonpoint sources loads are much more difficult to estimate. This is typically done using a watershed model designed for another purpose, which has been adapted to estimate mercury fate and transport in terrestrial systems. As alluded to above, these models rarely incorporate or simulate the mercury fate and transport processes that actually occur in natural systems. At best, runoff and erosion processes are addressed. In these models, mercury attached to eroded soil particles dominates loading to the water body. Soil erosion is almost always simulated using the Universal Soil Loss Equation (USLE). This method, developed by the U.S. Department of Agriculture (USDA) in the 1950s, was intended to be used as a tool for estimating soil loss for conservation purposes. It has subsequently been used as an underlying algorithm in many environmental models to simulate transport of contaminants attached to eroded soil particles. It does not simulate soil losses by particle size and enrichment of fine particles (to which mercury would be preferentially attached) during transport. Since the data to calibrate or validate these models for mercury is nonexistent, the estimates they produce are tenuous at best. Furthermore, since the nonpoint source load constitutes by far the greatest load to the waterbody, this analysis usually dictates the required load reductions. Mercury concentrations in bulk surface soils or measured concentrations in stream bed sediments typically are used to characterize the concentration of mercury in eroded soil particles. Either of these can lead to misrepresentations of actual concentrations and introduces considerable uncertainty into the calculations. Nonetheless, the results of these computations are often given to a surprising number of significant digits, implying accuracy far beyond what is possible. Estimates of uncertainty in these estimates are seldom, if ever, expressed, and the implications of this uncertainty are never dealt with. The reality is that the uncertainties are immense, probably greater than the load reductions themselves, and the load reductions border on being meaningless.

A review of watershed models typically employed in TMDLs highlighting assumptions, strengths and weaknesses of each is provided in Appendix B of this document.

Atmospheric load estimates are typically made using the output of atmospheric transport and deposition models or data from the Mercury Deposition Network (MDN). Where these estimates differ, the highest estimates are normally used. Since load reductions are normally equated to the reduction of water column or fish tissue concentration required to meet the water quality standard expressed as a percentage, the higher the current atmospheric load, the greater the absolute reduction required.

Often, the reduction in required air deposition is parsed between reductions assumed to be attained through implementation of existing Maximum Achievable Control Technology (MACT) regulations and that which will not be. The difference is that portion of the emission reduction associated with the power industry, as it is identified by EPA as being the greatest remaining industrial atmospheric source in the United States.

1.6.5.2 Receiving Water Analysis/Models

Once the watershed loads to the waterbody are generated, a receiving water model may be run to calculate water column concentrations or fish tissue concentrations for comparison to the TMDL target. If the TMDL target is a fish tissue concentration, and reductions in atmospheric emissions are equated to the percent reductions required in *observed* fish tissues as compared to the target, a receiving water model is not needed. In general, the receiving water models are more advanced than their watershed loading counterparts, in terms of their representation of key processes involved in mercury fate and transport. A review of receiving water models, including fish bioaccumulation models, is provided in Section 4.

The significant issues relative to the simulation of bioaccumulation in fish are methylation of inorganic mercury and bioaccumulation of methylmercury in the aquatic food chain. Unfortunately, as much as is known about these two phenomena, predictions of when, where, and to what extent they will occur in any given aquatic system cannot be made reliably. The prediction of methylmercury production and bioaccumulation is still empirical, based on methylation “translators” (i.e. the ratio of methyl to total mercury) and bioaccumulation factors (i.e. the ratio of methyl mercury in fish tissue to methylmercury in the water column). While these processes are briefly reviewed here, the reader is referred to EPRI (2003) for a more detailed assessment of the body of scientific knowledge, and knowledge gaps, concerning these processes.

1.6.5.3 Methylation

Methylation is the process by which inorganic mercury is converted to methylmercury, a more toxic and bioaccumulative form. Mercury methylation is influenced by a number of complex environmental variables and interactions, including pH, redox (Eh), temperature, salinity and microbial population, as well as organic (e.g. dissolved organic carbon or DOC) and inorganic (e.g. S^{2-}) complexing ligands. Methylation is thought to be primarily a microbially-mediated process although the precise mechanism of methylmercury formation is unclear. It is the complexity of the interactions of all these influencing variables that makes the prediction of methylation an intractable problem.

1.6.5.4 Bioavailability and Bioaccumulation

Bioaccumulation is the process by which methylmercury is incorporated into biota and becomes biomagnified (i.e. tissue concentrations are increased) as it moves upward through the food chain in aquatic systems.

In order for mercury to bioaccumulate is must be in a bioavailable form. Generally, bioavailable mercury is thought to be comprised of dissolved inorganic forms including “free” ionic mercury (Hg^{2+}) and uncharged soluble complexes (e.g. $HgCl_2$), although some low molecular weight charged species may also be bioavailable. These forms may constitute a minor portion of the mercury in an unfiltered water sample, where much of it may be adsorbed to inorganic particles, assimilated in particulate organic matter (e.g. detritus, algae), or complexed with dissolved organic matter (DOM). Studies required to speciate mercury are expensive, and even if the bioavailable species concentrations are estimated, the activity of sulfate reducing bacteria is modulated by environmental factors in natural systems that are difficult to predict. For example, it is well-established that sulfate reducing bacteria are primarily responsible in most aquatic systems for methylation, yet none of the available receiving water models simulate sulfur cycling.

1.6.5.5 Old versus New Mercury

While this issue, to the researcher’s knowledge, has not come up in a way that has materially affected TMDLs to date, it is worth mentioning, as it may be used as an argument by the agencies favoring the regulation of facilities currently emitting or discharging mercury to air or water. There is no absolute definition for “old” versus “new” mercury. However, the concern is “old” mercury that has resided in the terrestrial or aquatic system for a sufficient time to be bound in inorganic or organic complexes is less bioavailable than “new” mercury that has been recently introduced into the system. Thus, it may be argued that ‘’old” mercury loadings to an aquatic system, which may have come from preindustrial or older anthropogenic sources, can be dismissed or deemphasized vis-à-vis mercury in fish tissue. Such an argument would tend to favor control of current emission sources relative to resident mercury in watersheds. However, it seems premature to draw this conclusion at this time. While there is recent experimental evidence that mercury introduced into Everglades mesocosms is more bioavailable than resident mercury in the system (Gilmour et al. 2003), the overall impact of new mercury on methylation in the system may still be in question[4] and the phenomenon has by no means been shown to be ubiquitous.

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[4] Several aspects of this research are worth mentioning. First, the amount of mercury introduced into the WCA 3A-15 mesocosms produced initial concentrations of about 7 ng L-1, 22 ng L-1, and 35 ng L-1. The typical total mercury concentration in area WCA 3A-15 is about 1.9 ng L-1, so the introduced total mercury concentrations were atypically high. Next, even though methylation of introduced mercury appeared to be enhanced over older mercury, the percentage of new mercury methylated was quite low (from about 0.5% at lower concentrations to 1% at the highest concentration). A typical percentage of methyl to total mercury is 25% in area WCA 3A-15.

1.6.6 TMDL Development, Load Allocations, Wasteload Allocations

The essence of the TMDL is the establishment of loading capacity relative to the water quality standard. As originally envisioned, this is a relatively straightforward exercise. If the concentration of a given pollutant is 20% above the water quality standard in a waterbody, common sense suggests that the loading of a given pollutant should be reduced by 20% in order to meet the standard. Furthermore, if there is some uncertainty about the magnitude of that load, reducing it by some additional amount (a margin of safety) should provide greater confidence that the standard will be met. With mercury, however, this analysis is not straightforward. There is abundant evidence in the literature that the loading of total mercury to a waterbody does not correlate to water column concentrations of total mercury. There is abundant evidence in the literature that methylmercury concentrations in the water column are not related to total mercury concentrations in the water column. Even though there appears to be a more consistent relationship between methylmercury in water and bioaccumulated levels in fish, the lack of relationship between total mercury loadings, total mercury water column concentrations, and methylmercury water column concentrations precludes a straightforward analysis.

It has been suggested that a linear relationship exists between mercury loads and fish tissue concentrations and this assumption underlies the load reductions specified in most, if not all mercury TMDLs. This theory apparently has its roots in an analysis done in the Florida Everglades (FDEP 2001) and perhaps more generally due to the fact that early mercury studies were done on seepage lakes where atmospheric inputs were the dominant loads and fish response was more likely to be linear with these loads.

While the FDEP analysis predicted a linear response of fish tissue to atmospheric load reductions, it also specifically stated that "the predicted long-term response of fish tissue concentrations to changes in atmospheric deposition is governed, and to some extent uncertain, as a result of our current understanding of mercury cycling and the resulting assumptions in the model". Specifically, the following assumptions were identified as having a significant impact on the shape of the load-response curve:

- Mercury methylation depends on the bioavailable fraction of sediment porewater Hg^{2+};
- Porewater Hg^{2+}concentrations are not at saturation with respect to cinnabar (that is; formation of HgS did not control the porewater concentration of mercury);
- Hg and MeHg in inflows to the aquatic system were reduced in the same percentage as Hg^{2+} deposition; and
- Atmospheric methylmercury deposition was held constant when Hg^{2+} deposition was reduced.

Thus, higher than typical additions of new mercury produced much lower than typical yields of methylmercury. Therefore, the overall contribution of new mercury to methylmercury in the aquatic system may be small, depending on the quantities of new versus old mercury in the system. The researchers also comment on the rapid aging of new mercury in the mesocosms. This brings up an equally interesting point, the question being, "how quickly does "new" mercury become "old". This question is particularly relevant in systems where mercury may tend to be methylated only at certain times of the year in certain areas. The "dislocation" of "new" mercury additions in time and space from areas where methylation actively occurs may limit the importance of this phenomenon in many systems.

The assumption that porewater mercury concentrations were not controlled by precipitation of cinnabar is an assumption that may not hold true in many systems and would result in a distinct non-linearity in the response curve. Furthermore, the assumption that watershed loadings of mercury are reduced by the same percentage as, and in phase with, atmospheric reductions is unlikely, especially in waterbodies with larger watersheds, where releases from large terrestrial storages may continue to provide sufficient mercury to maintain fish tissue at elevated levels, regardless of atmospheric reductions.

1.6.6.1 Assessment of Loading Capacity

Loading capacity is established in TMDLs by two very uncertain calculations; the current loading to the waterbody, and the percent reduction in water column or fish tissue concentration required to meet the TMDL target.

The current load assessment usually is broken into two parts: direct atmospheric loadings to the waterbody and indirect loadings to the waterbody from the watershed. The direct loadings are normally derived from modeled deposition or from Mercury Deposition Network (MDN) data. A significant drawback of the MDN data is that dry deposition is not measured and thus its contribution must be estimated for a given location. Thus, the quantity of dry deposition is a source of considerable uncertainty. As previously mentioned, the higher are the estimated loads, the greater are the reductions required to meet the TMDL target.

Indirect loads, if calculated, are based on watershed models that have been developed with incomplete knowledge of the important physical, chemical, and biological processes which occur in watershed landscapes, in transit from the watershed to the waterbody, and with insufficient data to validate them. Because the indirect load to the waterbody is by far the largest component of the total load in most watersheds, this computation determines the analysis. Given the current state of the science and models, the resulting estimates of current loads are indefensible.

The quantification of the loading capacity is normally based on the estimate of the current load multiplied by the ratio of the TMDL target (water column concentration or fish tissue concentration) to the current estimate of ambient water or fish tissue concentration. The uncertainties are lower if the fish tissue concentration data are used as they are less variable and usually more abundant than water column data. Regardless of which target is used, however, the assumption of linearity between loads and water column or fish tissue concentrations comes into play when the allowable capacity is calculated based on this ratio. Thus, a highly uncertain load estimate modified by an untested assumption results in a loading capacity estimate that is tenuous, at best.

1.6.6.2 Specification and Allocation of Reductions

The reduction required is the difference between the current load and the loading capacity and must be viewed with the same degree of scientific skepticism. The allocation of loads on the other hand is usually based on agency policy; for instance, all sources must reduce by the same percentage as the percent reduction required to meet the target, or all sources must reduce in proportion to their magnitude with respect to the load. Rarely is the decision made on the basis of the ability (or inability) of a particular source to comply with the assigned reduction.

1.6.6.3 Unallocated Reserve

In some mercury TMDLs, an unallocated reserve is specified. In the case of other pollutants, for instance BOD, where there may be a reasonable chance that future development will result in additional loads and a reserve capacity is set aside for that future development, the specification of an unallocated reserve is sensible. In the case of mercury, however, in world where "virtual elimination" is the byword and where it is unlikely that an agency would permit a new or expanded source of mercury, the setting of an unallocated reserve only serves to lower much needed allocations to existing sources. It therefore functions as an additional margin of safety (MOS).

1.6.7 Margin of Safety, Seasonal Variations, and Critical Conditions

The MOS is supposed to account for "any lack of knowledge concerning the relationship between effluent limitations and water quality". However, the margin of safety is rarely identified or quantified in a rigorous way. More often than not, the MOS is incorporated in the TMDL by making conservative assumptions in the analysis. The problem with this approach is that the degree of protection afforded by the MOS is completely unknown. It may be adequate and appropriate. On the other had it may be excessive, creating a target so low that it may never be met. MOS is sometimes expressed as a percentage of the TMDL (e.g. 10%, 20%). In most cases these percentages appear to be arbitrary and decided more by policy than by consideration of the lack of knowledge involved. In such cases, it would seem appropriate to ask the regulatory agency to either justify the MOS, or remove it, as it reduces the allocation available to point sources.

Seasonal variations go largely unaccounted for in mercury TMDLs because data is typically so limited. Seasonal variation is less likely to be problematic when TMDLs are based on fish tissue targets, as fish tend to integrate seasonal and year-to-year variations. However, where TMDL targets are based on water column data, seasonality and year-to-year variations may be extremely important. In these cases, water quality targets based on a few data points may be unrepresentative of long-term average values and may skew the calculation of targets by hundreds of percent.

Critical conditions are not appropriate to mercury TMDLs as the analysis should be based on long-term average fish tissue or water quality concentrations. However, some state regulations require that critical conditions, such as the 7Q10 flow, be used to calculate water quality criteria for toxicants[5]. TMDL stakeholders should insist that that these provisions do not apply to the mercury problem, that they be revised in regulation, and that TMDLs be recalculated based on average flows.

[5] For instance, the TMDL may have been calculated based on the product of the water quality standard (e.g. 12 ng L^{-1}) and the 7Q10 flow to arrive at a mass per unit time load.

1.7 Implementation

Implementation plans have been ruled not to be part of the TMDL. However, many TMDL documents address implementation issues and advise the implementing authorities as to what must be done to meet the requirements of the TMDL. The implementing authorities are the agencies, usually the states, which issue and administer NPDES permits. However, for waterbodies affected solely by nonpoint sources or where point sources have been judges *de minimis*, the responsibility for implementation is less clear. In such cases, the state would normally identify a Designated Management Agency (DMA) to be responsible for implementation. In the short term, where the power industry is concerned and where existing or pending air regulations are identified as leading to the required reductions, it is likely that the only other necessary action will be continued monitoring of fish tissues in affected water bodies. If ambient monitoring shows that these controls are not leading to attainment of the water quality standard, this situation may change.

In cases where point sources are identified in the TMDL, two actions may be required, which may be written specifically into permits in the form of a compliance schedule. Monitoring using low-level techniques for some period of time is almost always required, since effluent data are typically sparse or nonexistent. This may extend to monitoring of influent (raw water) as well. Once monitoring data is available, a data report may be required, which will compare the effluent concentrations to the water quality standard (if the standard is water column-based). If effluent concentrations exceed the WQS and are greater than influent concentrations, a pollution minimization plan (PMP) may be required. This plan will typically require that all known sources of mercury in a facility be identified, quantified, and reasonable actions be taken to reduce the number and magnitude of these sources. In cases where the WQS is a tissue-based standard, effluent monitoring (and fish tissue monitoring) may be required. PMPs may be required, whether or not a connection has been established between a discharge and mercury in fish tissue. In power plants, the sampling and analysis required to produce a PMP, as well as potential actions to reduce mercury in effluent, can be involved and costly.

1.8 Alternatives to TMDLs

At this time, there appear to be few alternatives to TMDLs once a waterbody has been placed on a State 303(d) list. Options that may be available are discussed briefly below. Additional guidance relevant to these options is provided in Section 4.

1.8.1 Delisting

Delisting may represent the most reasonable opportunity to avoid a TMDL in a specific waterbody. Most often, the listing is the result of a fish consumption advisory. If the advisory is statewide and there are no data for the waterbody of interest, fish tissue data collection and interpretation vis-à-vis the water quality standard may be the best opportunity to avoid a TMDL. In the case where data already exists, it may be possible to analyze the existing data differently to show that tissue concentrations do not exceed the 303(d) listing threshold. If the listing is based on water column samples, especially if the data indicate very high (part-per-billion) levels, they may have been collected before the advent of clean sampling and analytical techniques. In such cases, it may relatively easy to convince the regulatory agency that new data should be collected and the listing revised.

1.8.2 Variances

Variances may or may not lead to the elimination of a TMDL. Although there would appear to be justification for states to place listed waters in categories other than Category 5 (for instance Category 4b) when a statewide variance is in place, most states have not taken this opportunity. Thus, the variance only serves to delay the establishment of the TMDL. In this researcher's opinion, it is unlikely that fish tissue levels will drop sufficiently within the term of the variance (normally 5 – 10 years) to avoid the TMDL. However, in cases where the fish tissue levels are only marginally above the listing threshold, this could feasibly occur.

1.8.3 Use Attainability Analysis

Use attainability analysis (UAA) is probably the least likely way to avoid a TMDL at this time. Although the states are keenly aware of this option in the case of mercury, it is an expensive and time consuming proposition. Moreover, most states would be reluctant to pursue a course of action counter to the conventional view that mercury levels in fish tissue can be abated through the use of air emission controls. As CAA regulations are implemented and fish tissue monitoring continues, it may become apparent that fishing uses are not attainable, as defined by the existence of fish consumption advisories. At such time, states may be more interested in pursuing this option.

A reality of the UAA provision is that uses cannot be changed (or standards lowered) where conditions existed in 1975 (when uses were originally established) such that the water body was meeting that use. Therefore, changing the fishing use of a waterbody would be tantamount to demonstrating that the use was not being attained in 1975. Since data is generally lacking, this would be difficult. It is worth noting however, that one of the justifications for changing a use is "substantial and widespread economic or social impact", a justification that has been used to establish mercury variances.

1.9 References

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2
IMPORTANCE OF MERCURY TMDLS TO THE POWER INDUSTRY

2.1 Background

Mercury TMDLs and the regulatory process of which they are a part are an important consideration for the electric power industry, especially at coal-fired power plants. Mercury in fish tissue and the resulting fish consumption advisories have been largely responsible for recent legislation aimed at controlling air emissions and reducing airborne transport and atmospheric deposition. This legislation will result in major expenditures by the industry to install air pollution control equipment at fossil fuel generation plants and to identify new technologies to reduce sources of mercury in their operations.

In addition to the attention fish consumption advisories have drawn to air emissions, fish consumption advisories have been a major motivation to place waterbodies on state 303(d) lists of impaired waters. Once on the 303(d) list, TMDLs must normally be performed to remove them from the list. Establishment of the TMDL is the first step in a regulatory process that may require expensive monitoring, mercury source identification and reduction, and results in limits for permitted outfalls. Furthermore, removal of mercury from combustion gases will likely lead to increased loadings to wastewater treatment systems. This mercury will ultimately either be discharged, accumulate in the wastewater treatment system (primarily bound to solids), or become incorporated into coal combustion products (CCPs)[6].

Dealing with this increased load to the wastewater treatment system is also an important issue for the industry. If increases in soluble mercury result, power plants may have difficulty complying with WQTs resulting from TMDLs. Perhaps as important are potential mercury increases in CCPs such as fly ash and flue gas desulfurization (FGD) scrubber sludge. Reuse of these materials is economically important to the industry and increasing health or environmental risks associated higher levels of trace metals may reduce their desirability for some reuse applications.

This chapter attempts to identify the elements of potential risk to the industry posed by mercury TMDLs. It begins by summarizing currently available low-level mercury data for power plants in the United States and comparing these data to WQTs that have resulted from the establishment of TMDLs. It then addresses conditions that may change this situation in the future, most notably the implementation of FGD systems and the advent of new regulations. Finally, it identifies sources of mercury in power plants and opportunities for risk management.

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[6] Alternatively referred to as coal combustion by-products (CCBs) and coal utilization by-products (CUBs).

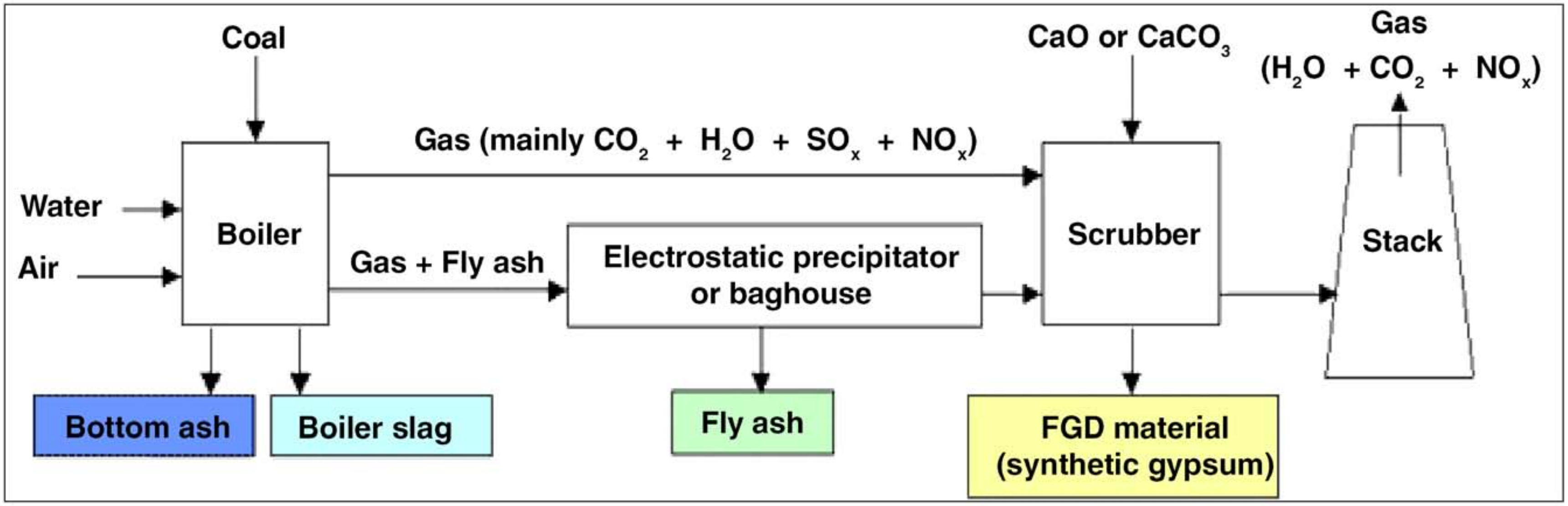
2.2 Mercury in Power Plants and Coal Combustion Products

When mercury enters a power plant in coal it is transformed in the combustion process. In order to describe mercury fate and transformation in the power generation process, it is necessary to define the process. Because processes vary widely among power plants, the description given here must necessarily be generic.

There are approximately 1140 coal-fired boilers in the United States (Berland et al. 2003). A generic process diagram is shown in Figure 2-1, taken from the USGS (2001a). In general, mercury will either accumulate in fly ash, FGD scrubber sludge, or be emitted in flue gas, with only a small percentage in bottom ash. According to Kalyoncu (2000), fly ash represents 58% of the CCPs in the United States, followed by FGD material (24%), bottom ash (15.5%) and boiler slag (2.5%). The amount of mercury captured in CCPs depends upon the design of the ash collection and desulfurization systems employed. The most widely-used FGD systems are wet scrubbers using calcium-based sorbents (Berland et al. 2003). Wet FGD scrubbers are currently installed on about 25% of U.S. coal-fired power plants, with dry scrubbers and sorbent injection technologies growing in popularity. Wet FGD systems produce either wet material (sludge or unoxided wet FGD material) or FGD gypsum (from forced oxidation systems). In both wet and dry systems, the chemical composition of FGD materials depends on the sorbent used and the proportion of fly ash in the FGD material.

According to Hassett et al. (2005) mercury present in flue gases of lignite and sub-bituminous coals tends to be elemental while the combustion of bituminous coal results in higher percentages of oxidized species. Elemental mercury tends to adsorb to unburned particulate carbon collected by electrostatic precipitators (ESPs) and fabric filters, while oxidized species can be sorbed onto fly ash, carbon, or calcium-based FGD materials. Meij et al. (2002) report that speciation of Hg in the flue gas makes a significant difference in removal efficiency. Oxidized forms such as $HgCl_2$ favor a high degree of removal and the conversion of Hg^0 to $HgCl_2$ is positively correlated with Cl content of the fuel. Lower vaporization percentages of Hg are observed when HCl concentrations are relatively high, and in these cases, more Hg is found in the fly ash. The formation of $HgCl_2$ and lower operating temperatures also favor removal in the FGD system. Implementation of SCR technology also favors the formation of Hg^{2+} from Hg^0, with subsequent adsorption onto particles. Senior et al. (2003) also report a relationship between unburned carbon content of fly ash (as measured by LOI), Cl and Hg in fly ash from a site burning low sulfur bituminous coal.

The quantity of mercury that may be present in the effluents of handling and storage facilities at a given power plant will depend upon the amount of mercury in these materials, the characteristics of the materials, the way in which they are handled, and prevailing environmental conditions.



Flow diagram of the flue-gas-desulfurization process based on lime (CaO) or limestone ($CaCO_3$), which are the sorbents used by 90 percent of FGD systems in the United States.

Figure 2-1
Generic Process Diagram for a Coal-Fired Power Plant with Flue Gas Desulfurization (Source USGS, 2001a)

According to Meij et al. (2002), the fate of mercury entering a typical power plant is as follows:

- <1% in bottom ash,49% in pulverized fuel ash (i.e. fly ash);
- 16.6% in FGD gypsum;
- 9% in wastewater treatment plant sludge;
- 0.04% in the effluent of the wastewater treatment plant;
- 0.07% in the fly dust (particulates leaving the stack); and
- 25% as gaseous Hg in the flue gases.

Tolvanen (2004) studied the mass balance of trace metals including mercury at three coal-fired power plants in Finland. Results are summarized in Table 2-1.

Table 2-1
Mercury Mass Balance in Three Finnish Coal-Fired Power Plants (% of Total Flux Out)

Waste Stream		Plant HB	Plant SB	Plant MB	Average
Bottom Ash		3.5	<0.05	0.12	~1
Pulverized Fly Ash		74	60	81	72
FGD Product		20	8.9	7.5	12
Flue Gas (downstream of FGD)	Particulate	0.02	1.3	.1	0.7
	Gaseous	1	30	10	14
Total		98.5	>100	99	

These percentages compare favorably with those of Meij et al. (2002), although total mercury in the flue gas exiting the plant is lower.

In terms of concentration, Eary et al. (1990) report that bottom ash may contain from 0.01 to 4 mg kg^{-1} of mercury, fly ash from 0.01 to 12 mg kg^{-1}, FGD sludge from 0.01 to 6 mg kg^{-1} and oil ash <1 mg kg^{-1}. By contrast, coal contains on the order of 0.01 to 1.6 mg kg^{-1}. Until the mid-1990s, methods with sufficiently sensitivity to measure mercury in water were lacking and characterization was only possible in the solid phase. Recently however, a number of studies have been undertaken to characterize mercury levels in wastewater and in the leachates of fly ash and other CCPs.

Kazonich et al. (2003) reported mercury at levels of 1.61 mg kg^{-1}, 89.3 mg kg^{-1}, and 1.09 mg kg^{-1} in high mercury fly ashes from a commercial utility boiler, a full-scale test of activated carbon injection (ACI), and an ACI pilot unit[7]. These ashes were leached with five different lixiviants, including synthetic precipitation and deionized water. Leaching with deionized water (pH = 6.0)

[7] The amount of mercury present in the fly ash was correlated with the amount of organic carbon or loss on ignition (LOI).

produced leachate concentrations of up to 10 ng L^{-1}, with the bulk of the concentrations less than 5 ng L^{-1}. The highest leachate concentrations were not associated with the fly ash with the highest total mercury, but were associated with non-ACI fly ash. Synthetic precipitation (deionized water adjusted to pH 4.2 using a 60/40 mixture of H_2SO_4/HNO_3) produced slightly higher leachate concentrations, up to 12 ng L^{-1} with most being less than 8 ng L^{-1}. Here again, the highest concentrations were associated with the non-ACI fly ash. On average synthetic precipitation leached slightly more mercury overall then deionized water (9 ng versus 7 ng) but the mass percentages of total mercury released were quite small, the highest being 0.0013%.

Kim and Schroeder (2005) reported mercury levels in 9 fly ash samples; 3 from high mercury coal (the same reported by Kazonich et al. above), 3 from pilot scale studies of powdered activated carbon (PAC), and 3 from full scale PAC injection tests using deionized water and synthetic precipitation (also as described above). With one exception, mercury leached by deionized water ranged from 9.9 ng L^{-1} to 43.2 ng L^{-1}, and mercury leached by synthetic precipitation ranged from 1.4 ng L^{-1} to 21.2 ng L^{-1}. One sample had much higher leachate levels, 222 ng L^{-1} (deionized water) and 152 ng L^{-1} (synthetic precipitation). This sample had a high LOI and the lowest Hg to LOI ratio. Total mercury leached by either of these two methods as a percentage of mercury in fly ash was less than 0.06%.

Pflughoeft-Hassett (2004) studied leaching of mercury from ACI fly ash. A synthetic groundwater leaching procedure – long term leaching (SGLP-LTL), developed at the North Dakota Energy & Environment Research Center (NDEERC) to mimic leaching under environmental conditions, was used in the tests. Forty (40) samples of fly ash from commercial facilities with no Hg controls, 22 samples from ACI fly ash collected in the primary particulate control device (PCD) and 5 samples from AI fly ash collected after the primary PCD were leached. Total mercury in non-ACI fly ash contained from 0.005 to 0.203 mg kg^{-1} total Hg, ACI fly ash from primary PCDs contained from 0.147 to 5.80 mg kg^{-1} total Hg, and ACI fly ash collected after the primary PCD contained from 17.7 to 120 mg kg^{-1} total Hg. While the value of this testing was limited by the detection limits of the analytical method (12 of 18 samples leached for 18 hours were reported <10 ng L^{-1}, and 15 of 16 samples leached for 30 and 60 days were reported <10 ng L^{-1}), detected leachate concentrations ranged from 10 to 30 ng L^{-1}.

Senior et al. (2003) reported leaching results for three fly ashes from power plants. The Brayton and Gaston plants were burning bituminous coal while the Pleasant Prairie plant was burning Powder River Basin coal at the time of the testing. Total mercury in fly ash from the Brayton tests ranged from 0.2 mg kg^{-1} to about 0.53 mg kg^{-1} and produced leachates (using the SGLP method) ranging from 10 ng L^{-1} to 50 ng L^{-1}. Leachates of the Gaston and Pleasant Prairie fly ash were all <10 ng L^{-1}.

Hassett et al. (2005) also reported leaching of samples of CCPs (fly ash and FGD material) from sites having both mercury and no mercury controls using the NDEERC SGLP-LTL procedure. In this study, leachates were observed with concentrations of up to 400 ng L^{-1}, with the bulk of the concentrations being below 150 ng L^{-1}. There was no correlation between total mercury in the solids (concentrations up to 6 mg kg^{-1}) and mercury in the leachate. The nature of the materials producing the highest concentrations was not noted. Details of the analytical method used for mercury were not provided in the report; however, methods used by the NDEERC are provided in Pflughoeft-Hassett (2005).

Cardone et al. (Undated) reported the release of mercury and ammonia leached with water from fly ash from a number of facilities having selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) devices for NO_x control. Ammonium was almost always released in the first 100 mL of leachate[8]. The two ashes that released most of the ammonium consistently released the least amounts of metals. Mercury levels in leachate exceeded 200 ng L^{-1} in one sample but were mostly less than 100 ng L^{-1}. Details of the analytical method used for mercury were not provided in the report.

In summary[9], the above studies report that mercury leached from power plants CCPs under conditions that emulate disposal environments are typically less than 50 ng L^{-1} but in some cases are as high as 400 ng L^{-1}. Complicating the picture with regard to mercury in power plant effluents is the reality that wastewater does not only contain effluent from coal combustion processes and by-product recovery. It can also contain effluent from:

- regenerate from the conditioning of makeup water and desalination of condensate;
- water used for washing condensate filters;
- effluent from coal handling and coal storage;
- pickling (oxide scale removal) wastewater;
- floor drains;
- water from the boilers, turbines and transformers; and
- cooling-tower discharge and makeup-water conditioning,
- among other sources. Wastewater effluent can contain entrained suspended solids, salts, other heavy metals, acids, alkalis, ammonia and oil. Thus, prediction of mercury concentrations in power plant effluents presents a daunting task. Better indications of the concentrations present are more likely to be found in measurements of actual effluents.

2.3 Mercury in Power Plant Effluents

Mercury is present at trace levels in coal, normally in the tens to hundreds of parts per billion range, and in other fossil fuels. The U.S. Geological Survey (USGS 2001b) has provided a map of mercury in major coal deposits in the United States, reproduced as Figure 2-2. Note that the units in the map are 1b Hg 10^{12} BTU^{-1} (British Thermal Units). To convert to concentration, these coal contents must be multiplied by the calorific content of the coal in BTU lb^{-1}. Calorific content of coal is also dependent upon the formation and ranges from a low of about 6,400 BTU lb^{-1} to a high of 13,200 BTU lb^{-1}. Median mercury concentrations in whole coal range from a low of 40 ug kg^{-1} to a high of 190 ug kg^{-1}. Western coals tend to be among the lowest in mercury, while the highest median concentration occurs in northern Appalachian coal. Thus, the quantity

[8] Ammonium concentrations reached 400 mg L^{-1} but for the most part were 100 mg L^{-1} or less.

[9] The papers cited in this section are thought to be among the most recent and representative of the research on mercury in power plants and in CCPs. However, as a body they by no means represent a comprehensive review of the available literature, and are cited for their illustrative value.

of mercury in waste streams from power plants in some way depends upon the amount of mercury in coal used for combustion. However, the concentration of mercury in power plant effluents may or may not be correlated with the content of the coal. Soluble mercury concentrations in effluents will depend upon other factors, including sulfur content, plant operations, and wastewater treatment system characteristics.

Three sources of information were investigated to assess the current levels of mercury in power plants effluents. The first was the PISCES database[10]. The second was through a data request made of EPRI member companies. The third was through a search comprised of power plants identified in various TMDL reviews (see Chapter 3) and subsequent searches of EPA Permit Compliance System (PCS) database, personal communications, and other miscellaneous sources. Information obtained from all three sources is discussed in subsequent sections of this report.

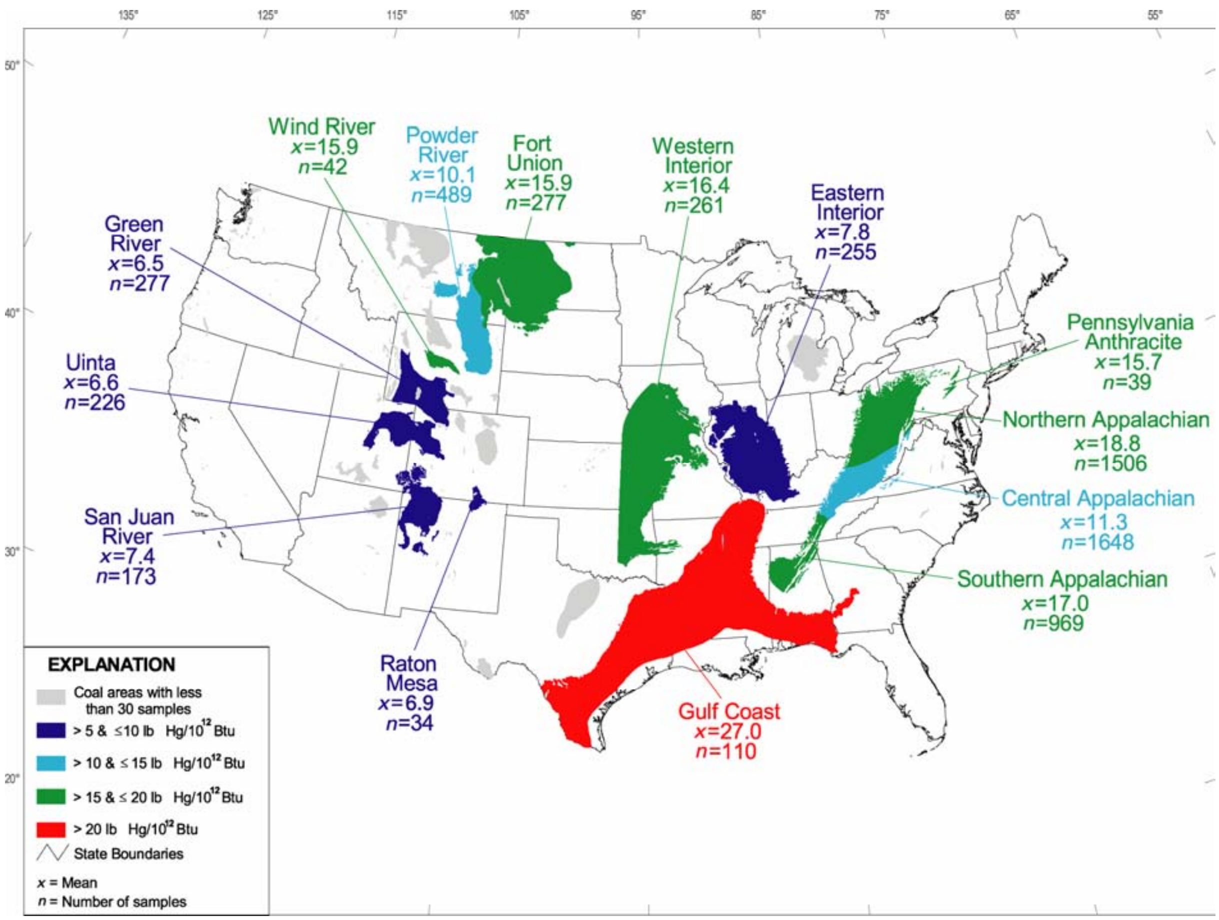


Figure 2-2
Map of Mercury in Major Coal Deposits in the United States (Source, USGS 2001b)

[10] Electric Power Research Institute. PISCES Database. Version 2005a.

In general, the PISCES data is thought to be the highest quality data obtained using these three searches. PISCES data has been subjected to scrutiny by sample analysts, EPRI contractors, and EPRI personnel. A data quality ranking was assigned to each data point in PISCES by an EPRI contractor and only those data of acceptable quality were used the analysis presented in this report. Data obtained from the member companies was judged to be the next most reliable, as they were obtained from a known and trusted source. In most cases, it was possible to contact a responsible, knowledgeable party for additional information and to answer questions. Although this data may be on somewhat lower quality that the “research-grade” data in the PISCES database, it is more likely to be indicative of the type and quality of data that most facilities will collect in response to monitoring pressures from the regulatory agencies. Data obtained from the PCS database and from miscellaneous sources was deemed to be the least reliable. PCS data is entered by third parties, can contain transcription errors, and units are sometimes ambiguous. Furthermore, it was rarely possible to contact the responsible party at a given facility to obtain additional information that would have been helpful in data interpretation.

2.3.1 Review of PISCES Data

A review of EPRI PISCES data was performed to assess levels of mercury in power plant effluents. Other relevant information that could be gleaned from the data was desired as well. In particular, it was hoped that differences in effluent Hg could be evaluated from facilities operating FGD systems and those that were not.

2.3.1.1 Data Acquisition

Data were obtained through the EPRI project manager. The PISCES database was searched by EPRI staff. Relevant information on mercury was retrieved and provided to the contractor in EXCEL spreadsheets. Preliminary review of this data led to a number of questions, to which EPRI and its contractors responded with answers and ancillary information.

2.3.1.2 Data Description

The PISCES database contained 365 relevant records. These records are grouped by facility (A through F). General descriptions of the data records for each facility are provided below:

Facility A – Records include total and total dissolved (filtered) mercury from the ash pond near the effluent outfall. Total and total dissolved mercury are further analyzed and reported as ionic mercury, zero-valent mercury, and methylmercury. Dissolved mercury is typically designated by the suffix “F” in the sample name (e.g. sample AAB500GF), although this designation is sometimes omitted (e.g. sample AAB501). Total mercury was sometimes analyzed by two independent laboratories and the results are reported separately. Samples with the “G” suffix were all analyzed by one of the two laboratories; if there is no “G” suffix, then the sample was analyzed by the other laboratory. Where plant intake data were collected on the same date as a sample from one of the operational units, it is included. Several data points for background lake water and once through cooling water are also included.

Facility B – Facility B records contain much the same information as those of Facility A except that Facility B includes some records of cooling tower blowdown water. There are also records (1 each) of demineralizer water and filter effluent, and of the river, upstream of the ash pond discharge and downstream of the plant (1 sample each).

Facility C – Records for Facility C are similar in content to Facility A.

Facility D – Facility D records contain much the same information as those of Facility A with the addition of data from an FGD stacking pond.

Facility E – Facility E records are much the same as Facility A with the addition of data from the cooling lake. Facility E has three ash ponds (North, East, and South) and some data is included for each. The South Pond data was not included in the analysis as the pond does not receive ash sluice water or FGD effluent.

Facility F – Facility F has the least amount of data, a total of six data points from the ash pond, taken on three closely grouped sampling dates, and analyzed for total and total dissolved mercury.

The reader is referred to several EPRI reports (EPRI 1997a; EPRI 1997b; EPRI 1998, EPRI 1999; EPRI 2000) for additional details concerning these facilities, sampling procedures, and data.

2.3.1.3 Data Analysis

There are two important factors in assessing the risk to power plants posed by mercury TMDLs, as follows:

- whether the discharged concentration is higher than the water quality target (WQT) established by the TMDL, and if so; and
- whether the plant is adding mercury across its operations.

Table 2-2 shows the most fundamental analysis performed on the PISCES data, the geometric mean concentrations of total mercury (THg) in various operations of the six facilities. THg in ash pond effluents are uniformly low, ranging from 0.94 to 3.84 ng L^{-1}.

Comparison of the average ash pond effluent to plant intake shows a range of -17% to +131%. Thus determinations of net mercury increases across operations for regulatory purposes will likely have to be performed on a case-by-case basis. The same is true for mercury concentrations in once through cooling water (OTWC), where mean concentrations with respect to plant intake range from -20% to +18%.

Concentrations in cooling lakes show a modest (33%) increase over plant intake at Facility E and a large (656%) increase over plant intake water at Facility C. Once through cooling water do not exhibit the same trends, however. At facilities A, B and C, OTCW showed minor differences from background of -5%, -7% and +4%, respectively. OTCW shows larger and more variable differences from plant intake water at Facilities D and E (-20% and +18%, respectively). This latter observation points to a unique situation for the power industry with regard to TMDLs: once through cooling water might not show a net increase when compared to cooling lake concentrations, but may show a net increase when compared to plant intake or makeup waters, from sources other than the cooling lake.

Table 2-2
Geometric Mean Concentrations of Total Mercury in Various Power Plant Operations and Percent Increase Over Intake

	Facility							
Operation	**A**	**B**	**C**	**ABC[1]**	**D**	**E**	**F**	**DE[2]**
Ash Pond Effluent (AP), ng L^{-1}	1.31	3.84	0.94	2.03	2.95	2.43	3.21	2.69
Plant Intake, ng/L	0.95	2.89	0.41	1.41	3.13	2.94		3.03
Once Through Cooling Water (OTCW), ng L^{-1}	0.90	2.68	0.42		2.50	3.48		
Cooling Tower Blowdown (CTB), ng L^{-1}		7.60						
Cooling Lake (CL), ng L^{-1}			3.07			3.93		
FGD Stacking Pond (FGD SP), ng L^{-1}					18.43			
AP Increase (%)	38	33	131	43	-6	-17		-11
OTCW Increase (%)	-5	-7	4		-20	18		
CTB Increase (%)		163						
CL Increase (%)			656			33		
FGD SP Increase (%)					490			
Coal Hg Content (lb/10^6 lb)	0.14	0.14	0.14		0.08 to 0.22	0.085	0.10 to 0.12	
[1] **Average of Facilities A, B, and C** [2] **Average of Facilities D and E**								

Approximate concentrations in the coal being used at these facilities during the time sampling were estimated using data provided by EPRI and the USGS (USGS 2001b). EPRI provided information on the geographic source and BTU content per pound of coal being burned. Information on the mercury content per BTU for various coal sources was taken from the USGS map showing the mercury content of various coal fields in the United States. Mercury content was estimated by multiplying the Hg/BTU value for the coal source by the BTU content of the coal being burned. Inspection of the coal mercury content and ash pond effluent concentrations reveals no obvious relationship.

None of the facilities A, B, or C had FGD scrubbers at the time of the sampling, while facilities D, E, and F did. Therefore, the average effluent pond concentrations for the non-FGD facilities were computed and compared to the average of the facilities with FGDs. On average, the three FGD facilities have higher mean concentrations in ash pond effluents than non-FGD facilities, which initially would seem to make sense. On further inspection, however, the facilities with FGD systems also have higher background levels of Hg in the plant intake water by roughly a factor of 2. The percent increase calculations (effluent versus background) show that the non-FGD ash ponds have higher percent increases than the ash ponds receiving FGD streams. In fact, both ash ponds at facilities with FGD systems show lower ash pond effluent concentrations than plant intake concentrations.

2.3.1.3.1 Seasonal Variation

Plots were made of the total mercury data over all the sampling dates for Facilities A through E. Samples for Facility F were collected during July only. The plots are shown in Figure 2-3. The data from Facilities A, C, and D do not show a consistent seasonal trend. Facility B data exhibits a seasonal trend with values tending to be greater in the winter and spring than in the fall. Data from the North and East Ponds for Facility E are also shown. The apparent trend in the North Pond is greatly influenced by two high values observed in March and November. There does not appear to be a consistent seasonal trend for total mercury in the East Pond.

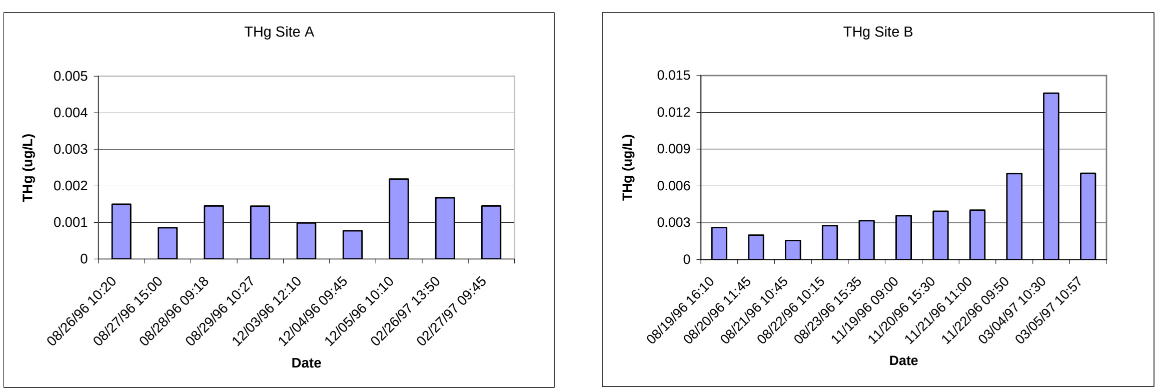


Figure 2-3
Time Series of Total Mercury Ash Pond Concentrations at Facilities A, B, C, D, and Facility E (North and East Ponds)

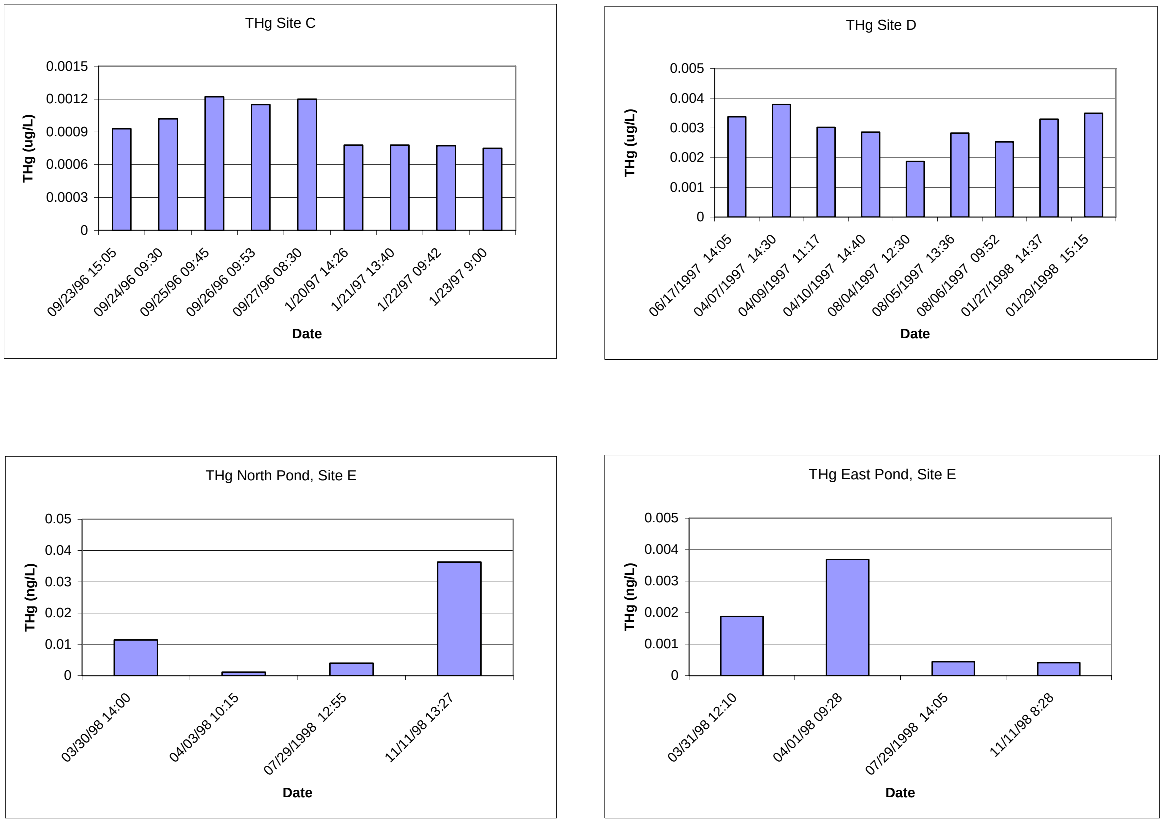


Figure 2-3
Time Series of Total Mercury Ash Pond Concentrations at Facilities A, B, C, D, and Facility E (North and East Ponds) (Continued)

2.3.1.3.2 Methylmercury

Methylmercury percentages were examined for those facilities having usable data. Table 2-3 shows the statistics developed. In general, methylmercury values are low, being uniformly less than 0.1 ng L^{-1}, and ranging from 0.005 ng/L to 0.093 ng L^{-1}. Methylmercury targets observed in TMDLs across the U.S. range from 0.029 ng L^{-1} to 0.46 ng L^{-1}. Thus, as with total mercury, the ranges overlap. Methyl to total mercury ratios are also low, ranging from 0.4% to 2.0%. Coefficients of Variation (CVs)[11] for the methylmercury measurements are about the same as those for total mercury, ranging from 30% to 90%.

[11] The Coefficient of Variation is the ratio of the standard deviation of a data set divided by its mean, normally expressed as a percentage, and as such represents a normalized expression of variability in the data.

Table 2-3
Methylmercury Concentrations and Methyl/Total Ratios in Ash Ponds (Facilities A & B) and Cooling Pond (Facility E)

	Facility					
Operation	**A**	**B**	**C**	**D**	**E**	**F**
Geomean Ash Pond, ng L^{-1}	0.005	0.027	NA	NA	0.090	NA
Average Ash Pond, ng L^{-1}	0.007	0.036	NA	NA	0.093	NA
CV (%)	90	72			30	
n	7	5			4	
Methyl/Total (%)	0.4	0.7			2.0	
NA = Data not available						

2.3.1.3.3 Bias in Analytical Laboratories

As mentioned earlier, some of the samples reported in PISCES were analyzed by two independent laboratories. Where possible, the total mercury results from the two labs were compared. For Facility A, Laboratory A and Laboratory B analyzed 6 samples in common. The geometric mean of the Laboratory A results is 1.85 ng/L and the geometric mean of the Laboratory B results is 0.76 ng/L, an RPD (Relative Percent Difference)[12] of 83%. At Facility B the laboratories analyzed 4 common samples. The geometric means of the results are 4.74 ng/L (Laboratory A) and 2.06 ng/L (Laboratory B), an RPD of 79%. At Facility C, two samples were analyzed in common. Laboratory A reported results with a geometric mean of 0.86 ng/L and Laboratory B reported results with a geometric mean of 0.79 ng/L, with a resulting RPD of 7.8%. In general, these differences are quite high and they are always biased in one direction, that is, Laboratory A's results are always greater than Laboratory B.

These results suggest that the laboratory should be carefully selected, considering that the difference between compliance and non-compliance may hinge on very small differences in sample results. This bias is not unique to the PISCES data, as this researcher has noted it in other low-level mercury studies where multiple laboratories have been used to analyze split samples. These other studies are discussed in the Section 4.

2.3.1.4 Limitations of PISCES Data

The major limitation of the analysis presented above is the relatively small number of data points. Therefore, the above observations should be viewed with healthy skepticism and far from being generalizations. Table 2-4 shows arithmetic mean concentrations, CVs, and the number of

[12] Relative Percent Difference (RPD) is the difference in the two results and divided by the average of the two results expressed as a percentage.

samples used in the computation of each mean value. Many of the means incorporate less than 5 data points.

Notice that in most cases, the arithmetic means (Table 2-4) and the geometric means (Table 2-2) are close to the same value, suggesting that the data are normally distributed. The exception is the ash pond means from Facility E, where the arithmetic mean is 6.71 ng/L and the geometric mean is 2.43 ng/L. This large difference occurs because the averages incorporate data from the North and East ponds and several values from the North Pond are an order of magnitude greater than the others. These values were combined in the analysis because North Pond ash is dredged and sluiced to the East Pond; therefore they receive the same wastestreams.

With the exception of the large CV in the ash pond data from Facility E, the CVs for the ash pond data range from 19% to 74%[13]. CVs for plant intake water range from 12% to 77% and OTCW from 10% to 81%. CVs for cooling tower blowdown, cooling lakes, and FGD stacking ponds are within the same ranges. Knowing the variability in the data is extremely important because the number of samples required to make statistical inferences about data populations (e.g. whether ash pond effluent concentrations are significantly greater than plant intake) is directly related to data variability. Thus, if too few samples of highly variable data are available, statistical tests may lack the ability to discern differences.

Table 2-4
Average THg Concentration in Various Power Plant Operations, Coefficients of Variation (CV) and Number of Data Points (n)

	Facility					
Operation	**A**	**B**	**C**	**D**	**E**	**F**
Ash Pond, ng L^{-1}	1.37	4.66	0.96	3.01	6.71	3.25
CV (%)	32	74	22	19	173	20
n	9	11	9	9	9	3
Plant Intake, ng L^{-1}	0.96	3.61	0.41	3.20	3.16	
CV (%)	15	77	12		41	
n	4	11	9	2	7	
Once Through Cooling Water, ng L^{-1}	0.91	2.69	0.48	2.51	3.74	
CV (%)		10	67		81	
n	2	3	4	2	5	
Cooling Tower Blowdown, ng L^{-1}		7.76				
CV (%)		20				
n		9				
Cooling Lake, ng L^{-1}			3.46		4.88	
CV (%)					42	
n			2		25	
FGD Stacking Pond, ng L^{-1}				19.1		
CV (%)				25		
n				6		
NV = No CV computed for less than 3 data points						

[13] CVs were not computed for means that incorporate less than 3 data points.

2.3.1.5 Conclusions

Based on review of the PISCES data, the following observations are made:

- The PISCES database contains very useful information for assessing the range of ash pond effluent mercury concentrations from a small number of power plants. For the purposes of this analysis, the database contained about 365 relevant data points from six facilities. Geometric mean total mercury concentrations for the ash pond effluents are uniformly low, ranging from 0.94 to 3.84 ng L^{-1}.
- CVs for the ash pond data range from 19% to 74%. CVs for plant intake water range from 12% to 77% and from 10% to 81% for once through cooling water. The magnitudes of these statistics indicate that the measurements can be quite variable.
- Comparison of ash pond effluent to plant intake shows that the effluent may be higher or lower than the intake water, ranging from -17% to +131% at these facilities. The same is true for mercury concentrations in once through cooling water, where the mean concentrations with respect to plant intake ranged from -20% to +18%.
- At these six facilities, non-FGD ash ponds have higher percent increases of ash pond effluent to plant intake water than ash ponds receiving FGD wastestreams. In fact, ash ponds at facilities with FGD systems show lower effluent concentrations than plant intake concentrations (negative percent increases).
- Two of the six facilities exhibit a seasonal trend in total mercury concentrations in ash pond effluents, with winter/spring values being higher than summer/fall values. At three facilities, no consistent trend is observed. At the remaining facility there is no seasonal data to analyze.
- Methylmercury values are low, being uniformly less than 0.1 ng L^{-1}. Methylmercury targets observed in TMDLs across the U.S. range from 0.029 ng L^{-1} to 0.46 ng L^{-1}. Thus, as with total mercury, the ranges overlap. Methyl to total mercury ratios are also low, ranging from 0.4% to 2.0%. Coefficients of Variation for methylmercury measurements are about the same as those for total mercury, ranging from 30% to 90%.
- Laboratory bias is a concern. RPDs of the geometric mean sample results are 8%, 79%, and 83% between laboratories for samples collected and analyzed in common from three of the six facilities. In two instances, these differences are quite high. They are always biased in one direction: that is, one laboratory's results are always greater than the other.
- A major limitation of the data is the small number of samples. Given the variability in the data, larger numbers of samples will generally be required to test hypotheses concerning the data. Comparisons of importance for regulatory purposes include ash pond effluents to plant intake water and ash pond effluents to TMDL targets.

2.3.2 Additional EPRI Member Data

Data other than those available through the PISCES database were researched. Emphasis was placed on monitoring data using Method 1631 and information relevant to assessing potential increases in mercury concentration in power plant effluents due to the implementation of FGD systems. In June 2005, a request for data was made of the member companies through the EPRI project manager. Responses were received from several companies, and all data are total mercury, unless otherwise stated.

Four member companies provided low-level mercury data from their operations. These four utility companies are designated by the letters M, N, O, and P and the facilities represented by number (e.g. 1, 2, 3, etc.) in the discussion that follows.

2.3.2.1 Utility M

This utility is located in the upper Midwest. Utility M provided data on three power plants. The WQS in the receiving water for plant M-1 is 6.8 ng L^{-1} and it has permit limits of 17 ng L^{-1} (daily maximum) and 10 ng L^{-1} (monthly average). The WQS at plants M-2 and M-3 is 1.3 ng L^{-1} with permit limits of 3.2 ng L^{-1} (daily maximum) and 1.8 ng L^{-1} (monthly average).

Data were collected between January, 2001 and October, 2005. Results of the data analysis are presented in Table 2-5. All ratios of discharge concentrations to intake were computed by subtracting the intake value from the process value, dividing the difference by the intake value, and expressing the result as a percent. There were only seven dates in the dataset where sampling of the plant intake (river) was concurrent with the discharge. Taking these dates into consideration, however, there was an inverse relationship between the river mercury levels and the discharge levels as evidenced by the negative correlation coefficient (r = -0.69). There were nineteen dates where the sampling of the cooling lake inlet was concurrent with the plant discharge sampling, which also exhibited an inverse relationship (r = -0.43). River concentrations were positively correlated with cooling lake inlet concentrations (r = 0.83).

Table 2-5
Mercury in Effluent and Intakes for Utility M

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Plant M-1					
Discharge (D-1)	6.87	9.76	10.15	104	20
Discharge (D-2)	3.58	3.98	2	50	12
Intake	0.60	0.82	0.59	72	18
D-1/Intake (%)	1045				
D-2/Intake (%)	496				
Plant M-2					
Pre-discharge 1[1]	0.76	0.88	0.52	59	4
Intake	0.63	0.73	0.45	61	3
Pre-discharge/Intake (%)	21				
Plant M-3					
Discharge (D-1)	5.12	7.20	7.26	101	32
Cooling lake inlet	3.95	4.35	2.29	53	20
Intake	3.69	3.91	1.34	34	7
Cooling lake/Intake (%)	7				
D-1/Intake (%)	39				

[1] One discharge data point was reported for this plant with a value of 32.2 ng L^{-1}. It was noted that this sample was associated with a high total suspended solids (TSS) value.

Figure 2-4 demonstrates the year-to-year variability in the discharge data from this plant. The plot shows the average mercury concentration discharged for each of the five years in which samples were collected and demonstrates considerable variation. Annual mean values ranged from 3.17 ng L^{-1} to 12.1 ng L^{-1}, with the ratio of the highest to the lowest year being 3.8. The data also has a seasonal component. The mean for data collected during the 3rd quarter is the lowest (4.74 ng L^{-1}) while the mean of the data collected during the 1st quarter of the year is highest (13.8 ng L^{-1}), with the ratio of the highest to the lowest of 2.9. Means for data collected during the 2nd and 4th quarters are 6.05 ng L^{-1} and 8.37 ng L^{-1} respectively. Thus it appears that total mercury exhibits cyclical behavior at this facility over an annual period, with the highest values occurring in late winter and the lowest in the late summer/early fall.

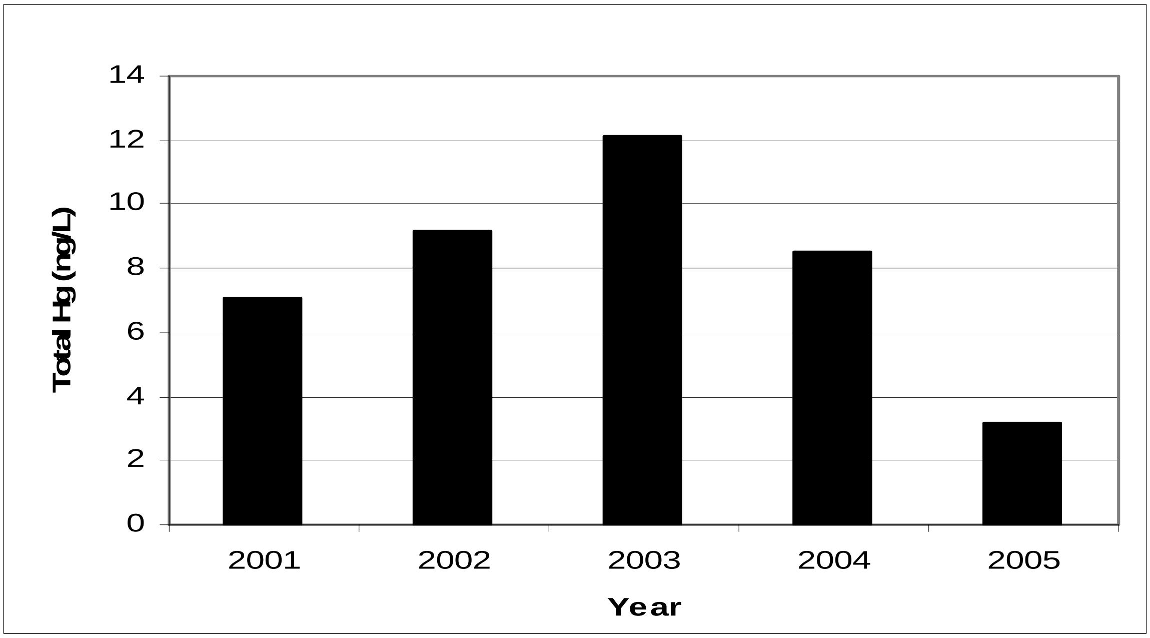


Figure 2-4
Average Annual Mercury Concentrations Discharged from Plant M-1 During the Period from 2001 to 2005

2.3.2.2 Utility N

This utility is located in the Ohio Valley. Utility N provided discharge data on two power plants. Two additional process streams were reported; one entitled "cooling water discharge with ash pond inlet" and one for leachate from an FGD landfill. These data were collected primarily from 2002 to 2005. No intake data were provided. Results of the data analysis are presented in Table 2-6. All ratios of process concentrations to intake were computed by subtracting the intake value from the process value, dividing the difference by the intake value, and expressing the result as a percent.

This dataset had two discharges with a larger number of data points than the others. For these discharges, seasonal and year-to-year means were calculated. Table 2-7 shows these values. Neither discharge exhibited a pronounced year-to-year variability. The ratios of the highest to lowest year-to-year values were 1.5 for the cooling water and 1.6 for the landfill leachate. Ratios of the highest to lowest seasons were 1.5 for the cooling water and 2.0 for the landfill leachate, with the landfill leachate discharge showing a slightly more pronounced seasonal effect. Interestingly, the highest quarterly value for the landfill leachate occurred in the third quarter. This is a different pattern than for surface waters, where the lowest values appear to occur in the summer/fall with higher values in the winter/spring.

Table 2-6
Mercury in Effluent of Utility N

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Plant N-1					
Fly ash pond discharge	0.945	1.05	0.429	41	15
Plant N-2					
Cooling water Discharge w/ash pond inlet	12.8	14.6	8.06	55	38
Plant N-3					
FGD landfill leachate	9.70	13.0	14.9	114	38
Plant N-4					
Bottom/fly ash pond discharge	3.69	4.71	3.99	85	15

2.3.2.3 Utility O

This utility is located in the Southeastern U.S. and provided data for one of its power plants. This midsize fossil fuel plant generates 470 megawatts by burning pulverized coal in three units that can also burn natural gas as an alternate fuel. The facility consumes about 130 tons of coal per hour when operating under full load. Unit 1 came on line in 1962, Unit 2 in 1964, and Unit 3 in 1967. The plant is equipped with electrostatic precipitators that remove 99 percent of the unburned carbon and fly ash from the boiler gases and a baghouse. Baghouse collections are stored in a permitted on-site landfill. Units 2 and 3 are equipped with low-NO_X burners. Low-NO_X burners were due to be installed in Unit 1 in 1999. Drainage from the plant grounds and equipment is passed though a series of settling ponds before being discharged to the river. The plant has a “closed cycle” cooling system, in which three cooling towers are used to provide condenser water and plant service water in a closed loop.

Table 2-7
Year-to-Year and Seasonal Means for "Cooling Water with Ash Pond Inlet" and "FGD Landfill Leachate" Discharges for Utility N

	Cooling Water w/Ash Pond Inlet ng L^{-1}	FGD Landfill Leachate ng L^{-1}
Year-to-Year Means		
2002	13.7	8.95
2003	18.5	14.1
2004	12.1	14.6
2005	13.4	11.8
Seasonal Means		
1st Quarter	19.0	9.33
2nd Quarter	14.8	7.39
3rd Quarter	12.6	14.5
4th Quarter	12.8	8.11

Utility O provided data on two discharges from this power plant. Data were collected during 2004 and 2005. Discharge D-1 receives low volume waste, coal pile runoff, cooling tower blowdown, ash pit overflow, runoff from a sulfuric acid/caustic containment and unloading area, and non-chemical metal cleaning waste. D-2 is a discharge pond for the ash pond. The facility has a permit limit for mercury at only one outfall (interim 400 ng L^{-1}, final 50 ng L^{-1}). The WQS for mercury in the receiving water is 51 ng L^{-1}. Based on this WQS and measurements made of plant discharges, the NPDES authority concluded that there was no reasonable potential to exceed the standard at other outfalls.

Results of the data analysis are presented in Table 2-8. All ratios of process concentrations to intake were computed by subtracting the intake value from the process value, dividing the difference by the intake value, and expressing the result as a percent.

Table 2-8
Mercury in Effluent and Intake for Utility O

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Plant O-1					
Discharge (D-1)[1]	5.89	6.14	1.75	28	13
Discharge (D-2)	4.93	5.58	2.74	49	8
Intake	–	4.93	–	–	–
D-1/Intake (%)		24			
D-2/Intake (%)		13			

[1] One of the discharge data points reported for this facility had an abnormally high value of 64 ng L^{-1}. There was no plausible explanation for the anomaly. It was excluded from the statistical analysis.

Outfall pH and TSS data was also provided with this dataset. Analysis of this data with total mercury indicated no relationship between TSS and pH of the discharge and total mercury in the discharge.

2.3.2.4 Utility P

This utility is located in the Ohio Valley. Utility P provided data on three power plants. Results of the data analysis are presented in Table 2-9. Data were collected from 2002 to 2005. All ratios of process concentrations to intake were computed by subtracting the intake value from the process value, dividing the difference by the intake value, and expressing the result as a percent.

Table 2-9
Mercury in Effluent and Intakes for Utility P

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Plant P-1					
Discharge (D-1)	9.2	18	21	121	5
Cooling pond	5.8	11	11	106	5
Intake	4.3	10	12	119	5
D-1/Intake (%)	114				
Cooling pond/Intake (%)	35				
Plant P-2					
Cooling Pond	4.2	9	11	123	5
Intake	2.2	7	11	171	5
Cooling pond/Intake (%)	91				
Plant P-3					
Discharge (D-1)	1.7	4	7	168	5
Intake	3.5	6	6	96	5
D-1/Intake (%)	-51				

2.3.2.5 Conclusions

Based upon the data received and analyzed from EPRI member companies, the following observations and conclusions can be drawn:

- Geometric mean mercury concentrations in discharges for these plants[14] ranged from 0.76 ng L^{-1} to 9.7 ng L^{-1}. Although at the low end of the range the value is comparable to plants in the PISCES database, the upper end of the range is two to three times higher than the plants in the PISCES database. This may be due to natural variability in sampling but could also be due to less rigorous cleanliness in the sampling technique that may have resulted in low-level sample contamination.
- CVs for the discharges measured from these plants ranged from 28% to 121%, although most of the CVs fell in a range from about 50% to 100%. This range of variability is greater than that observed for the plant discharges in the PISCES database (19% to 74%). Higher variability could be due to several factors. One could be a less consistent sampling technique, which may have resulted in low-level contamination of some samples but not in others. Another could be that the sampling extended for longer periods of time than in the PISCES sampling, with results incorporating more seasonal or year-to-year variation.
- CVs for plant intakes ranged from 34% to 171%. However, the three highest CVs are all from one utility (Uitility P), and it is known that this utility did not analyze samples in a clean laboratory. If these are removed, the range of CVs becomes 34% to 72% and is comparable to the range observed at the plants in the PISCES database (12% to 77%).
- Comparison of ash pond effluent to plant intake shows that the effluent may be higher or lower than the intake water for these plants, ranging from -51% to +1045% at these facilities. However, only one plant in this group had an effluent that was less than the intake. Excluding the one plant with very high effluent to intake ratios for both discharges, the range of effluent to intake ratios for these plants ranged from 13% to 114%. The PISCES plants ranged from -17% to 131%.
- Several sets of data from the member companies had sufficient data to investigate seasonal variations. Lowest total mercury concentrations in discharges normally occurred in late summer/early fall and highest concentrations in late winter/early spring. In one plant the ratio between the highest and lowest seasonal values was about 3:1[15]. At a second plant, the seasonal effect was much less pronounced. At a third plant, the ratio of highest to lowest

[14] The highest geometric mean for any of the data provided was 9.7 ng L^{-1} for an FGD landfill leachate. However, it is not known if this is a direct discharge or if it receives additional treatment. The second highest discharge is 9.2 ng L^{-1} from Plant P-1. However, a conversation with the person responsible for this data indicated that although the samples were collected using "clean hands" the samples were not analyzed in a clean laboratory. Thus, both of these "highest" discharge means are subject to some speculation. The third highest geometric mean is from Plant M-1, at 6.87 ng L^{-1}.

[15] Higher total mercury values in the winter may be associated with poorer settling of solids in ash ponds or clarifiers. In ash ponds where thermoclines form in the summer, higher winter values may also be associated with fall turnover of the pond.

quarterly means for leachate from an FGD landfill was about 2:1, with the highest mean occurring in the third quarter (late summer/early fall).

- Year-to-year variability was also investigated were adequate data were available. In one discharge where total mercury was measured over a five year period, the ratio of the highest to the lowest year's annual mean was almost 4:1. At another plant, the year-to-year was less pronounced, with the highest to lowest year ratio being about 1.5:1.

2.3.3 Additional Miscellaneous Data

In the review of TMDLs from across the U.S., one of the features noted was the availability of effluent monitoring data. If effluent monitoring data were available, special note was made if the data were from power plants. Once the TMDLs reviews were completed, searches of EPA's PCS database were made to see if relevant data could be obtained for these facilities. In this way, several additional data sources were identified including a small coal-fired power plant in the Upper Midwest, a natural gas-fired power plant in the Far West, and a petroleum coke-fired power plant in Far West.

A difficulty encountered in using and interpreting data obtained from PCS was the lack of information about the plant and its wastewater treatment system configuration. This research attempted to overcome this impediment by making contact with the responsible party named in the PCS database. However, this generally did not meet with success. As a fallback, attempts were being made to obtain permits and permit applications from the permitting agencies or through Freedom of Information Act (FOIA) requests. This resulted in some additional useful information. Personal communications with utility contacts, where possible, generally resulted in the highest quality, least ambiguous and most reliable information.

2.3.3.1 Coal-Fired Power Plant – Upper Midwest

This 55MW coal-fired plant was built in the early 1980s. It burns approximately 150,000 tons of high sulfur bituminous coal annually and has an additional oil/gas-fired capacity of 40MW. Plant operations include coal handling, boiler/steam generation, cooling water, a cold-side electrostatic precipitator (ESP), a limestone in-situ forced oxidation FGD stack scrubber, as well as wastewater treatment. The facility has two wastewater outfalls. Outfall 001 contains cooling water filter backwash and serves as the backup for cooling tower blowdown. Flow is routed through a settling/evaporation pond with a volume of approximately 300,000 gallons. Outfall 002 contains controlled cooling water blowdown and discharge from the waste treatment facility. Process wastes include ion exchange demineralizer regenerant, scrubber blowdown, and excess flow from the coal pile basin as well as floor drains from the boiler and scrubber buildings.

Process waters are collected and routed through a thickener, with the overflow reused internally as clarified recycle water (CRW). Sludge generated in the thickener is sent off-site for recycling in the manufacture of gypsum board. Excess CRW is treated via a new on-site process waste treatment facility that was constructed and initiated operation in 1995. The treatment facility employs a multi-step metals removal scheme that includes acidification (lowering pH to 2-3 SU with sulfuric acid for chelant destruction), hexavalent chromium reduction (with sodium bisulfite) if necessary, precipitation (raising pH to 10-11 SU with lime slurry), flocculation/clarification (via polymer addition and routing through a Claricone®), and neutralization (lower pH to approximately 8 SU with sulfuric acid). Sludge from the treatment process is routed back to the CRW thickener. The facility currently has a permit limit for mercury of 86 ng L^{-1}, is required to monitor monthly using EPA Method 1631, and has a requirement to develop an approvable Mercury Minimization Plan.[16]

Table 2-10 provides the available data (total Hg and TSS) for Outfall 002. No intake data was available for this facility. Data was collected between October, 2002 and June, 2005. Data were obtained from a regulatory document and supplemented by searching the PCS database. No intake data was available for this facility. Effluent concentrations at this plant are among the highest observed at any of the facilities investigated in this research.

Table 2-10
Mercury and Total Suspended Solids in Effluent, Coal-Fired Plant in the Upper Midwest

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Discharge (002) T-Hg[1]	36.9	52.2	48.3	92	30
Discharge (002) TSS	13.7	15.3	7.6	49	32

[1] Units of total mercury are ng L^{-1}, units of TSS are mg L^{-1}.

While the reason for this is unknown, additions of sulfuric acid and lime in the WWTP containing trace levels of mercury could be responsible. Analysis of the data reveals a weak relationship between total mercury and TSS as shown in Figure 2-5.

[16] Information on plant operations and wastewater treatment processes was taken from the facility's NPDES permit.

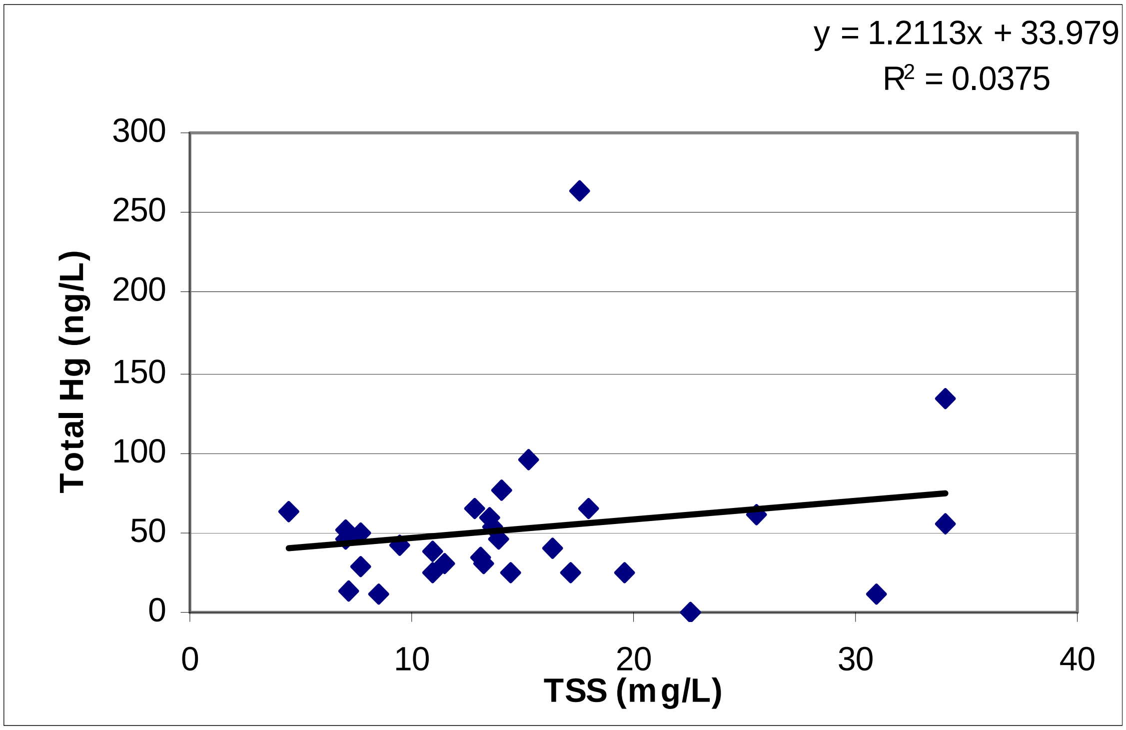


Figure 2-5
Relationship of Total Mercury and Total Suspended Solids in Plant Effluent from a Small Coal-Fired Power Plant in the Upper Midwest

2.3.3.2 Gas-Fired Power Plant – Far West

This plant has a capacity to generate approximately 2,060 Megawatts (MW) from seven steam-electric generating units. Water is withdrawn via two shoreline intake structures to cool the condensers. Cooling water drawn from both intakes passes through separate bar racks and screens. Units 1 through 4 have been in operation since 1954. Units 5 and 6 came online in 1960 and 1961, respectively. Unit 7 came online in 1972. The plant has been in operation in its current facility design and discharge configuration since 1972.

Wastewater is discharged through 11 shoreline outfalls. To the best this researcher can ascertain from the facility permit, Outfall 001 discharges once-through cooling water from Units 1 through 6, Unit 7 Cooling Water Blow Down, and other low volume wastes. Outfall 01B is believed to consist of water from the pretreatment system that has been treated by sedimentation and microstraining, and untreated water from the reverse osmosis building drains. This plant is on a waterbody listed on the state 303(d) as being impaired by mercury and the permit makes a finding of reasonable potential based on a maximum mercury effluent concentration of 160 ng L^{-1} as compared to a maximum ambient background concentration of 21.9 ng L^{-1} and the WQS of 25 ng L^{-1}.

Data summarized in Table 2-11 were collected between January, 2004 and June, 2005 and were obtained from the PCS database.

Table 2-11
Mercury in Effluent and Intake of a Gas-Fired Power Plant, Far West

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Discharge (001)	6.64	7.94	3.68	46	16
Discharge (01B)	3.43	4.64	3.63	78	17
Intake (INF)	7.66	9.50	5.90	62	17
001/Intake (%)	-13				
01B/Intake (%)	-55				

2.3.3.3 Petroleum Coke-Fired Power Plant – Far West

This facility is an electric power plant that uses water for steam generation and cooling. The only liquid discharge is a blowdown stream from the cooling tower system. Nearly all the liquid at the facility is recycled through the cooling tower. Only a small fraction is discharged as cooling tower blowdown. Makeup water to the cooling system is a combination of purchased fresh water, stormwater collected on site, and equipment washdown water. Trace constituents in the source water are likely increased in concentration through water evaporation in the cooling tower.

Data were collected between August 1999 and September 2005. Because much of the data collected from the beginning of the record and August, 2001 was reported at less than the detection limit, only the data from August, 2001 through September, 2005 were used in the data analysis shown in Table 2-12. The data were provided by the regulatory agency to which this facility reports. No comparable intake data were available for the facility.

Table 2-12
Mercury in Effluent of a Petroleum Coke-Fired Power Plant, Far West

Plant/Location	Geometric Mean ng L^{-1}	Arithmetic Mean ng L^{-1}	Standard Deviation ng L^{-1}	Coefficient of Variation %	n
Discharge (D-1)	30.0	26.0	12.8	49	55

This dataset has the longest period of record found and greatest number of data points of any discovered in this research. As such several interesting features can be pointed out.

Figure 2-6 shows a time series plot of the data. The data appear to have a periodic component, with higher values occurring in the second quarter (spring) of the year. To confirm this, seasonal means were computed from the data set. Means of data from the third and fourth quarters of the year (20.2 ng L^{-1} and 23.3 ng L^{-1}) are lower than those for the first and second quarters (28.5 ng L^{-1} and 30.3 ng L^{-1}), indicating a definite seasonal trend for total mercury data in the effluent of this plant. The ratio of the highest to the lowest quarter is 1.5:1.

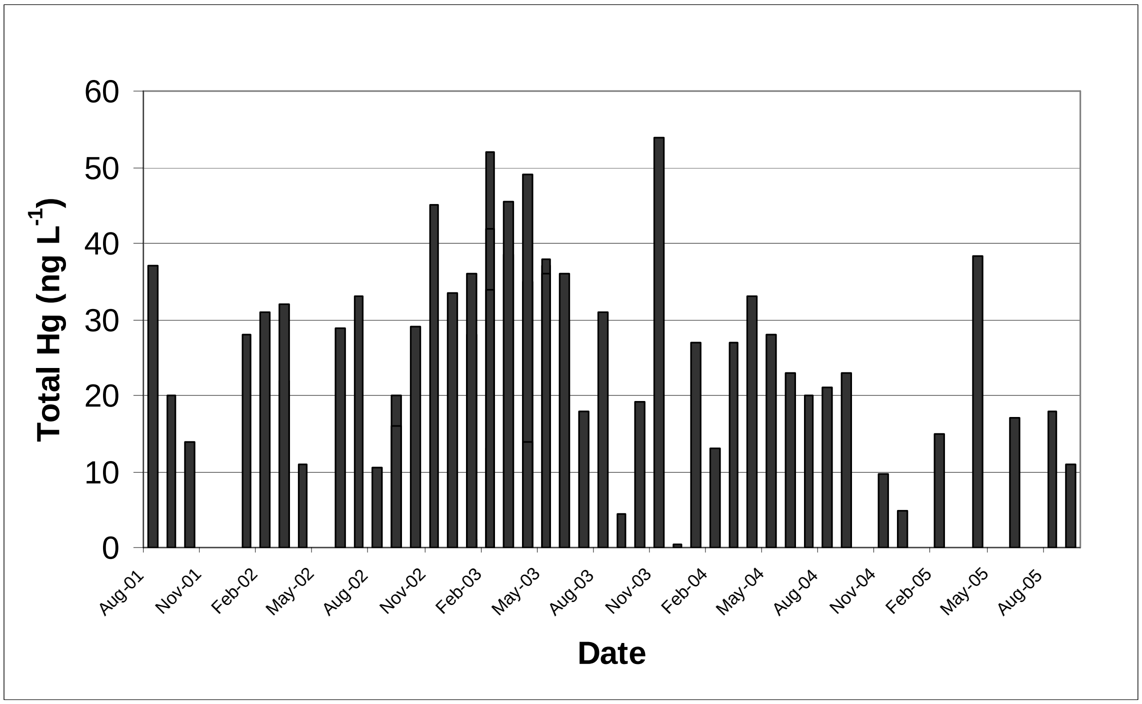


Figure 2-6
Total Mercury in the Discharge of a Petroleum Coke-Fired Power Plant in the Western U.S.

The data set also affords the opportunity to investigate year-to-year variability. Analysis of years beginning 8/2001-7/2002, 8/2002-7/2003, 8/2003-7/2004, and 8/2004-9/2005 yielded the following means, 25.7 ng L^{-1}, 30.7 ng L^{-1}, 23.4 ng L^{-1}, and 17.5 ng L^{-1}. The ratio of the highest to lowest annual mean is 1.75:1. From this analysis, it is evident that year-to-year variability is important and that a long-term record should be used to develop any statistics of central tendency.

2.3.3.4 Small Former Coal-Fired Power Plant – Southeast

This facility is a two-unit, oil-fired steam electric generating peaking plant with nine combustion turbines for a combined producing total of 596 megawatts. The plant began generation in 1952 with Unit 1 originally designed as an oil-fired unit. Unit 2, a coal-fired unit, began operation in 1952. Unit 1 was converted from oil to coal, and began operating as a coal-fired unit in 1960. In 1971 and 1972, partially as a result of limited ash storage facilities, both units were converted back to oil.

On September 17, 2003, clean technique sampling was conducted of the intake water, Outfall 01 - Once Through Condenser Cooling Water and Outfall 02 - Ash Transport Water and Low Volume Waste Discharge. Analyses were conducted by two independent laboratories. These analyses yielded the following results:

Laboratory A

Sample:	Total Hg, ng L^{-1}
Intake source water	4.3
Intake source water duplicate	4.4
01 - Once Through Condenser Cooling Water	3.9
01 - Once Through Condenser Cooling Water duplicate	3.4
02 - Ash Transport Water and Low Volume Waste	<0.2
02 - Ash Transport Water and Low Volume Waste duplicate	<0.2

Laboratory B

Sample:	Total Hg, ng L^{-1}
Intake source water	7.84
Intake source water duplicate	8.07
01 - Once Through Condenser Cooling Water	14.7
01 - Once Through Condenser Cooling Water duplicate	15.7
02 - Ash Transport Water and Low Volume Waste	1.75
02 - Ash Transport Water and Low Volume Waste duplicate	1.70

The analyses of this one time sampling event show that:

- Outfall 002 concentrations are below the plant intake water values, as measured by both laboratories. As reported by Laboratory B, concentrations are lower across plant operations (-78%);
- Outfall 001 concentrations show concentrations above plant intake levels (94%) from one laboratory and below plant intake levels from the other laboratory (-16%);
- The interlaboratory RPD was 57% for the plant intake water and 122% for outfall 001. The bias in these interlaboratory results was consistently in one direction (i.e. Laboratory B results were always higher); and
- The water quality target established by a TMDL for the receiving waterbody in this case is 2.5 ng L^{-1}. Thus far, the plant has received no notice of any further action following submittal of these results.

2.3.3.5 Conclusions

Based on the observations of the data presented in this section, the following additional conclusions can be drawn:

- At one plant geometric mean effluent concentrations were the highest of any plant investigated in this report with a mean concentration of 36.9 ng L^{-1}. Data analysis showed a weak relationship with TSS;
- At a gas-fired power plant in the western U.S., effluent total mercury concentrations were below plant intake levels in two outfalls from -13% to -55%;
- At a petroleum coke-fired power plant in the western U.S., geometric mean total mercury effluent concentrations were the second highest of the plants investigated in this research. The long-term effluent record confirmed significant year-to-year and seasonal variability observed in the EPRI member data; and
- At a small, former coal-fired, power plant in the Southeast, ash pond effluent was significantly lower than intake values (-78%) and were below the WQT; however, results from two different laboratories conflicted on OTCW results, one showing concentrations elevated above intake by 94% and one showing concentrations below intake by 16%. These data also confirm that interlaboratory bias is a significant issue. Interlaboratory RPDs ranged from 57% to 122% on two split samples and were consistently biased in one direction.

2.4 Comparison to Mercury TMDL Targets

In summary, the PISCES data, EPRI member company data and other data obtained through permit searches, show geometric mean concentrations in power plant discharges ranging from 0.76 ng L^{-1} to 36 ng L^{-1}. Comparison of these concentrations to the range of typical water quality targets observed in mercury TMDLs across the country (0.52 to >10 ng/L) indicates that the ranges overlap substantially. Given this overlap it may be difficult to make generic statements concerning risk of mercury TMDLs to the power industry and risk may need to be determined on a regional or facility-by-facility basis.

Another concern that TMDLs raise is whether the discharge exceeds the plant intake; that is, whether mercury is being added by the facility. For the PISCES plants, the change in concentrations across the facilities ranged from -17% to 131%. In the EPRI member company data, the range was from -15% to 1045%, with the most of the plants being in the 13% to 114% range. One gas-fired power plant in the west discharged effluent at concentrations below its intake values. However, the majority of plants investigated as part of this project appear to be adding mercury to their effluent as a result of operations. At this time, there appears to be no way to predict what the discharge concentrations are likely to be at a given plant and levels can only be established through monitoring.

2.5 Assessment of Future Risk Factors

Two future conditions are discussed here as factors that may alter the importance of mercury TMDLs to the power industry. The first is the implementation of FGD systems. The purpose of FGD implementation is to reduce releases of sulfur and trace elements, such as mercury, in flue gases, thus preventing some mercury from entering the atmospheric mercury pool. The reality is that when mercury is scrubbed from flue gases, it is incorporated into other solids or liquids that each facility must treat, dispose of, or reuse. A portion of this mercury represents an increased load to wastewater treatment systems. The second factor is changing water quality standards or targets. Outside of changes to the methylmercury criterion to accommodate site-specific conditions or sensitive human subpopulations, the most significant alterations may come in the form of lowered standards for the protection of wildlife.

2.5.1 FGD System Implementation

Ash pond effluents from facilities in the PISCES database with FGDs are quite low, averaging 2.43 ng L^{-1} to 3.21 ng L^{-1}, and are below plant water intake levels. On the other hand, data obtained from a small coal-fired power plant in the Upper Midwest with an FGD system has discharge mercury levels among the highest of all the facilities investigated as part of this project (37 ng L^{-1}). The conclusion of a recent EPRI study (EPRI 2003) that characterized ash sluice wastes, FGD scrubber waste, plant sump discharges, cooling tower blowdown, coal pile runoff, water treatment residuals and plant intake water at six facilities was that mercury is captured by wet scrubbers resulting in higher concentrations in the wastewater entering treatment ponds. The ratio of FGD influent to ash pond influent concentrations at Facility F was on the order of 20:1.

Assuming that mercury *loads* to plant water systems are higher given the implementation of FGD systems, it may be the case that higher sulfur levels combined with low redox in some ash ponds may provide an opportunity for precipitation of Hg as a sulfide, which would tend to reduce mercury levels in discharged effluent. Chloride levels may also be a factor, as Hg complexed with chlorides may be held in solution and unavailable for precipitation by sulfides. This would tend to increase mercury levels in effluent. At this time, it is not possible to predict mercury levels in effluent from power plants, with or without implementation of FGD systems. Geochemical modeling of ash pond effluents using complete sets of major and minor chemical constituents would be necessary to develop a better understanding of these interactions.

2.5.2 SCR/SNCR System Implementation

The implementation of SCR and SNCR systems for the reduction of NO_X may have a significant impact on the loadings of mercury to wastewater treatment systems in some facilities, especially when they are combined with FGD systems to scavenge oxidized mercury. Research done by EPRI (EPRI 2003a) demonstrates that SCR systems can assist in converting Hg(0) to Hg(II). This effect appears more likely to occur with bituminous coals where at the particulate control device inlet, Hg(II) species predominate (90+%). The three bituminous coal-fired power plants tested in the cited study achieved 84% to 92% mercury removal with SCR operation as compared to 43% to 51% without SCR operation. The increased removal efficiency was thought to be due to the combined effect of the SCR to increase mercury oxidation and reduce reemissions of Hg(0) from the FGD system. In another series of independent tests, an SCR/air heater combination converted more than 98% of the elemental mercury to oxidized and particulate forms at a 1300MW unit burning bituminous coal with 3% sulfur content. Mercury removal on a coal-to-stack basis was 86% (EPRI 2006). At another site burning 3.7% sulfur coal, 98% oxidation was achieved with overall mercury removal of 90% (EPRI 2006a). Without the SCR/air heater operation at these same plants only 61% of the mercury was in oxidized forms and the average coal-to-stack removal rate was only 66%. At a pulverized coal-fired power plant burning high sulfur eastern bituminous coal with a SCR, cold-side ESP and a FGD system, significant mercury oxidation occurred with subsequent capture in the FGD. Results of testing spanning a three year period from 2001 to 2003 indicated that there was no apparent decrease in oxidation or capture with the aging of the catalyst (EPRI 2004b).

The SCR co-benefit was not observed in a power plant that burned Power River Basin (PRB) coal, and may be less significant for low-chloride bituminous coals as well (EPRI 2004d). That SCR has little if any effect when PRB coal is burned was observed at another site as well (EPRI 2004a). Mercury removal results at another site burning PRB basin coal were inconclusive (EPRI 2005). On the other hand, at a site that burned a blend of Powder River Basin and eastern bituminous coal, the operation of a SCR did have a significant effect on the oxidation of mercury (EPRI 2004). However, because this site did not have a wet FGD, the oxidized mercury was not efficiently captured so the overall benefit of SCR operation was not realized.

Other environmental control practices such as the injection of ammonia can also affect the mercury load to the wastewater treatment system. At two power plants burning PRB coal, the impact of ammonia injection in combination with SCR or in flue gas conditioning appeared to be minor. However, at a power plant burning Texas lignite, ammonium sulfate injection upstream of the air heater appeared to significantly increase the mercury fraction in particulates and removal by the ESP (EPRI 2004c).

2.5.3 Mercury Standards for Protection of Wildlife

The focal points for the regulation of mercury in fish tissue have been fish consumption advisories and the methylmercury criterion for the protection of human health. In some TMDLs, however, concerns for the protection of wildlife have been evaluated. In several TMDLs established in California, the U.S. Fish and Wildlife Service (USFWS) has provided consultation to the regulatory agencies as to the level of protection afforded wildlife by the human health criterion (see Section 3). This type of analysis may take two approaches; the first based on the protection of lethal and sublethal effects in wildlife in general, and the second based on the protection of endangered species. The first may be viewed as analogous to protecting the general human population against adverse effects of fish consumption. The second is analogous to protecting sensitive subpopulations of consumers.

To date, the conclusion of the USFWS has been that the methylmercury criterion, when implemented as an average over all trophic levels of fish (i.e. the average tissue residue over all trophic levels would be 0.3 mg kg^{-1}), may not be protective enough for several endangered species. When implemented as an upper limit for the highest tropic level (i.e. trophic level four fish would have no more than 0.3 mg kg^{-1} in tissues), the methylmercury criterion is viewed as *more* protective, but still not protective enough for several endangered species (USFWS 2003). These analyses are admittedly based on very limited data. In light of the uncertainties involved, they make use of a number of conservative assumptions. As better data becomes available on mercury reference doses and exposure data for these species, it is possible that these conclusions will be validated. In some cases, they may be found to be inadequate, which may force regulatory targets for mercury to lower levels.

Thus far, regulatory agencies responsible for these TMDLs and for implementation of the methylmercury criteria have taken a variety of positions regarding the USFWS' conclusions. The State of Idaho (IDEQ 2004) opined that the methylmercury criterion, implemented as an average over all trophic levels should be protective of wildlife. As a result of the Cache Creek mercury TMDL, the Central Valley [California] Regional Water Quality Control Board recommended an alternative in its proposed basin plan amendments to adopt water quality objectives of 0.23 mg kg^{-1} in trophic level 4 fish and 0.12 mg kg^{-1} in trophic level 2 fish, specifically intended to protect fish consuming wildlife (CVRWQCB 2005). This translates into an aqueous methylmercury goal of 0.13 ng L^{-1}. In a more famous incident, the Great Lakes Water Quality Initiative proposed a goal of 1.3 ng L^{-1} for total mercury in the Great Lakes, a standard driven by exposures to wildlife, which has subsequently been adopted as a water quality standard by the Great Lakes states. In the Mercury Study Report to Congress (U.S. EPA 1997), a total mercury value of 0.91 ng L^{-1} was proposed for wildlife protection that considered several piscivorous avian and mammalian species. Of course, the criterion adopted will normally be based on the most sensitive of the endangered species under consideration. In New Jersey, out of consideration for the peregrine falcon, the State recommended a total mercury WQS of 0.53 ng L^{-1} (NJDEP 2001). A recent study sponsored by the Water Environment Research Foundation (WERF) proposed an approach for developing site-specific values for wildlife protection (Moore et al. 2003).

The USFWS, in ongoing consultation with the EPA, are said to be formulating new recommendations (acute and chronic criteria) for the protection of aquatic life. At this time, based upon USFWS' analysis, methylmercury concentrations expected from implementation of the methylmercury criterion appear to be well below observed effects levels for fish. However, in their words "increasing emphasis on examining more subtle methyl mercury-induced effects may reveal even lower tissue-based threshold effects concentrations for fish" (USFWS 2003). Thus, it is not inconceivable that fish health could dominate the establishment of future mercury TMDL targets.

It is possible, even likely, that future TMDLs will consider exposures to wildlife as well as human health in establishing WQTs. The presence of endangered species in a given water body may well establish a lower target than would otherwise have been established for the protection of human consumers.

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3

REVIEW OF MERCURY TMDLS NATIONWIDE AND RELATED REGULATORY DOCUMENTS

3.1 Background

The utility industry faces an evolving regulatory landscape vis-à-vis mercury in NPDES permitted discharges. EPA's first recommendation of a Section 304(a) water quality criterion for mercury dates to 1976. In 1985, the water quality standard recommended by the EPA for the protection of aquatic life was 12 ng L^{-1} and this standard was adopted by many of the States. In 1995, the EPA revised its 304(a) acute criterion to 1.7 ug L^{-1} and the chronic criterion was increased from 0.012 ug L^{-1} to 0.91 ug L^{-1}. Meanwhile, the U.S. Food and Drug Administration (FDA) had recommended fish tissue guidance of 1 mg kg^{-1} for protection of human health and a number of states had adopted this guidance for the purpose of issuing fish consumption advisories. Other states have used a risk-based approach to set thresholds for fish consumption advisories. In many cases, the states have also used these thresholds as the targets in their TMDL analyses. As the reader will note in the following TMDL reviews, these values typically range from about 0.2 mg kg^{-1} to 0.4 mg kg^{-1}, depending upon the specific assumptions each states makes concerning parameters in the risk equations.

In January, 2001, the EPA recommended a human health criterion for mercury that was the first of its kind; a water quality criterion measured in fish tissue rather than in the water column. While many agree that this is a reasonable approach for mercury and other bioaccumulative substances, the Agency has left the states with virtually no guidance as to how this criterion should be implemented in the regulatory process. This in turn has created a situation in which the use of the criterion for 303(d) listing, TMDLs, and NPDES permitting by EPA Regions, the states, and potentially tribes, varies widely.

Table 3-1 shows the water quality standards for the twenty-eight states in which Program 53 supporting EPRI members operate. A few states have adopted a tissue based standard but only two have adopted 0.3 mg kg^{-1} as their water quality standard for mercury for the protection of human health. Others have adopted the *approach* EPA used to derive the criterion but have adapted it for local conditions by changing parameters such as fish consumption rates, relative source contribution, etc. with resulting values ranging from 0.2 to 12 mg kg^{-1}. Still others retain water column based standards with values ranging from 1.8 ng L^{-1} to 600 ng L^{-1}. Many states have also interpreted their narrative toxics standard by placing waterbodies on their 303(d) list when fish consumption advisories are posted. Table 3-1 also shows the lowest threshold level used for posting advisories which in essence has the force of a WQS. These values range from 0.05 mg kg^{-1} to 12 mg kg^{-1}. Thus, the power industry is faced with confusing array of standards in the various states in which they operate.

Table 3-1
Water Quality Standards for Selected States for Mercury Including Fish Consumption Advisory Thresholds

State	Freshwater Aquatic Life Acute (ng L^{-1})	Freshwater Aquatic Life Chronic (ng L^{-1})	Human Health (Fish Tissue) (mg kg^{-1})	Human Health (Water Column) (ng L^{-1})[1]	Wildlife (ng L^{-1})	Fish Advisory Threshold (mg kg^{-1})	Anticipated Changes:	Standards Website Address:
Alabama	2400	12		12		1.0[8]		http://www.epa.gov/waterscience/standards/wqslibrary/al/al.html
Alaska	2400	12		50/51		See footnote 7	Proposed 2400 ng L-1and 770 ng L-1for acute and chronic aquatic life protection	http://www.epa.gov/waterscience/standards/wqslibrary/ak/ak_10_toxics_manual.pdf
Arizona	2400 D	10 D		600		0.3 to 0.6		http://www.epa.gov/waterscience/standards/wqslibrary/az/az_9_wqs.pdf
Arkansas	2400	12				1.0		http://www.epa.gov/waterscience/standards/wqslibrary/ar/ar_6_wqs.pdf
Colorado	1400	10		10		0.5		http://www.epa.gov/waterscience/standards/wqslibrary/co/reg31-20051231.pdf
Florida		12		12		0.5		http://www.epa.gov/waterscience/standards/wqslibrary/fl/fl_4_62-302t.pdf
Georgia	1400	12	0.3			0.23		http://www.epa.gov/waterscience/standards/wqslibrary/ga/ga_4_wqs.pdf
Hawaii	2400	550		47		See Footnote 9		http://www.hawaii.gov/health/environmental/env-planning/wqm/wqm.html
Illinois	2600	1300		12[10]		Statewide for predator fish		http://www.epa.gov/waterscience/standards/wqslibrary/il/il_5_c302.pdf
Illinois[4]	1700	910		3.1	1.3			
Indiana	2400	12		140		See footnote 11		http://www.epa.gov/waterscience/standards/wqslibrary/in/in_5_wqs.pdf
Indiana[4]	1694	908		1.8	1.3			
Iowa[5]	1700	910		50		0.2		http://www.iowadnr.com/water/standards/files/table1.pdf
Kansas	1400	770	12	146		12		http://www.epa.gov/waterscience/standards/wqslibrary/ks/ks-tables-20041206.pdf
						Statewide for all		
Kentucky	1700	910		51		fish		http://www.epa.gov/waterscience/standards/wqslibrary/ky/ky_4_wqs.pdf
Maine	1700	910	0.2			0.2	DEP directed by legislature (2001) to establish a BAF protective of 95% of waters and wildlife criterion	http://www.maine.gov/sos/cec/rules/06/096/096c584.doc
Michigan	1400	770		1.8	1.3	0.5, statewide for predator fish		http://janus.state.me.us/legis/statutes/38/title38sec420.html
Minnesota	2400			6.9		0.2		http://www.epa.gov/waterscience/standards/wqslibrary/mn/mn_5_0222.htm
Minnesota[4]	2400				1.3			
Mississippi	2100	12		153/151		1.0		http://www.epa.gov/waterscience/standards/wqslibrary/ms/ms_4_wqs.pdf
Missouri	2400	500				0.3	May change the way the State assesses mercury impairments in next triennium	http://www.dnr.mo.gov/env/wpp/rules/index.html
Nebraska	1400	51[2,3]	0.215[3]			0.215		http://www.deq.state.ne.us/RuleandR.nsf/Pages/Rules
New Mexico	1400	770	0.3			0.3		http://www.nmenv.state.nm.us/swqb/Standards/index.html
North Dakota	1700	910		50/51		0.3		http://www.epa.gov/waterscience/standards/wqslibrary/nd/nd_8_swq.pdf
Ohio	1700	910				0.05		http://www.epa.gov/waterscience/standards/wqslibrary/oh/oh_5_3745-1-07_wqs.pdf
Ohio[4]	1700	910		3.1				http://www.epa.gov/waterscience/standards/wqslibrary/oh/oh_5_3745-1-33_wqs.pdf
Ohio[6]	1700	910		12				http://www.epa.gov/waterscience/standards/wqslibrary/oh/oh_5_3745-1-34_wqs.pdf

Table 3-1
Water Quality Standards for Selected States for Mercury Including Fish Consumption Advisory Thresholds (Continued)

State	Freshwater Aquatic Life Acute (ng L^{-1})	Freshwater Aquatic Life Chronic (ng L^{-1})	Human Health (Fish Tissue) (mg kg^{-1})	Human Health (Water Column) (ng L^{-1})[1]	Wildlife (ng L^{-1})	Fish Advisory Threshold (mg kg^{-1})	Anticipated Changes:	Standards Website Address:
Tennessee	1400	770		50/51		1.0	Consider adopting EPA methylmercury	http://www.epa.gov/waterscience/standards/wqslibrary/tn/tn_4_wqs.pdf
Texas	2400	1300		12		0.7	criterion during next triennium Consider adopting EPA methylmercury	http://www.tceq.state.tx.us/nav/eq/eq_swqs.html
Virginia	1400	770		50/51		0.5	criterion during next triennium Public hearings mid-2006 for Ohio River issues with topics to include mercury	http://www.deq.state.va.us/wqs/documents/WQS06.pdf
West Virginia	2400	12 M	0.5			0.05	criteria	http://www.epa.gov/waterscience/standards/wqslibrary/wv/wv_3_series1.pdf
Wisconsin	830	440		1.5	1.3	0.05		http://www.epa.gov/waterscience/standards/wqslibrary/wi/wi_5_nr105.pdf
Wyoming	1400	770		50/51		No advisories		http://soswy.state.wy.us/RULES/4475.pdf

Footnotes:

[1] Where two entries are provided, the first is for consumption of water and organisms, and the second is for consumption of organisms only.
[2] Current standard, State has proposed that chronic criteria should be 770 ng L^{-1} but USFWS has testified it should remain at 51.
[3] Proposed standards currently awaiting governor's approval.
[4] Waters draining to the Great Lakes.
[5] There are multiple criteria for various uses. Those listed are the most stringent.
[6] Waters draining to the Ohio River.
[7] The State of Alaska recommends unrestricted consumption of marine and freshwater fish citing the health benefits of fish consumption.
[8] The State of Alabama currently uses FDA guidance of 1 ppm to post fish consumption advisories. However, according to Dr. Neil Sass, the state toxicologist, Alabama will likely begin using the EPA methylmercury criterion as it's listing threshold, either this year or in 2007.
[9] The State of Hawaii appears to have no listings based on fish consumption.
[10] The WQS for certain waters designated as secondary contact and indigenous aquatic life is 500 ng L^{-1}. See Illinois Administrative Code Title 35, Subpart C, Chapter I, Parts 302.407 and 303.441
[11] The standard Indiana uses for calculating consumption values for mercury in fish is 0.3 ug/kg/day for the general population, and 0.07ug/kg/day for the sensitive population, defined as pregnant women and nursing mothers, women of childbearing age and children under the age of 15. Additional information could not be obtained.
D Dissolved
M Methylmercury
All values total recoverable unless otherwise noted.

It is this researcher's belief that most states and tribes will move towards adopting EPA's criterion (or an allied criterion adjusted by State specific preferences) and the older criterion of 12 ng L-1 will fall into disuse. The 12 ng L-1 standard was confusing at best. Even though it was recommended as an aquatic life protection criterion, it was derived as a human health criterion (using the FDA guidance of 1 mg kg^{-1} and dividing by a bioconcentration factor). Many states had adopted it as "protective of all uses" since the acute and chronic criteria for protection of aquatic life were much higher. Many states appear to be waiting for EPA's final guidance on implementation of the methylmercury criterion to be released to adopt a tissue-based standard.

The review of mercury TMDLs was performed to achieve two objectives, as follows:

- to aid in the assessment of the risk that mercury TMDLs pose to the electric power industry; and
- to help develop a basis for providing guidance for individual power plants that may be faced with mercury TMDLs.

In terms of the first objective, the reviews focused on the water quality targets (WQTs) developed for each specific water body. It was hoped that these WQTs could be compared to wastewater effluent concentrations from power plants in the PISCES database to assess the ability of industry facilities to comply with current or proposed water quality targets. In terms of the second objective, the reviews focused on the approaches used by the EPA Regions and states in various mercury TMDLs. These reviews therefore provide an opportunity to assess the defensibility of existing mercury TMDLs and provide a basis to develop strategies for individual facilities.

Seventy-three (73) TMDLs were reviewed for this project[17,18]. Because many of these TMDLs have been done by specific states and EPA Regions, the reviews are grouped along geographic lines in the following discussion. It will also be evident to the reader that the development of strategies for coping with mercury TMDLs at individual power plants must be tailored to the specific approaches used by the regions or states that have developed them, as each regulatory agency thus far has taken somewhat unique approaches. Single page summaries of each review are provided in Appendix A and citations for each individual TMDL are provided in the summaries.

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[17] The number of TMDLs does not correspond to the number of listed water bodies. In most instances, a single TMDL is done for all the listed segments in a waterbody or watershed. Therefore the TMDLs reviewed represent a much greater number of listed segments of waterbodies.

[18] The Florida Everglades pilot mercury TMDL study was not reviewed as part of this effort. The study is not a TMDL *per se* and did not address many of the issues of importance to this work. Furthermore, no point sources are identified in the TMDL and thus it is not particularly relevant to the current project. Having said this, one of the major conclusions of the Florida study was that mercury reductions in air emissions lead to 1:1 mercury reductions in biota. While the caveats attached to this statement in the report are largely ignored, it has become the basis of the assumption in most TMDLs that reductions in air emissions and other sources to waterbodies will lead to 1:1 (percentage) decreases in fish tissue concentrations.

In addition to reviews of the mercury TMDLs, EPA's draft guidance document for implementing its 2001 methyl mercury criterion (U.S. EPA 2001), the State of Idaho's recent mercury water quality criterion implementation guidance (IDEQ 2004), the State of Michigan's permitting strategy (MDEQ 2004), the State of Ohio's Mercury Variance Guidance (Ohio EPA 2000), and the Clean Air Mercury Rule (CAMR) Regulatory Analysis (U.S. EPA 2005) were reviewed. These documents give insights into the way that subsequent TMDLs may be developed and inform the discussion of risk to the power industry.

In reviewing the TMDLs, instances were noted when specific power plants were identified. In some cases, mercury data from these facilities were summarized or available in the TMDL. In other cases, NPDES permit numbers were given and EPA's PCS (Permit Compliance System) database was researched to determine if data were available. In some cases, data was found in PCS. The results of these findings are reported in Section 2 of this report.

3.2 Key Findings

The following is a summary of the key findings from the TMDL reviews. Findings are summarized in four categories:

- Use of Fish Tissue Criterion as a Water Quality Standard;
- Water Column Targets Derived from Fish Tissue Targets;
- Approaches for Deriving Water Column-Based Criteria; and
- Approaches to TMDL Allocations and Implementation.

3.2.1 Use of Fish Tissue Criterion as a Water Quality Standard

Regardless of whether EPA's tissue-based criterion has been formally adopted by the States, the criterion is used liberally in the establishment of TMDLs by the States and EPA Regions. It is rare, in the TMDLs reviewed for this project, that the state or region uses the 0.3 mg kg^{-1} criterion without some modification of the assumptions used to derive it. The TMDLs done in the State of Georgia by EPA Region 4 are among the few in which the 0.3 mg kg^{-1} criterion is used without modification.

In some cases, the criterion is adjusted for local fish consumption rates. A case in point is the TMDL for San Francisco Bay, wherein the tissue-based target is calculated to be 0.2 mg kg^{-1}, based on a fish consumption rate of 32 g day^{-1} rather than the 17.5 g day^{-1} used by EPA to derive the 0.3 mg kg^{-1} criterion. The criterion is not often adjusted for the relative source contribution (RSC) although this has been done in some TMDLs (e.g., Minnesota). In some cases the tissue-based criterion is above the 0.3 mg kg^{-1} criterion, as in the Cashie River, NC, where the target is 0.4 mg kg^{-1} and is based on the criterion the State used to list the waterbody.

In a number of cases, the state or region makes additional conservative assumptions with regard to the use of the tissue-based criterion. Although EPA derived the criterion using mean tissue concentrations in trophic levels 2, 3, and 4, and consumption-based weights for each trophic level, the criterion is often compared to the tissue concentrations in trophic level four fish only. The criterion is often compared specifically to largemouth bass, northern pike, walleye, or other top-level predator in the system tending to have the highest observed tissue levels. This adds an additional, but normally unquantified, margin of safety into the TMDL calculations.

In yet other cases, the states or regions standardize the criterion to a fish species of a certain length or age-class. For instance, the criterion may be stated as 0.4 mg kg^{-1} in a three-year old largemouth bass or 0.2 mg kg^{-1} in a 40 cm walleye. This is helpful in that it guarantees that the oldest, largest specimen with the highest observed tissue level is not used in the analysis.

While the states and tribes are free to develop their own criteria, alternative criteria must be based on scientifically defensible methods. It is not clear how EPA makes this determination as part of the TMDL review process.

3.2.2 Water Column Targets Derived from Fish Tissue Targets

In a number of TMDLs, the state or EPA Region derives a water column-based target from a fish tissue target. This results in a criterion for either total mercury or methyl-mercury in the water column. Table 3-2 gives a summary of the derived criteria by EPA Region. Inspection of the table shows that the results vary widely across the country, depending not only of the aquatic ecosystems involved but also the assumptions used by the permitting agency establishing the TMDL. Total mercury values range from a low of 0.52 ng L^{-1} in the northern forests and wetlands of Minnesota to over 10 ng L^{-1} in California affected by mining activities[19]. Methylmercury criteria range from a low of 0.06 ng L^{-1} in mining affected systems in California to 0.46 ng L^{-1} (nearly two orders of magnitude difference) in a blackwater Coastal Plain stream of North Carolina Coastal Plain.

Table 3-2
Summary of Water Column-Based Criteria used in Mercury TMDLs Nationwide

Region (State – Type)	Total Mercury ng L^{-1}	Methylmercury ng L^{-1}
EPA Region 3 (MD – Lakes)	1.32[20]	
EPA Region 4 (GA – Rivers)	3.8[21]	
EPA Region 4 (GA – Lakes)	7.0[22]	
EPA Region 4 (NC – River)	1.5 to 3.9[23]	0.464[24]
EPA Region 5 (MI – River)	1.3[25]	
EPA Region 5 (MN – Statewide)	0.52	
EPA Region 9 (CA – Cache Creek & tributaries)	13 - 41[26]	0.06 to 0.14[27]

[19] These California rivers and streams tend to have low methyl to total mercury ratios.
[20] Average of 9 lakes.
[21] Average of 21 rivers.
[22] Average of 6 lakes.
[23] Estimated for this report based on the range of ratios of total methylmercury to total mercury given in the TMDL.
[24] Total methyl mercury.
[25] Great Lakes Initiative (GLI) value for wildlife protection.
[26] Estimated for this report using ratios of total methylmercury to total mercury given in the TMDL.
[27] Total methyl mercury.

Table 3-2 (continued)
Summary of Water Column-Based Criteria used in Mercury TMDLs Nationwide

Region (State – Type)	Total Mercury ng L^{-1}	Methylmercury ng L^{-1}
EPA Region 10 (OR – Willamette River)	0.92	0.029[28]
Range	0.52 - 41	0.029 to 0.46

3.2.3 Approaches for Deriving Water Column-Based Criteria

Water-column based criteria are derived in several ways from the tissue-based criterion, as follows:

- division of the tissue-based concentration by a bioaccumulation factor (BAF). In most cases these are calculated from measurements made in the waterbody. In limited instances, the TMDL uses default EPA BAFs;
- regression of waterbody-specific fish tissue concentrations on methylmercury concentrations in water; and
- regression of regional fish tissue concentrations on methylmercury concentrations in water.

3.2.4 Approaches for TMDL Allocations and Implementation

Calculation and allocation of load reductions and implementation of the TMDL in NPDES permits is of great importance to dischargers. In the TMDLs reviewed, calculation of load reductions has been accomplished in a variety of ways involving comparison of fish tissue, water column concentrations and sediment concentrations to targets developed for these media, as follows:

- Fish tissue concentrations are often compared directly to the fish tissue target (e.g. Region 6 TMDLs). As mentioned above, there are different ways the TMDLs make this comparison that increase the required load reductions;
- In some cases, ambient water quality concentrations are compared to the derived water quality targets (e.g. Willamette River TMDL, Maryland lake TMDLs);
- In the Georgia TMDLs, modeled water quality concentrations were compared to the water quality target; and
- In the San Francisco Bay TMDL, current sediment concentrations were compared to a target level of 0.2 mg kg^{-1}.

[28] Dissolved methyl mercury.

In all cases, load reductions are required in the same percentage as the reductions required by comparison to fish tissue or water quality concentrations to the targets. Once the load reductions are estimated, allocations are assigned to point and nonpoint loading sources to the watershed. Of particular importance to this review is the way in which allocations are made to the point sources. In the TMDLs reviewed, these allocations have been made in the following ways:

- In the event that a point source is categorized as a "major" source, it may receive an individual waste load allocation (WLA). The definition of a major source varies some state to state;
- In TMDLs where point sources taken together are considered *de minimis*, they may receive an aggregated WLA;
- In TMDLs where the point sources taken together are considered *de minimis*, they may receive no WLA with language that there is to be no net increase in the discharged load;
- In some TMDLs point sources have been assigned a zero WLA. This is particularly problematic since all point sources will discharge mercury at some level; and
- In some TMDLs, wasteload allocations are deferred until monitoring results can be used to assign a WLA.

Implementation plans are not a required TMDL element. However, almost all TMDLs have some language with implementation recommendations for the permitting authority:

- While the language varies from state to state, in almost all cases point sources are required to monitor for mercury using an approved low-level method (i.e., Method 1631 for total mercury or Method 1630 for methylmercury);
- In almost all cases where a water quality target is assigned, point sources are required to monitor influent and effluent mercury and assess whether the facility discharge levels are above or below the WQT and whether the facility is adding mercury in its wastewater. This is almost always done on a concentration basis. Point sources whose effluents exceed the WQT and are adding mercury to the discharge are often required to develop plans of study to identify sources and mercury to their effluents and develop minimization plans to control those sources;
- In a number of cases where the state water quality standard is 12 ng L^{-1} and the point sources are considered *de minimis*, the TMDL has recommended no action with regard to changes in permits;
- In States such as Michigan and Ohio where general permit variances have been established, permittees are required to take limits based on "achievable levels" and develop characterization and minimization plans as a condition of the variance. In these States, the general variance appears to have been implemented in lieu of performing TMDL analyses (at least on a temporary basis); and
- In some states, guidance has been formalized for assessment of "reasonable potential (RP)". In Michigan, a statistical procedure is outlined to determine RP for facility effluents and in the draft Idaho guidance, the procedure for finding RP is based on fish tissue data exceeding a threshold in the waterbody to which the permittee discharges.

3.3 Review of TMDLs by EPA Region

This section provides reviews of individual TMDLs grouped by EPA Region. Within each region, the individual states are arranged alphabetically. Within each state, TMDLs are also arranged alphabetically. This should provide the reviewer with an easy means of locating TMDLs that have been done in the EPA Region or state of interest.

3.3.1 EPA Region 1

3.3.1.1 Massachusetts

Although no mercury TMDLs were identified for waterbodies in the State of Massachusetts, it is worth mentioning that the State has drafted a proposal as a supplement to its "2004 Integrated List of Waters" describing an alternative approach to performing TMDLs for specific water bodies. This approach is limited to those waterbodies identified as being affected by air deposition of mercury alone. The plan relies on a number of educational and source reduction adaptive management strategies to reduce mercury emissions and eliminate mercury use. In addition, the Massachusetts Department of Environmental Protection (MADEP) has promulgated regulations limiting mercury emissions from coal-fired power plants that are more aggressive (both the percent reductions and in implementation time frames) than EPA's proposed requirements.

While specific numerical targets are not called for by the plan, the plan makes use of very conservative assumptions in assessing the levels of reduction needed to achieve "safe" fish consumption levels. As with several of the individual TMDLs which will be discussed below, MADEP takes data from trophic level four fish (in this case large-mouth bass), develops a 95% percentile statistic for the tissue concentrations, and makes the presumption that fish will be "safe" to eat (i.e. the "fishable" use will be restored) when 95% percentile levels in largemouth bass reach the methyl mercury criterion level of 0.3 mg kg^{-1}. It is thus concluded that "in-region" reductions alone will not be sufficient to bring fish tissue to safe levels and that aggressive reductions from outside the region will also be required.

The plan is silent on potential sources of mercury from power plants other than air emissions.

3.3.2 EPA Region 2

3.3.2.1 New York (NY/NJ Harbor)

TMDLs for mercury were proposed in 1994 and finalized in 1996 for the New York/New Jersey Harbor. The listing is based on exceedance of the 25 ng L^{-1} marine water quality standard. WLAs and LAs were developed for municipal/industrial dischargers, combined sewer outfalls (CSOs), stormwater, and atmospheric deposition. Allocation is based on capping municipal and industrial dischargers at current levels. Some reductions are required of CSOs (10%) and stormwater (30%) sources; however, the bulk of the reductions are slated to come from atmospheric deposition (60%). Rationale for the allocations is not given in the TMDL notice in the Federal Register. Review of the TMDL reveals that the allocation for atmospheric deposition comes from an assumption that the atmospheric load will be reduced by 85% through implementation of CAA regulations. Applying a 30% MOS yields (0.85 x 0.3) yields the 60% allocation. The allocation for CSOs and stormwater sources are also based upon assumptions that enforcement of CAA regulations will bring about the indicated reductions. No further rationale is provided.

3.3.3 EPA Region 3

3.3.3.1 District of Columbia

This TMDL covered metals (including mercury) in Rock Creek, located in the Middle Potomac/Anacostia/Occoquan watershed. Although there is a fish consumption advisory for Rock Creek, the TMDL is for exceedance of the 12 ng L^{-1} water column water quality standard. Exceedances of the total mercury criterion were based on data collected from 1989 to 2003, with samples being analyzed using EPA Method 245 with a detection limit of 200 ng L^{-1}. Some of the data may therefore be suspect. Allocations of the existing mercury load were assigned to CSOs and stormwater outfalls, which samples were found to have 400 ng L^{-1} and 190 ng L^{-1} respectively. Reductions of 88% to 95% from the current mercury load were projected in order to meet the water quality standard.

3.3.3.2 Maryland

Nine TMDLs were identified for the State of Maryland. All of these TMDLs were for lakes or reservoirs, as Maryland has a statewide advisory for its lakes. For all of these lakes, the State used a listing criterion of 0.235 mg kg^{-1} in fish tissue. The criterion was lowered from 0.3 mg kg^{-1} because the State used a higher Relative Source Contribution (RSC) for consumption of marine fish. In all cases, data from largemouth bass were used to compare to the standard for listing purposes.

All TMDLs were established in a similar manner. First, bioaccumulation factors (BAFs) were determined using fish tissue and water column methylmercury data. The BAF was then used to calculate methyl and total mercury concentrations in the water column that would yield the “safe” fish tissue concentration of 0.235 mg kg^{-1} (essentially, the safe tissue concentration was divided by the BAF). The total current mercury load was calculated as the product of the current mercury concentration in the lake and the lake outflow. This load was apportioned into “direct to lake” and “watershed” loads. The current “direct to lake” mercury load was calculated from current atmospheric deposition estimates. The watershed load was then calculated as the difference between the “total” load and the “direct-to-lake” load. The load reduction was calculated by assuming that the load reduction required to achieve the water quality target is proportional to the ratio of “current” to “target” water column concentrations. Allocations were made to the direct and watershed sources in proportion to their relative magnitude. A small portion of the load (3%) was set aside for future allocation. The water quality targets and load reductions required for each of the nine lakes are summarized in Table 3-3.

Table 3-3
Summary of WQTs in Maryland Lakes and Reservoirs

Lake/Reservoir	Water Quality Target (Total Mercury, ng L^{-1})	% Atmospheric Load Reduction Required
Deep Creek Lake	1.01	45
Big Piney Run Res.	0.75	71
Lake Lariat	0.45	82
Liberty Res.	0.87	38
Loch Raven Res.	3.11	35
Pretty Boy Res.	2.15	48
Savage River Res.	0.42	62
St. Mary's Lake	0.78	63
Tuckahoe Lake	2.42	42
Average	1.32	54

As can be seen from the table, the water quality targets for total mercury are quite low, ranging from 0.42 to 3.11 ng L^{-1}.

3.3.3.3 Pennsylvania

The approach taken for Wallenpaupack Lake is identical to that taken for the nine Maryland lakes. Differences in execution are that 0.3 mg kg^{-1} is used for the target fish tissue criterion and national (50% percentile) values are used for the BAF and methylation translators, as no water column data were available with sufficiently low detection limits. The derived water quality target is 1.53 ng L^{-1} total mercury (similar in magnitude to those derived for the Maryland lakes) and a 40% reduction from the current load was calculated in order to meet the WQT.

3.3.4 EPA Region 4

3.3.4.1 Georgia

The State of Georgia has the distinction of having the most mercury TMDLs of all the 50 states, 27 to be exact. All of the TMDLs have been established using a similar approach, as they were all established by EPA Region 4. Originally all the waterbody listings resulted from fish consumption advisories using the Georgia risk methodology as an interpretation of the narrative water quality standard. This had the effect that waterbodies were listed if tissue concentrations in a single species exceeded 0.23 mg kg^{-1}. However, during the course of performing the body of required TMDLs, the State of Georgia adopted EPA's methylmercury criterion in fish tissue of 0.3 mg kg^{-1}. Using the "trophic level weighting" embodied in the calculation of the methylmercury criterion, the State of Georgia recomputed average fish tissue concentrations for the listed waterbodies.

Those waterbodies having trophic-weighted tissue values of greater than 0.3 were retained on the 303(d) list. Although TMDLs were required by court order for all waterbodies, waters with tissue values less than 0.3 mg kg^{-1} were eventually removed from the 303(d) list and the TMDLs were withdrawn. These waters are numbered in the 27 TMDLs counted above. It is a peculiarity of the Georgia procedures that although these waters have been removed from the 303(d) list, the fish consumption guidelines are still in effect. In essence, Georgia has retained its fish consumption guidelines as a public service if the fish tissue for tested species exceed 0.23 mg kg^{-1}, and uses the 0.3 mg kg^{-1} level as a trigger for placing or keeping waters on the 303(d) list. Thus, the two programs have been divorced and fish consumption guidelines are no longer used for regulatory purposes.

TMDLs were established by EPA Region 4 for waters whose trophic weighted fish tissue averages are above 0.3 mg kg^{-1}. BAFs and water quality targets were established from limited sampling data collected from the waterbodies of interest. A watershed model (based on EPA's Watershed Characterization System (WCS) with an added mercury module) was used to generate loads to the WASP5 model, which was in turn used to calculate sediment and water column mercury concentrations. The WCS and WASP5 models were calibrated using the limited data collected. The required load reduction was calculated by taking the difference between the highest *simulated* value in any river reach and the water quality target, and dividing their quotient by the highest simulated concentration. This ratio was then applied to the current load to calculate the required load reduction. WQTs for the Georgia TMDLs that established targets are shown in Tables 3-4 (rivers) and 3-5 (reservoirs/lakes)

It is also important to note that the loads from point sources (in almost all cases) were considered *de minimis* (less than 1% of the total load) and atmospheric deposition was considered to account for 99% of the current loading to the watershed. On this basis, it was recommended that point sources test for mercury in their raw water and effluent using Method 1631. If an increase across the facility was identified at the effluent level greater than the WQT, then the facility was asked in the permitting process to develop a minimization plan. The State did not require facilities to meet the WQT at the end-of-pipe.

Table 3-4
Water Quality Targets and Associated Load Reductions for Georgia Rivers

Rivers/Streams	Water Quality Target (Total Mercury, ng L^{-1})	% Atmospheric Load Reduction Required
Alapaha River	5.8	56
Altamaha River	4.0	(N/A)[29]
Beaver Creek	3.2	49
Brier Creek	4.3	45
Canoochee River	9.3	38

[29] If designated N/A, water body was removed from 303(d) list and no reductions were required.

Table 3-4
Water Quality Targets and Associated Load Reductions for Georgia Rivers

Rivers/Streams	Water Quality Target (Total Mercury, ng L^{-1})	% Atmospheric Load Reduction Required
Chattahoochee River	1.0	(N/A)
Etowah River	2.2	(N/A)
Kinchafoonee Creek	3.2	31
Ochlockonee River	1.9	70
Ocmulgee River	7.4	(N/A)
Oconee River	4.9	(N/A)
Ogeechee River	1.7	45
Ohoopee River	3.4	27
Satilla River	2.0	67
Savannah River	2.8	44[30]
Spring Creek	2.2	(N/A)
St. Mary's River	2.3	60
Suwannee River	3.4	47
Talking Rock Creek	2.2	(N/A)
Taylors Creek	12[31]	(N/A)
Withlacoochee River	8.3	29
Average	3.8	47

[30] The Savannah River was also removed from the 303(d) list, but after the load reduction had been established by the TMDL.

[31] This TMDL was established due to exceedances of the numerical water quality standard of 12 ng L^{-1} and therefore was not derived in the same manner as the other TMDLs in the table. It is not included in the average.

Table 3-5
Water Quality Targets and Associated Load Reductions for Georgia Lakes and Reservoirs

Lakes/Reservoirs		
Big Haynes Res.	4.1	(N/A)
Jackson Lake	7.4	(N/A)
Lake Bennett	7.1	(N/A)
Lake Oconee	17.6	(N/A)
Stone Mountain Lake	4.4	(N/A)
Lake Yonah	1.3	(N/A)
Average	7.0	

3.3.4.2 Mississippi

Four mercury TMDLs were identified for the State of Mississippi; Escatawpa River, Yacona River and Enid Reservoir, Bogue Chitto River and Pearl and Yockanookany Rivers. All of these TMDLs were for mercury in fish tissue resulting from the exceedance of the FDA consumption guideline of 1 mg kg^{-1}. Unlike the State of Georgia, the Mississippi Department of Environmental Quality (MSDEQ) decided to establish its own mercury TMDLs rather than relying on EPA Region 4 to do so; therefore, the approach used differs from the Georgia TMDLs. The Mississippi TMDLs were approved, however, by EPA Region 4.

The MSDEQ performed Phase 1 TMDLs that address only the permitted point sources discharging to these waterbodies. In the Escatawpa River, the analysis uses Mississippi's established water quality standard of 12 ng L^{-1} for the freshwater (non-tidal) segments. The TMDL for the non-tidal segments is established as the product of the water quality standard (WQS) and the 7Q10 low flow for the segment. The current load allocation (LA) is established by the product of the ambient water column concentration (one measurement) and the 7Q10 low flow. The TMDL document places a moratorium on mercury discharges from point sources. Interestingly, all of the point source dischargers to the Escatawpa are in the tidal segment, for which there is no fish consumption advisory[32]. Therefore, there is a zero WLA allocation for the non-tidal segments, and the difference between the TMDL and the LA is assigned to the Margin of Safety (MOS). Thus, this allocation scheme gives 25% of the TMDL to the LA and 75% to the MOS.

The Yacona River/Enid Reservoir, Pearl/Yockanookany, and Bogue Chitto TMDLs take a similar approach. The TMDL documents, like the Escatawpa River TMDL document, place a moratorium on mercury from point sources. The current waste load allocation (WLA) is computed by as the product of the WQS and the sum of the permitted discharges. The MOS is allocated 50% of the TMDL and the LA is computed as the TMDL less the WLA and MOS.

[32] A mercury TMDL was not done for the tidal segment because there was no exceedance of the 1 mg kg^{-1} FDA fish consumption advisory.

No water quality targets that differ from the State's water quality standard of 12 ng L^{-1} are established by these TMDLs.

Note that because the 7Q10 low flow is used in the MSDEQ analysis rather than the average annual flow (used in Georgia and most other TMDLs for mercury), the absolute values of these TMDLs are significantly lower than the values established by other states for rivers with similar flows. These TMDLs will be revisited as part of the Phase 2 analysis or when the State adopts new water quality standards for mercury, as it indicates its intention to do so in both TMDL documents.

3.3.4.3 North Carolina

Two TMDL projects have been performed in the State of North Carolina. The Lumber River TMDL was done first, and takes an admittedly simplistic approach. The Cashie River TMDL was performed more recently and uses a methodology similar to the EPA Region 4 TMDLs for Georgia.

No water quality target was developed in the Lumber River TMDL as it used the existing state water quality standard of 12 ng L^{-1}. However, in the Cashie River TMDL several alternative approaches were investigated to develop a WQT from the fish tissue target of 0.4 mg kg^{-1}. The use of a 40 cm trophic level 4 fish to compare to the standard introduces an unquantified, implicit margin of safety into the Cashie River TMDL.

The first approach involved the use of eight fish samples and one methylmercury sample taken from the Cashie River itself. A regression of tissue residue on length was used to calculate the tissue burden for a 40 cm largemouth bass. The single dissolved methyl- mercury value was then used in conjunction with this tissue concentration to calculate a BAF.

The second approach involved the use of data from 8 Coastal Plain sites in addition to the Cashie River. A multivariate linear regression model was developed using parameters that explained the highest percentages of the variance in fish tissue concentration, which were fish length, total methylmercury in the water column and dissolved organic carbon (DOC) in the water column. The R^2 for this relationship was 0.724.

A third approach used a log-linear regression with the same independent variables as the previous approach. This yielded a regression relationship with an R^2 of 0.76; however, total MeHg and DOC in the water column were found not to be significant predictors of fish tissue concentration.

The fourth approach involved the use of the ratio of fish tissue concentration to length for the Cashie River samples. The ratios for all fish were calculated and the average was computed. This was then multiplied by 40 to yield the average tissue concentration in a 40 cm reference fish. This concentration was divided by the average total MeHg concentration from the Cashie River samples to yield a BAF.

The conclusion from this work was that the computed BAFs were all in close agreement, with estimates by the various approaches being within 25% of one another. The BAFs thus calculated ranged from 0.686E6 to 0.877E6. Method 3 (the log-linear regression model) was deemed to be the most appropriate of the four, having a BAF of 0.706E6. However, an additional margin of safety was inserted into the analysis by calculating the 75th percentile confidence value on the reference fish concentration from the regression analysis. This added 1.05 standard errors to the reference value yielding a BAF of 0.862E6 of total MeHg; a value about the same as the highest BAF resulting from any of the four methods. The resulting total mercury water quality target ranges from 1.5 to 3.9, depending on the methylation translator used. This value is in general agreement with those developed in the Georgia TMDLs.

3.3.5 EPA Region 5

Few TMDLs have been established in EPA Region 5. The one waterbody-specific TMDL was done on a creek in Michigan for which the only identified mercury source was an abandoned mine. The other is a proposed statewide TMDL for the State of Minnesota.

3.3.5.1 Michigan

This TMDL, established by the Michigan Department of Environmental Quality (MDEQ), used the Great Lakes criterion for the protection of wildlife of 1.3 ng L^{-1}. The current load from the Osceola Copper Mine was calculated by using the geometric mean of the mine discharge data (127 ng L^{-1}) times the average discharge flow rate. The critical flow condition of 90Q10 used by the State is in statute. However, since the 90Q10 for Hammell Creek is zero, the TMDL was taken, therefore, as the load calculated for the mine discharge. The mine is required to achieve the water quality target of 1.3 ng L^{-1} in its discharge and therefore must effect a 99% reduction in total mercury. There is no discussion of the feasibility of this reduction or how it might be achieved.

3.3.5.2 Minnesota

The Minnesota TMDL is one of the few regional or statewide TMDLs that have been attempted to date. The State was divided into two regions (NE and SW) along ecoregional lines. As with a number of TMDLs developed after EPA recommended its fish tissue criterion for methylmercury, the State used a fish tissue criterion as the endpoint for the TMDL. The fish tissue criterion of 0.2 mg kg^{-1} is equivalent to EPA's 0.3 mg kg^{-1} criterion using a fish consumption rate of 30 g day^{-1} versus the 17.5 g day^{-1} used by EPA, and a zero RSC. The 30 g day^{-1} fish consumption rate is derived from information generated in the State. The 0.2 level is also consistent with Minnesota's risk based consumption guidelines which advise 1 meal per week if tissue concentration in the consumed species is between 0.05 and 0.2 mg kg^{-1}.

Minnesota Pollution Control Agency (MPCA) made a number of conservative assumptions in interpreting fish tissue data relative to the criterion including, the following:

- the 90% percentile value on fish tissue measurements were used to compare to the criterion for the purposes of computing reduction factors[33];

[33] The 90th percentile walleye concentration used to establish the percent reduction in the TMDL is from 2 to 3 times higher than the median concentrations for these fish species in the NE and SW regions.

- walleye was selected as the reference species because it had the highest 90th percentile tissue concentration, and therefore required the highest reduction factors to meet the criterion;
- the 30 g day^{-1} consumption rate is for *all* fish, not just walleye, therefore the exposure to the consuming population is overestimated; and
- the highest reduction factor (calculated for walleye in the NE region) is applied to the entire State.

Although this TMDL does not make use of a water column-based criterion to assess the required reductions, a water column concentration equivalent to the 0.2 mg kg^{-1} in fish tissue was computed. It was compared to the 1.3 ng L^{-1} criterion for the protection of wildlife to assure that it was as stringent. The resulting water column value of 0.52 ng L^{-1} was computed using BAFs calculated from 14 Minnesota lakes.

Monitoring and minimization plans will be required of facilities with permitted discharge rates >0.2 MGD. Statewide, the WLA is limited to 1% of the atmospheric deposition load or 11 kg yr^{-1}. Due to the phase out of mixing zones required by the Great Lakes Initiative (GLI), all point sources within the Lake Superior Basin will have to meet a 1.3 ng L^{-1} permit limit by March 23, 2007.

3.3.6 EPA Region 6

3.3.6.1 Arkansas

Ten mercury TMDLs have been completed in the State of Arkansas covering 40 listed segments. All of these TMDLs have used essentially the same approach. None have made use of a water column based WQT. Rather, the target is a fish-tissue based criterion based on the FDA criterion (1 mg kg^{-1}) as an interpretation of the narrative water quality standard for mercury[34] with a 20 % MOS, yielding a fish tissue target of 0.8 mg kg^{-1} [35]. Required load reductions are estimated as 1 minus the ratio of the average concentration in largemouth bass in the waterbody to the target of 0.8 mg kg^{-1}. Current load allocations are given to MACT sources, a WLA assuming that point sources discharge 15 ng L^{-1} on average (the State water quality standard for mercury is 12 ng L^{-1}), an LA consisting of a natural geologic and soil sources, and atmospheric sources consisting of local and regional sources. Point sources are considered *de minimis* and no reductions are recommended from the current WLA. In all the TMDLs, except for the Ouachita River, MACT and anticipated air emission reductions are expected to achieve the fish tissue criterion (proportionality of reductions in emissions and fish tissue concentrations is assumed). In the Ouachita River, where there is a significant geologic source of mercury, additional controls (e.g. sediment controls) are estimated to be needed to achieve the target.

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[34] Also the State Action Level for fish consumption advisories.

[35] As with many other TMDLs, these make the conservative assumption that trophic level four fish need to meet the TMDL rather than a representative assemblage of fish typically caught and consumed.

Two electric generating plants are identified as regional air emission sources in these TMDLs, but no effluent data is identified for them and no wasteload reductions are assigned to them as part of the TMDL.

3.3.6.2 Louisiana

The Louisiana TMDLS have used a variety of approaches, which appear to vary with the contractor used by EPA Region 6 to establish them. None of the approaches, however, use a water column-based water WQT. For the most part, linearity is assumed between the current fish tissue concentration and the target and the load reductions required to achieve the target.

3.3.6.2.1 Coastal Bays and Gulf Waters

This TMDL uses an implicit MOS with a 0.5 mg kg^{-1} target for fish tissue. The target species is King Mackerel and the average concentration in this species is used to compare to the criterion to estimate required load reductions.

This recent (April 2005) TMDL embodies the most detailed approach yet taken to Louisiana mercury TMDLs but still relies on a number of conservative simplifying assumptions. Air deposition estimates are made using EPA's REMSAD (Regional Model System for Aerosols and Deposition). Wastewater loads are estimated using permitted flow rates and an assumed effluent concentration of 12 ng L^{-1}. Contribution of the Mississippi River is estimated using mercury concentrations in water and sediment and TSS concentrations measured between 2001 and 2004, assuming that mercury in suspended sediments have the same concentrations as mercury in bottom sediments. The watershed load is calculated using BASINS, with REMSAD deposition rates as inputs. 100% of generated mercury loads are assumed to reach the aquatic systems. A 59% reduction in the nonpoint source mercury load is required.

Point source reductions, *per se*, are not required by the TMDL. Municipal WWTPs over 0.1 MGD are assigned an individual WLA and will be required to monitor for mercury using Method 1631. If the water quality standard is exceeded, they will be required to implement a mercury minimization plan. A group allocation is provided for other point sources but facilities <0.1 MGD are exempt from allocation. Industrial point sources greater than 0.1 MGD are required to monitor using Method 1631. If mercury is detected, they are required to develop a mercury minimization plan.

3.3.6.2.2 Coastal Waters of the Calcasieu

The TMDL for the coastal waters of the Calcasieu River Basin is similar to the other in this group. The target species of interest is King Mackerel. The TMDL establishes reductions for two targets; one for 0.4 mg kg^{-1} in fish tissue and one for 0.24 mg kg^{-1} (the latter being EPA's methylmercury criterion with an additional 20% MOS). The document concludes that reductions of 56% or 74% from current atmospheric loads will achieve the fish tissue target (depending upon the target) and that existing and proposed air emission regulations will be sufficient to accomplish this.

A unique facet of this TMDL is the conclusion that the 80 some point sources in the Calcasieu Ship Channel *do* contribute a significant waste load to the Calcasieu coastal waters. Even though this conclusion is based on very sketchy data, the TMDL assigns a load reduction of either 56% or 74% to the point sources. Despite this conclusion, the TMDL "does not include wasteload allocations". Rather, the LA is defined to include the Calcasieu River, which includes point sources. However, in two of the cases investigated for load reductions (including the "most likely" scenario), point sources in the Calcasieu Ship Channel would have to totally eliminate mercury to meet the required reductions, assuming air emission reduction from existing and proposed regulations.

This TMDL sets a precedent because of the way in which the point source discharges are treated, being lumped in to a Load Allocation. It also sets a precedent in that the point sources under some scenarios would be assigned a WLA of zero. If there is a redeeming quality of this TMDL, it is that the conclusions reached are so vague that almost any implementation outcome is possible. Two electrical generation plants are identified as point sources contributing to the mercury load in the Calcasieu Ship Channel.

3.3.6.2.3 Little River/Catoula Lake

The approach taken to the Little River/Catoula Lake TMDL differs from the two previous TMDLs. Rather than using 0.4 mg kg^{-1} in a predator species as the target, this TMDL uses 0.5 mg kg^{-1} (the advisory listing with no explicit MOS[36]) and the "watershed average" fish tissue concentration for all species. This results in a more generous TMDL than for other water bodies in Louisiana and a load reduction of only 32%. The current mercury load was estimated using EPA's BASINS PLOAD model. This model generates watershed estimates of runoff and sediment production. For the purposes of this TMDL, mercury in runoff was conservatively assumed to be at the same concentration as mercury in rainfall. Estimates of mercury concentrations in soil were estimated by using concentrations measured in the soils of the Savannah River Basin by EPA Region 4, and adjusting them using the ratio of wet deposition to the Little River/Catoula Lake watershed to wet deposition in the Savannah River watershed (assuming that soil levels respond linearly to the depositional load).

The aggregate WLA calculated for this TMDL gives all municipal and industrial dischargers a load equivalent to the permitted discharge rates times the water quality standard of 12 ng L^{-1}. A certification process is proposed by which a discharger could demonstrate that nothing in its operations would reasonably be expected to cause discharge of mercury. If certification cannot be made, monitoring using EPA Method 1631 is proposed. If monitoring were to reveal levels in excess of 12 ng L^{-1}, then a mercury minimization plan would be required. Interestingly, the TMDL states that even if emissions regionally and nationally are brought to anticipated levels with existing and proposed regulations, minimization plans would still be required due to localized emissions and/or watershed response than may cause localized exceedances of the criterion.

[36] In this TMDL, in contrast to earlier Louisiana mercury TMDLs, conservative modeling assumptions are assumed to provide an implicit margin of safety and the 20% explicit MOS is not applied to the fish tissue target.

3.3.6.2.4 Mermenteau and Vermilion-Teche Rivers

In the TMDLs for the Mermenteau and Vermilion-Teche River Basins, the target fish tissue concentration is again 0.4 mg kg^{-1}. However, instead of using the average concentration in a predator species to compare to the tissue criterion, these TMDLs use a “worst case” value, specifically, the average tissue concentration measured in bowfin from Bayou Plaquemine Brule (1.191 mg kg^{-1}). The current waste load is computed assuming the point sources contribute 15 ng L^{-1} at the permitted facility flow rate. The current nonpoint source load is the sum of annual wet and dry deposition to the entire basin. The anticipated reduction required to meet the fish tissue target is computed to be 66%. Since atmospheric reductions are only anticipated to result in a 50% reduction in fish tissue concentration, additional controls are needed to meet the target.

During implementation, point sources that are identified as having reasonable potential to exceed water quality standards will be required to monitor for mercury. Determination of reasonable potential would be based on background ambient water concentrations, discharge concentrations, and application of a water quality standard, criterion, or other target protective of human health. Mercury control would be affected through permit limits and/or minimization plans.

3.3.6.2.5 Ouachita River

The TMDL for the Louisiana portion of the Ouachita River basin used the same approach as the Arkansas TMDLs. However, the target fish tissue level is 0.4 mg kg^{-1} rather than the 0.8 mg kg^{-1} used in Arkansas. This difference arises because the State of Louisiana uses a 0.5 mg kg^{-1} threshold for listing of impaired segments. The 0.4 mg kg^{-1} results from an application of a 20% MOS to the target. Like the Arkansas TMDL, the average concentration in largemouth bass is used to compare to the fish tissue target in order to compute the required load reductions.

3.3.7 EPA Region 7

3.3.7.1 Kansas

This TMDL was established due to exceedances of the State’s 12 ng L^{-1} water quality criterion. The major contribution to impairment is assumed to be due to atmospheric deposition and nonpoint sources. The REMSAD and Generalized Watershed Loading Functions (GWLF) models were used to establish the current load using various conservative simplifying assumptions. The WLA was calculated using the design flow of the waste water treatment plant (WWTP) and the 12 ng L^{-1} state WQS. No reductions are required under the TMDL for this point source. Therefore, all of the reduction must come from the nonpoint source load. A 10% explicit MOS was also used and the LA was calculated as the TMDL minus the WLA and the MOS. No specific implementation actions other than continued monitoring of the receiving water were identified.

3.3.8 EPA Region 8

3.3.8.1 Colorado

The only TMDL established in Colorado is for two hydrologically-linked reservoirs. The target for the analysis is an average concentration of 0.5 mg kg^{-1} in a 15 inch smallmouth bass from McPhee Reservoir and an 18 inch walleye from Narraguinnep Reservoir. The target species allegedly differ because of the different fish community structure of the two reservoirs. Although the largemouth bass is the top predator in McPhee Reservoir, the smallmouth bass was selected as a better indicator of exposure to the consuming population, as creel surveys indicate that largemouth bass constitute less than 1% of the annual harvest. No water column-based target is proposed in the TMDL.

Pollutant sources are identified to be atmospheric and mining operations within the watershed. Atmospheric emissions in the region are shown to be dominated by two large coal-fired power plants. Direct atmospheric loads were calculated to the reservoirs using Mercury Deposition Network (MDN) data, although no MDN sites are close enough for a direct assessment and a technique involving the use of atmospheric deposition of sulfate and nitrate was used to scale the mercury deposition data. The watershed load was developed using the GWLF model utilizing water column and sediment samples collected from tributaries to the reservoirs. The Dynamic Mercury Cycling Model (D-MCM) was used to simulate tissue fish concentrations in the two reservoirs given the watershed loads. Model simulations with 15% load reductions for McPhee and 50% reductions for Narraguinnep produced the desired reductions in fish tissue levels. A 25% MOS is added to the largest of these, resulting in a recommendation of a 75% load reduction for both reservoirs to achieve the targets. On top on this, a proposed 50.8% reduction in loads from mining sources is recommended. The rationale for the magnitude of this reduction is not provided in the TMDL.

3.3.9 EPA Region 9

3.3.9.1 Arizona

The two Arizona mercury TMDLs (Pena Blanca and Arivaca Lakes) are similar to those developed for the McPhee and Narraguinnep Reservoirs in Colorado (likely because they were both performed by the same contractor). The primary difference arises from the fact that the fish tissue target in Arizona is the 1 mg kg^{-1} FDA advisory and the tissue target is applied to a five-year old largemouth bass.

Both lakes have mining as well as atmospheric sources. In both cases, the GWLF model was used to calculate runoff and sediment loads. Observed sediment concentrations were used to estimate “potency factors” for the eroded soils and thence the mercury load associated with erosion. Outputs from the GWLF model were used as inputs to the D-MCM model to model mercury cycling and bioaccumulation in the lakes. Based on this analysis, a 38% reduction in the watershed load was required in Arivaca Lake. The proposed remediation of a former gold mining site in the Pena Blanca Lake watershed (86% reduction in the current load) was judged to be sufficient to bring the fish tissue levels in this lake into compliance. No water column-based WQTs were established in either of these TMDLs.

3.3.9.2 California

Five TMDLs were identified as having been completed by the State of California. These include Hernandez Reservoir, Clear Lake, Cache Creek, San Francisco Bay and the Sacramento/San Joaquin River Delta. A sixth mercury TMDL is underway for the Guadalupe River, a tributary to San Francisco Bay, and a conceptual model report has been prepared. This report was not reviewed for this project for the following reasons:

- Although there will eventually be a TMDL for the Guadalupe River, the modeling report does not have the typical scope of a TMDL, does not identify TMDL endpoints or develop an approach for load reduction or allocations to sources;
- The sources are primarily legacy mining operations which are less directly applicable to the objectives of this report; and
- Although the data collection and modeling approach is a valuable addition to the study of mercury in watersheds, the available data far exceeds that which would normally be available for most TMDLs.

The following TMDLs are quite different, having been done by different Regional Water Quality Control Boards (RWQCBs) within the State. They are important, however, in that they all focus on sediment as a primary linkage between mercury in the waterbody and mercury in fish tissue.

3.3.9.2.1 Cache Creek

Fish tissue targets are established as 0.12 mg kg^{-1} in trophic level 3 fish and 0.23 mg kg^{-1} in trophic level four fish for the protection of human health and wildlife. In one of the tributary creeks, Harley Gulch, a fish tissue target of 0.05 mg kg^{-1} in trophic level 2 fish is established. Based on regressions of trophic level 3 and trophic level 4 fish tissue concentrations on unfiltered (total) methylmercury concentrations, total methylmercury WQTs are established for Cache Creek of 0.14 ng L^{-1}, 0.06 ng L^{-1} for Bear Creek (a tributary), and 0.09 ng L^{-1} for Harley Gulch. Using the data provided in the appendices to the TMDL report to calculate estimates of the MeHg to THg ratios, these methylmercury targets would translate to approximately 13 ng L^{-1} THg in Cache Creek, 6 ng L^{-1} THg in Bear Creek, and 41 ng L^{-1} THg in Harley Gulch.

Load reductions required to meet the fish tissue targets for the various tributaries to Cache Creek range from 35% to 96%. It is of interest to note that a concentration of 0.2 mg kg^{-1} appears in this TMDL as the “background” mercury concentration. Source areas having soil and sediment concentrations above this level are cited for control measures. It is also interesting that atmospheric deposition is thought to contribute a minor load in these watersheds and therefore reductions are neither sought nor specified from atmospheric sources. It is expected that bringing fish tissue to target levels will take from several decades to several centuries.

3.3.9.2.2 Clear Lake

The Clear Lake TMDL uses fish tissue targets of 0.09 mg kg^{-1} in trophic level three fish and 0.19 mg kg^{-1} in trophic level four fish based on protection of human health and wildlife, including bald eagles. The TMDL then proposes sediment targets for various parts of the lake in order to meet the fish targets. Sediment targets range from 0.8 to 16 mg kg^{-1}, depending on their location in the lake. In order to meet the sediment targets, it is estimated that concentrations in the active sediment bed must be reduced by 70%, the loads from the Sulfur Bank Mercury Mine by 95%, and the loads from tributary creeks by 80%. The linkage between mercury in sediments and mercury in fish tissue in the TMDL is presumptive and no scientific evidence is presented to defend it. The TMDL cites other remediation studies of contaminated sites where declines in fish tissue over 15 to 25 year periods following remediation have occurred as the basis. Another feature of interest is the 80 year time frame estimated to achieve the sediment and fish tissue targets.

3.3.9.2.3 Hernandez Reservoir

The Hernandez Reservoir TMDL is the most simplistic of the five. The fish tissue target is EPA's recommended 0.3 mg kg^{-1}. However, as in many other TMDLs, this is applied to trophic level four fish in order to introduce an MOS. This TMDL also has a WQT of 50 ng L^{-1}, which is the California Toxics Rule health-based mercury objective considering consumption of organisms and water for the Municipal and Domestic Water Supply beneficial use.

The TMDL for Hernandez Reservoir is based on the mean annual flow through the reservoir times the WQT of 50 ng L^{-1}. A TMDL is also established for Clear Creek, its principal tributary, using the mean annual flow of the creek and the WQT. The difference in these two loads is taken to be the nonpoint source load to Hernandez Reservoir. The surrounding watershed has a history of mining and efforts have been underway by the U.S. Bureau of Reclamation (BLM) to remediate the disturbed areas. Limited data suggests that mercury levels in water and sediment are declining and the TMDL suggests that nothing beyond the BLM's plans are required to meet the fish tissue targets. It is of interest to note that the "background" sediment level is judged to be 0.2 mg kg^{-1} in this TMDL as well and that "achieving an acceptable level of mercury [in sediments] will also achieve acceptable fish tissue concentrations (below the 0.3 mg kg^{-1} health-based criterion)". This linkage is presumptive and no evidence is presented in the TMDL to scientifically defend it.

3.3.9.2.4 Sacramento/San Joaquin Delta

The Sacramento/San Joaquin Delta TMDL document establishes TMDLs for both total and methylmercury. The methylmercury target is based on a fish tissue target of 0.28 mg kg^{-1} in a 350 mm reference largemouth bass. The 0.06 ng L^{-1} methyl mercury WQT is derived from a regression equation of largemouth bass fish tissue data on total methylmercury measurements in the water column and the use of an 18% MOS. The total mercury TMDL for the Sacramento/San Joaquin Delta is based on coupling to the San Francisco Bay TMDL which calls for a target of 330 kg yr^{-1} to the Bay from the Delta.

Percent reductions for methylmercury are based on the comparison of current ambient methylmercury concentrations in various subbasins of the Delta to the target. Required reductions range from 0 to 73%. A reduction of 26% in total mercury is required from the Sacramento River (because it is estimated to contribute some 80% of the input load of total mercury to the Delta). No reductions are required of other subbasins.

There are three identified electric generating facilities in the Delta. Of these, one is operated by the State, one is a petroleum coke-fired facility, and one is a natural gas-fired facility. Mercury measurements were made for all three of these facilities. In the course of the TMDL study, however, it was determined that these plants contribute a minor quantity of methylmercury relative to other sources and there is little if any net addition above water intake levels. Therefore, no additional regulation of these facilities was recommended. Effluent monitoring will continue to be conducted as they are currently required to measure mercury in their discharges. In the future, it is possible that mercury discharges could be capped at 2005 levels and minimization plans could be required if discharged loads were to exceed the cap.

3.3.9.2.5 San Francisco Bay

The San Francisco Bay TMDL has multiple targets including 0.2 mg kg^{-1} in fish tissue (EPA's methylmercury criterion of 0.3 mg kg^{-1} adjusted for a fish consumption rate of 32 g day^{-1}, the reported 95^{th} percentile consumption rate), 0.5 mg kg^{-1} in bird eggs, and 0.2 mg kg^{-1} as a median concentration in sediment. No water column criterion is established by this TMDL, although the TMDL estimates that lowering total mercury sediment concentrations by 50% will result in a total mercury concentration in the water column of 4.75 ng L^{-1}.

This TMDL also concludes that the key to reaching the fish tissue and bird egg targets is to reduce the concentration of mercury in sediments coming into the Bay. The required reduction is 50% based on lowering the average tissue concentration in striped bass to 0.2 mg kg^{-1} [37]. The TMDL suggests that a reduction of 50% in fish tissue is consistent with the reductions required to reach bird egg and sediment targets as well. The TMDL requires a 52% reduction in bed sediment concentrations, a 25% reduction in the load from the Central Valley (i.e. the Sacramento/San Joaquin Delta), 49% in urban stormwater, and 98% from the Guadalupe River. No reductions are required from atmospheric sources, non-urban stormwater runoff, or wastewater treatment plants.

As a group, industrial wastewater discharges and petroleum refineries are given a WLA of 3 kg yr^{-1}. Specific load allocations for several power plants are given in the TMDL. Ranging from 1 g yr^{-1} to 22 g yr^{-1}, they are computed based on each facility's fraction of the total mercury load from 2000 through 2003. Two of these facilities use petroleum coke to generate electricity, two are natural gas fired, and one is natural gas and distillate fuel-fired. Two of the facilities appear to have expired permits (as of 1999).

[37] Striped bass was chosen as the target species because of the typically elevated tissue values and because it is consumed by a high percentage of subsistence and recreational Bay fisherman.

3.3.10 EPA Region 10

3.3.10.1 Oregon

The Willamette River mercury TMDL is unique in its use of a stochastic food web model to establish the WQT. The establishment of a WQT begins with a fish tissue target of 0.3 mg kg^{-1}. This level has an explicit 15% MOS built in because Oregon's listing criteria is 0.35 mg kg^{-1}.

The Willamette River consists of a number of subwatersheds. Notable among these are the Coast Fork which contains the Dorena and Cottage Grove watersheds and reservoirs, both of which have elevated mercury levels most likely due to historic mining activities. In spite of this obvious spatial difference, the State combined all the fish tissue data from the Willamette when it made its 303(d) listing decision. Thus, the entire river is listed as being impaired, although analysis of fish tissue data from the mainstem indicate that it may not be (ORACWA 2004).

Nonetheless, the State's procedure selects the species with the highest tissue concentration, the northern pikeminnow, as the target species. Using the food web model, the Oregon Department of Environmental Quality (ODEQ) calculates that a WQT of 0.92 ng L^{-1} (THg) is required to bring the median northern pikeminnow to the target of 0.3 mg kg^{-1} for the Willamette. Using flow, suspended sediment and mercury in sediment concentrations, ODEQ computed an "average" total mercury concentration of 1.25 ng L^{-1} in the Willamette River. The required load reductions were then computed as one minus the ratio of the WQT to the average concentrations or 27%. A similar methodology was followed for the Dorena and Cottage Grove subwatersheds. The average total mercury concentration in the Dorena Reservoir was determined to be 1.31 ng L^{-1}, requiring a load reduction of 30%. The average total mercury concentration in the Cottage Grove Reservoir was determined to be 2.86 ng L^{-1}, necessitating a load reduction of 68%.

Current loads are estimated using a variety of available data and simplified techniques. Although runoff and surface soil erosion from agricultural and disturbed forest lands are estimated to be the greatest contributors to mercury loads to the river, the 27% load reduction is applied to all identified sources, including wastewater treatment plants and industrial discharges. No power plants (or other individual dischargers) were specifically identified in the TMDL.

3.4 Other Regulatory Documents

Selected regulatory documents in addition to the TMDLs were reviewed to provide a perspective on where TMDLs may be headed in the future and to assist in the assessment of risk of regulatory actions to the power industry.

3.4.1 EPA's Draft Methylmercury Guidance Document

EPA has drafted guidance for states and tribes for the implementation of the methylmercury criterion in fish tissue. This guidance covers the adoption of standards, the adjustment of the methylmercury criterion for site-specific concerns, monitoring and assessment techniques, coordination with other water quality standards, and TMDLs. NPDES permitting issues are reserved for later guidance.

3.4.1.1 Adoption of Standards

EPA recommends adoption of the methylmercury standard but leaves states and tribes the option of deciding whether to adopt it as a fish tissue concentration or as a water column-based concentration. This guidance is directly relevant to the issue of translating a tissue-based criterion to a water column-based criterion in a TMDL. If the standard is to be adopted as a water column-based standard, EPA gives three options to translate the fish tissue criterion into a water column criterion:

- deriving site-specific methyl mercury BAFs;
- using bioaccumulation models[38]; or
- using EPA's default methyl mercury BAFs;

with the first being the recommended option. A significant problem with this recommendation, however, is that EPA does not have an approved Part 136 method for measurement of methylmercury in water or fish tissue. This may present legal issues for the states and tribes in terms of the adoption of methylmercury as a water quality standard. EPA also touches on the subject of variances for the adopted standards and reviews Ohio's statewide variance and Michigan's multiple discharger variance (reviewed in this document below). EPA discusses the conditions under which Use Attainability Analyses (UAAs) might be pursued. To date, this researcher is not aware of any states or tribes that have performed UAAs because they feel that mercury impairments cannot be addressed by other means. However, if mercury reduction programs are implemented and waterbodies do not respond as expected, there may be more motivation for the agencies to use this as a future regulatory option.

3.4.1.2 Sampling and Assessment

EPA addresses monitoring and assessment in the next section of its guidance and discusses the available methods for methylmercury analysis, sampling designs (including guidance of which species to monitor, timing of sampling, number of samples), and the use of data to make listing decisions. This guidance is linked subsequently to TMDLs because the same fish tissue data will likely be used for both purposes. In essence, EPA defaults to its sampling guidance for fish consumption advisories. There are several troublesome or conflicting recommendations in this section that have bearing of the assessment of risk to the power industry. While these are discussed in the guidance document as "listing issues" they have direct relevance to the use of establishing water quality targets and reductions required to meet those targets in a TMDL analysis. These recommendations are discussed briefly below:

- EPA recommends the use of filets. While this may be appropriate for fish of a size to be consumed by humans, it is inappropriate for assessment of wildlife exposures, where whole fish samples may be more appropriate. EPA is silent on the collection of fish tissue data for

[38] In practical terms, this is really not a separate option. The existing models that EPA cites in tits guidance all use the BAF as an input. Even the Food Web Biomagnification Model used by the State of Oregon in the Willamette TMDL used BAFs as a "calibration" tool, and thus relied on site specific BAFs to predict fish tissue concentrations given methyl mercury concentrations in the water column.

the protection of wildlife, although this is clearly a poignant issue in current mercury TMDLs;

- EPA suggests that larger fish of species that tend to bioaccumulate mercury be targeted. This approach would inappropriately bias the results, however, and does not seem appropriate given that EPA's methylmercury criterion is an average over all species and sizes caught and consumed from fresh waters and estuaries. EPA goes so far as to recommend an option of monitoring trophic level fish four only. A sampling program of this type would clearly bias the results toward false positives (listing when there is no reason to do so) and, when applied in the context of a TMDL, inflate the reductions required to meet the standard. On the other hand, EPA suggests that matching the sampling to consumption patterns is also an option. In fact the guidance goes on to suggest that samples should be collected such that they represent "the average exposure to those who eat fish from the waterbody". These two sampling recommendations clearly conflict; and
- EPA suggests that the regulatory agencies may apportion all of the 17.5 grams of fish consumption to trophic level four fish. However, EPA offers no guidance as to the margin of safety that this imparts into the assessment. This guidance conflicts with a later statement that fish creel data may be used to provide a justifiable basis for weighting the tissue data.

3.4.1.3 Coordination with Other Water Quality Standards

EPA recognizes that multiple standards exist for mercury and that this problem may be exacerbated with the adoption of a fish tissue criterion to interpret narrative standards. While the document discusses the issues, it offer little in the way of actual guidance. Left on their own, states and EPA Regions have come up with a variety of ways to coordinate the various criteria. The most thorough treatment of this issue has been in TMDLs recently developed by the RWQCBs in California.

3.4.1.4 TMDLs

The section on TMDLs guidance covers several topics discussed in the following paragraphs:

- EPA recommends regional or statewide approaches if the loadings are dominated by air deposition driven; otherwise, waterbody-specific approaches are recommended. Statewide approaches have the advantage of relieving the regulatory agency of performing many individual TMDLs. The danger is that the agency will make conservative assumptions relative to the most sensitive condition or portion of a state or region and apply it to the entire state or region. This is what has been proposed in Minnesota, where the less sensitive Southwestern ecoregions are being asked to make the same reductions as the more sensitive Northeastern ecoregions of the State, amounting to overregulation in the less sensitive areas;
- EPA recommends regional alternatives to TMDLs by using screening analyses along the lines of Mercury MAPS or the SPARROW models being applied in New England. Although discussed in the TMDL section, these approaches seem more related to listing impaired water bodies. States typically do not need to predict where the problems are, as they already know this based on fish tissue data. The use of Mercury MAPS is unnecessary to predict

reductions in loadings as reductions determined by comparing the fish tissue residue to the standard would produce an identical result (proportionality between loads and fish tissue concentration reductions is assumed in either case). It seems unlikely that regulatory agencies will adopt this approach, except in the New England States where it is apparently being implemented;

- EPA discusses the quantification of various mercury sources including point discharges, atmospheric, mining, sediments and natural background (which it terms geologic sources) but offers little guidance as to how to assess the magnitude of the loadings from each. There are several topics not addressed in the guidance. The first is urban stormwater. Few if any of the models which have to date been used to establish TMDLs where nonpoint sources are considered address this source. The recent Sacramento/San Joaquin TMDL does perhaps the best analysis to date. The second is that EPA fails to distinguish between older anthropogenic atmospheric deposition, which is uncontrollable with existing or proposed air regulations, and current deposition, which is controllable through air programs;

- EPA discusses linkage issues by reviewing, in a very general sense, with approaches ranging from the simple (example, Mermenteau-Teche TMDL approach) to the complex, including mass balance, dynamic, and spatially-detailed models. Recommended factors to be considered when selecting a model are methylation, BAFs, and the importance of sediment in the TMDL. EPA's guidance on this topic suffers from a lack of understanding of the models. First and foremost, there are no available models that adequately predict when, where, or to what extent methylation occurs. Second, there are no available models that predict when, where and the extent to which bioaccumulation occurs. Most of the available models use BAFs as inputs. Finally, the "importance of sediment" issue is really a methylation issue. For instance, it is observed that in TMDLs in the western states sediment mercury levels are typically much higher than in the eastern states. However, methylation percentage appears to be lower in the west (e.g. 1 to 3% in Cache Creek) than in the east where the methylation percentage may be much higher (up to 30% in southern blackwater streams). On balance, the fish tissue concentrations in these systems tend not to be radically different, especially given the substantial differences in sediment concentrations;

- On the issue of load allocation, EPA suggests that in most cases atmospheric sources (that is, current controllable sources) are dominant and a key issue is whether current and proposed air regulations provide reasonable assurance. What is truly important is whether the load allocations to sources are technically feasible and implementable at a reasonable cost. For instance, it may not be feasible to expect to control 75% of the mercury entering a water body due to erosion and runoff. Once again it may not be reasonable to expect a point source discharger to reduce its loading by 30%, when that means going from 10 ng L^{-1} in its effluent to 7 ng L^{-1}; and

- EPA recommends that a phased approach may be appropriate for some TMDLs. However, the guidance is silent on perhaps the most important facet of this issue, antibacksliding. If a state or tribe, in a Phase I analysis, using conservative assumptions, derives a low water quality target for a waterbody, it may not be possible to relax this standard in a subsequent TMDL.

3.4.2 State of Idaho Mercury Water Quality Criterion Implementation Guidance

This document implements the mercury water quality criterion in Idaho and as a result covers may of the same topics as the EPA draft guidance, reviewed above. However, because the State's program provides for the direct interface between the regulatory agency and the regulated community, it is valuable to see what has been done. The document also includes permitting guidance, whereas the EPA document does not.

3.4.2.1 Criterion Adoption

Idaho has elected to adopt a fish tissue criterion of 0.3 mg kg^{-1}, and therefore does not intend to translate the fish tissue criterion into a water column-based criterion. Idaho Department of Environmental Quality (IDEQ) believes that the 0.3 mg kg^{-1} criteria, if applied to trophic level 4 fish, is likely protective of aquatic life, including bald eagle and threatened and endangered fish species. It has reserved the adoption of acute and chronic mercury criteria for protection of aquatic life for a later date.

The State gives three options to insure that the criterion is locally acceptable including:

- modification of the criterion to reflect local conditions;
- granting of temporary variances to specific discharges; and
- using UAAs where it is determined that the criterion cannot be feasibly attained.

3.4.2.2 Monitoring

Idaho proposed that monitoring be implemented on two levels: statewide and at the facility/source level. The State will encourage dischargers to participate in statewide monitoring of fish tissue. Facilities would be required to monitor effluent monthly (industrial) and quarterly (municipal) until it has 12 monitoring points, at which time the monitoring frequency would drop to quarterly or semi-annually, respectively. Idaho recommends following protocols developed for the Idaho Fish Consumption Advisory Program for sampling, except where deviations are needed to apply data to TMDL and NPDES programs. Idaho is proposing that the target species be in trophic level 4. Bass are proposed for lakes and recommends that the target species for rivers and streams would depend upon the fishery use of that stream.

3.4.2.3 TMDLs

In terms of its TMDL program, Idaho intends to adopt a phased approach and adaptive management. A very positive aspect of Idaho's TMDL approach is the targeting of specific subbasins for analysis. TMDL analyses are expected to focus primarily on air deposition and legacy mining sources. A 5% MOS would be applied to all proposed load reductions.

3.4.2.4 NPDES Permits

Recommended permit conditions would depend upon whether a point source is considered significant. A source would be considered significant if it has been given a WLA in a TMDL or has reasonable potential to exceed the mercury criterion. Idaho's guidance imposes no special conditions on industrial or municipal stormwater permits.

The Idaho permitting guidance is troublesome in that it assumes a facility has RPTE if the concentration in fish in the water body exceeds 0.24 mg kg^{-1}. Since Idaho is targeting trophic level four fish in its listing assessments, it is likely that many stream/reservoirs will exceed the 0.24 mg kg^{-1} threshold. Any facilities discharging to these waterbodies will have RPTE, even if those sources add little or no mercury to their discharge. If RTPE exists, facilities will be required by their permits to:

- take non-numeric restrictions (i.e. implement BMPs for pollution prevention);
- monitor effluent; and
- monitor fish tissue in the receiving water, unless the facility opts in to the statewide monitoring program.

In terms of new or increased discharges, IDEQ admits that the use of a tissue-based criterion poses a particular challenge. The suggested approach is to calculate the resulting concentration of mercury in the water body "after complete mixing" with the receiving water and assume that fish tissue concentrations will increase in proportion to the increase in the fully mixed concentration. This approach has several shortcomings. On the one hand, it does not specify the point at which the discharge is fully mixed, a technicality that might favor dischargers. Second, it allows predicted increase in fish tissue concentrations up to 0.24 mg kg^{-1}, which seems incompatible with antidegradation. Third, it in effect allows for a mixing zone for the discharge, which EPA, other states, and environmental groups have fought against elsewhere. It does not consider any loss mechanisms for mercury. Neither does it consider that the discharge is likely to consist primarily of divalent mercury and it gives no allowance for the fact that only a fraction of this mercury may be methylated and become available for bioaccumulation by fish.

3.4.3 Michigan Permitting Strategy

In May, 2004 the State of Michigan updated its 2000 permitting strategy based on implementation of Method 1631 and several years' worth of data collection and evaluation. The 2000 strategy established a multiple discharger variance to avoid widespread noncompliance with NPDES permits. It included a 30 ng L^{-1} "Level Currently Achievable" (LCA) and required pollution minimization plans in continuing effort to meet the State water quality standard of 1.3 ng L^{-1}. Because monitoring has shown that most NPDES discharger concentrations are significantly less than the 30 ng L^{-1} LCA, the 2004 strategy revises the LCA to 10 ng L^{-1}.

The State has two approaches to determining reasonable potential. If ten or more effluent samples are available, the predicted average effluent concentration equals the 95^{th} percentile of the data (Approach 1). If less than ten samples are available, the predicted average concentration is equal to the maximum concentration times a multiplying factor (Approach 2). If either approach demonstrates reasonable potential to exceed 1.3 ng L^{-1}, a limit based on the LCA is included in the permit.

The multiple discharger variance requires that a permit limit for mercury be set at the LCA and that reasonable progress is made toward achieving the WQS (as outlined in the facility's mercury minimization plan). Individual dischargers may apply for a site-specific LCA of greater than 10 ng L^{-1}.

3.4.4 Ohio Permitting Strategy

The Ohio permitting strategy is similarly based on the intent to prevent widespread social and economic impacts from the implementation of a very low WQS for mercury, contending that the average cost to remove mercury below 12 ng L^{-1} is in excess of ten million dollars per pound. Permittees that are unable to achieve an annual average mercury effluent concentration (AAMEC) of 12 ng L^{-1} are eligible to apply for the mercury variance. The application must contain a Plan of Study (POS) that includes the following:

- data on current influent and effluent concentrations;
- preliminary identification of all known mercury sources;
- description of plans to eliminate known sources;
- preliminary identification of "other" sources;
- a proposed schedule for evaluating sources; and
- a proposed schedule for identifying and evaluating potential reduction, elimination and prevention methods.
- Permits based on an acceptable application will include the following key elements:
- an initial limit, which represents the currently achievable level;
- a pollutant minimization program; and
- monitoring and analysis requirements using the most sensitive EPA-approved method.

If, after implementation of the Plan of Study (POS) and Pollution Minimization Plan (PMP), the discharger still cannot meet the 12 ng L^{-1} limit (unless it can demonstrate that the reason is mercury in its intake water), it must apply for an individual variance.

3.4.5 Regulatory Impact Analysis of the Clean Air Mercury Rule

The regulatory impact analysis (RIA) of Clean Air Mercury Rule (CAMR) is a substantial body of work performed by the U.S. EPA in support of the Clean Air Mercury Rule. Overall, its goal is to provide an analysis of the benefits, costs and net benefits of the rule. It is not the intent here to provide an exhaustive review of this 550+ page document. Rather, it is reviewed in the context of speculating about the future of mercury TMDLs.

The document consists of twelve sections and appendices, as follows:

- Introduction
- Impact of mercury on human health, ecosystems, and wildlife
- Ecosystem scale modeling for mercury benefits analysis

- Profile of fishing in the U.S.
- Mercury concentrations in fish
- Profile of the utility sector
- Cost and energy impacts
- Air quality modeling: changes in Hg deposition to U.S. waterbodies
- Analysis of dose-response relationship between maternal mercury body burden and childhood IQ
- Exposure modeling and benefit methodology with an application to a no-threshold model
- Benefits of mercury reduction considering established health-based benchmarks and overall benefits conclusions
- Co-benefits resulting from reductions in emissions of PM2.5
- Appendix A-1: Mercury load reduction analysis and response for Eagle Butte (South Dakota)
- Appendix A-2: Mercury load reduction analysis and response for Pawtuckaway Lake (New Hampshire)
- Appendix A-3: Mercury load reduction analysis and response for Lake Waccamaw (North Carolina)
- Appendix A-4: Mercury load reduction analysis and response for the Brier Creek watershed (located in the Savannah River basin, Georgia)
- Appendix A-5: Mercury load reduction analysis and response for Lake Barco (Florida)
- Appendix B: Qualitative ecological review of mercury literature
- Appendix C: Cardiovascular effects of methlymercury
- Appendix D: Normalization of mercury in fish tissue samples
- Appendix E-1: Analysis of travel distance for freshwater anglers
- Appendix E-2: Methodology for estimating freshwater fishing days by watershed

Of particular interest to the present discussion are Section 3 which discusses the ecological scale modeling effort, Section 4, that deals with the establishment of fishing profiles, Section 5, dealing with mercury concentrations in fish, Section 8, that deals with air quality modeling, and Section 10, that summarizes the results of the analysis. Also of interest are the appendices that deal with the application of various environmental models to the five case studies. Because the review of the case study appendices is more relevant to the discussion of mercury environmental models presented in Appendix B, comments related to the case studies can be found there.

3.4.5.1 Ecological Scale Modeling for Mercury Benefits Analysis

To perform the benefits analysis, EPA had to first estimate changes in deposition resulting from the implementation of the CAMR and the Clean Air Interstate Rule (CAIR). This was done using air quality models discussed in Section 8 of EPA's report. EPA's Mercury Maps (MMaps) model (U.S. EPA 2001) was then applied to estimate changes in freshwater fish tissue mercury concentrations resulting from changes in mercury deposition after implementation of air regulations. MMaps assumes a proportional relationship between reductions in air deposition and concentrations in fish tissue at steady-state. The basic formulation is

$$\frac{C_{fish}(t_2)}{C_{fish}(t_1)} = \frac{L_{air}(t_1)}{(L_{air}(t_1) + L_{Other})} * \frac{L_{air}(t_2)}{L_{air}(t_1)} + \frac{L_{Other}}{(L_{air}(t_1) + L_{Other})}$$ **Equation 3-1**

where:

$C_{fish}(t_2)$ is the concentration in fish tissue at time $t_{2,}$

$C_{fish}(t_1)$ is the concentration in fish tissue at time $t_{1,}$

$L_{air}(t_2)$ is the air deposition load at time $t_{2,}$

$L_{air}(t_1)$ is the air deposition load at time $t_{1,}$ and

L_{Other} is the sum of all non air deposition sources to the waterbody.

The MMaps report notes that equation 3-1 is of the form y = mx + b and that m+b=1. From the Everglades TMDL pilot project it is noted that m = 0.94 and b = 0.06. In order for the assumption of proportionality to be valid, it is important that systems are chosen such that m is close to 1 and b is close to zero. These are systems in which direct air deposition, rather than other sources, dominates the loading scenario.

MMaps does not consider the dynamics of ecosystem-specific factors that affect mercury methylation and bioaccumulation in fish tissues in different waterbodies over time; rather it assumes that these processes are unchanged by the loading of mercury to the waterbody. The RIA MMaps application does not consider the inputs of non-air sources to the watershed (coefficients "m" and "b" are chosen so that m = 1 and b = 0). A shortcoming of the application of MMaps to the estimation of benefits is that it does not consider the lag time between the reduction of mercury loads and the resulting reductions in fish tissue concentrations. This is important because benefits are estimated for the year 2020 relative to a base case of 2001. Within this time frame some waterbodies may respond and other may only partially respond to reductions in air deposition. The principal reason that ecological models were run was to provide estimates of this time lag.

EPA used several models to simulate the response of the five ecosystem cases including:

- SERAFM;
- WASP;
- WCS; and
- BASS.

SERAFM is a spreadsheet model that simulates mercury response in water, sediments, and fish in a two-layered (epilimnion, hypolimnion) lake with direct deposition and runoff and erosional inputs of mercury from four land use types[39]. WASP (Water Quality Analysis Simulation Program) is a fully dynamic mass balance model for predicting response of water and sediment in waterbodies to loadings of mercury from any number of sources. However, WASP requires linkage to a watershed model to provide the loads and linkage to a food chain bioaccumulation model to predict fish tissue responses. In EPA's analysis, the WCS (Watershed Characterization System) is used to provide loadings for the Bier Creek case study. In all the other case studies, the only load was direct deposition to the waterbody. For the Eagle Butte case study, the BASS (Bioaccumulation and Aquatic System Simulator) model was used to predict fish tissue response to changes in water and sediment mercury concentrations predicted by WASP.

Because of the uncertainties in modeling methylation and bioaccumulation in various systems, EPA suggests that no model can be considered *a priori* predictive of ecosystem responses at this time. Thus, ecosystem models were calibrated using five test cases. The test cases were:

- Eagle Butte, SD; a shallow, well-mixed lake of 0.2 km^2 with a watershed:lake area ratio of 22.6;
- Pawtuckaway Lake, NH; a medium-sized seepage lake (0.36 km^2) near Nottingham, NH, with a watershed:lake area ratio of 13.7;
- Lake Waccamaw; a Large Bay lake in the coastal plain of southeastern, NC with a surface area of 35 km^2 and a watershed:lake area ratio of about 6;
- Brier Creek, GA; a tributary of the lower Savannah River characterized by extensive riparian wetlands; and
- Lake Barco, FL; a small seepage lake in northeastern Florida with a surface area of 0.12 km^2 and a negligible contributing watershed.

The range of response times for these systems were estimated by selecting sediment layer characteristics and diffusion coefficients to affect fast, medium, and slow response times. The depth of the active sediment layer was selected to be either 1, 2, or 3 cm and the diffusion coefficient between sediments and the overlying water were chosen to be between 10^{-4} and 10^{-5} cm sec^{-1}. Smaller active sediment layer depths and larger diffusion coefficients accelerate the release of sediment bound mercury into the water column, thereby shortening the response time of the waterbody to changes in atmospheric loading.

Based on this modeling and assessment of the literature, EPA concludes that the most likely response times (i.e. time to reach steady state given decreased load reductions) for freshwater ecosystems is between 5 and 30 years (for those primarily affected by direct deposition), recognizing that some systems will likely take more than 50 to 100 years (for those where indirect sources play a larger role).

[39] Additional details of these models can be found in Appendix B.

EPA assessed five scenarios in addition to the 2001 base case:

- 2001 “zero-out” case in which all utility sources are assumed to be eliminated;
- 2020 base case with CAIR implementation;
- 2020 “zero-out” case with all utility sources eliminated;
- 2020 case with CAMR Control Option 1[40]; and
- 2020 case with CAMR Control Option 2 implemented.

In its analysis of the five case study locations, EPA found that total elimination of mercury from coal fired utilities would only result in a reduction of atmospheric deposition rates of between 4 and 15 percent. These values are relatively small compared to maximum reductions of 70% observed in the U.S. under the “zero-out” scenario. Thus, EPA ran a scenario of 50% reduction associated with larger declines in atmospheric deposition. One of the significant findings of this analysis was that the magnitude of the uncertainty in the atmospheric and ecosystems models used is greater than the signal derived from a change in loading following elimination of coal-fired utilities at the five locations investigated in the report. EPA added that the effects of expected land use changes can alter the magnitude and timing of fish tissue response to load reductions, adding yet another degree of uncertainty to the results.

In general, statements made by EPA in the CAMR RIA (e.g. no model can be considered *a priori* predictive of ecosystem responses at this time) are not supportive of using ecosystem level models for the establishment of waterbody specific TMDLs. In fact, the results of the ecosystem scale modeling done in the RIA are used only indirectly to estimate the time lag between reduction of atmospheric loadings and fish tissue response. EPA’s hesitancy to use this type of model for a regulatory impact analysis of its own rules runs counter to its draft guidance for implementing the methylmercury criterion which suggests that such models may be used. Instead, EPA’s approach validates EPRI’s comments to the Agency (EPRI 2003) that “it will take many years (>10 years) before scientifically-defensible TMDLs can be developed”. EPRI further stated that “where TMDLs must be initiated before adequate research or site-specific data collection can be completed, a phased TMDL should be performed. The MMaps analysis performed by EPA in the CAMR RIA constitutes a screening level analysis that could potentially be used by states in the establishment of a phased TMDL. It quantifies loadings, provides a linkage of loads to fish tissue response and estimates a time to attainment. Such an analysis could certainly serve as a surrogate for a TMDL in waterbodies where no significant point sources exist, as perhaps in many where point sources are present but judged to be *de minimis*.

[40] CAMR Option 1 assumes a 38 ton yr^{-1} cap on mercury emissions through 2017 and 15 ton yr^{-1} thereafter. CAMR Option 2 assumes a 38 ton yr^{-1} cap on mercury emissions through 2014 and 15 ton yr^{-1} thereafter. CAIR implementation assumes SO_2, N_{OX} (annual) and N_{OX} (summer) caps of 3.6 Mtons yr^{-1}, 1.5 Mtons yr^{-1}, and 0.6 Mtons yr^{-1}, respectively, through 2014 and 2.5 Mtons yr^{-1}, 1.3 Mtons yr^{-1}, and 0.5 Mtons yr^{-1}, respectively, thereafter.

3.4.5.2 Profile of Fishing in the U.S.

In this section of the RIA, EPA provides a characterization of the U.S. commercial and recreational fishing industry, including production, demand, pricing, and outlook. EPA also characterizes the populations that consume fish and quantifies the pathways by which fish from various sources are consumed. This is precursory to the next section in which concentrations in consumed fish are estimated and thence exposures in later sections of the RIA.

There are several interesting points to be made concerning EPA's analysis that relate to mercury TMDLs. First, EPA states that its estimates of fish consumption highlight the fact that the primary benefits of reducing atmospheric deposition of mercury affect a "relatively small" fraction of overall fish consumption. Specifically, the recreational freshwater angler population represents only 13% of the total fish consumption in the U.S. Second, EPA suggests that the average daily fish consumption of the general population is 6 g day^{-1}, the "recommended" freshwater fish consumption rate for freshwater anglers is 8 g day^{-1}, and the average daily consumption of general adult females of child-bearing age (15 to 44 yrs) is 4.3 g day^{-1}. This appears to be in conflict with the consumption rate of 17.5 g day^{-1} on which the methylmercury criterion is based. Finally, EPA states that data for freshwater recreational harvest are not available. While this may have been the case within the scope and timeframe of the RIA, this statement neglects the body of data that exists from creel surveys done by state game and fish agencies. Although it is dispersed, this source may represent the most comprehensive data that exists. For the purposes of performing TMDLs in individual states, this data is certainly relevant if it is available for the waterbody of concern.

3.4.5.3 Mercury Concentrations in Fish

In this section, EPA estimates the concentrations in consumable fish. The RIA examines two databases, the National Listing of Fish and Wildlife Advisories (NLFA) and the National Lake Fish Tissue Study (NLFTS). By comparing the frequency distributions of the two datasets, the Agency concludes that they cannot be judged to be drawn from different populations and therefore combines them for the analysis. This resulted in over 92,000 data points. However, the database was cleaned by eliminating data collected prior to 1990, samples that were not georeferenced, and samples that had unreasonable recorded lengths compared to world record length for that species. Only freshwater species were used. EPA analyzed the resulting dataset using a procedure developed by the USGS referred to as the National Descriptive Model of Mercury and Fish (NDMMF).

According to the NDMMF, the data are fitted to a power function model of the type $Y = aX^b$, in which X is fish length and Y is the methylmercury tissue concentration. Two assumptions of interest are made. First, that the exponent 'b' is unique to each fish species but is the same at all locations, and second, that the coefficient 'a' is unique to each location but is the same for all species. This procedure results in "normalized" fish tissue concentrations that are somewhat lower than their "non-normalized" counterparts. For instance, the mean of non-normalized largemouth bass concentrations is 0.57 mg kg^{-1}, whereas the mean of the normalized concentrations is 0.31 mg kg^{-1}. Differences typically are less for other species with the exception of walleye, whose non-normalized and normalized means are 0.66 mg kg^{-1} and 0.42 mg kg^{-1}, respectively.

Interestingly, the average fish tissue concentration in the NLFA database is 0.29 mg kg^{-1} and the average in the NLFTS database is 0.22 mg kg^{-1}. Since the data are lognormal, this suggests that the better part of the U.S. waters sampled have fish tissue values less than EPA's methylmercury criterion of 0.3 mg kg^{-1}. In fact, EPA states in its report that 226 8-digit Hydrologic Unit Code (HUC) watersheds have average concentrations higher than the 0.3 mg kg^{-1} criterion. This represents 18% of the watersheds in the U.S. Samples in these two databases were concentrated mainly in the eastern and far western U.S.

3.4.5.4 Air Quality Modeling: Changes in Hg Deposition to U.S. Waterbodies

EPA used the Community Multiscale Air Quality (CMAQ) modeling system. CMAQ is a three-dimensional grid-based Eulerian air quality model design to simulate atmospheric concentrations and deposition over large spatial scales. Model simulations are performed using plant-specific emissions of mercury by species provided by the Integrated Planning Model (IPM).

Results of the simulations for the 2001 base case indicate 50% percentile annual mercury deposition for the U.S. of 15.9 ug m^{-2}. In the 2001 "zero-out" case, this figure drops to 14.6 ug m^{-2}, a reduction of only slightly over 8%. Under CAIR plus CAMR Option 1 in 2020, median deposition drops to 14.4 ug m^{-2}, an overall reduction of about 9% from current levels. According to EPA's analysis, in the 2001 base case 90% of the HUCs have utility-attributed depositions below 4.08 ug m^{-2}, whereas in 2020 under the CAIR plus CAMR Option 1, 90% of the HUCs have utility-attributable depositions below 1.16 ug m^{-2}. One question that this analysis raises, not addressed in EPAs report, is whether any of the HUCs with higher percent reductions in deposition coincide with those having higher fish tissue concentrations. Alternatively, do the greatest reductions in deposition come where they are will have less environmental benefit? EPA does state that the higher declines in depositions are predicted to occur in Illinois, Michigan and Missouri whereas higher fish tissue concentrations tend to occur in the northeastern and southeastern U.S.

3.4.5.5 Exposure Modeling and Benefit Methodology with an Application to a No-Threshold Model

The methodology used in the RIA is to project changes in Intelligence Quotient (IQ) of a population of children due to mercury exposures *in utero* given projected changes in fish tissue concentrations resulting from CAMR implementation. Although by EPA's admission, there is limited evidence directly linking IQ and methylmercury exposure, EPA adopted IQ as a surrogate for the neurobehavioral endpoints that the National Academy of Sciences (NAS) and EPA relied on in the development of the reference dose (RfD). Study predictions indicate that a typical child of freshwater fishers lost approximately 0.06 to 0.07 IQ points due to mercury exposure in 2001. Implementing CAIR reduces this loss by a little less than 0.007 to 0.009 IQ points in 2020. Implementation of CAIR plus CAMR Option 1 or Option 2 reduces the loss by an additional 0.0006 to 0.0009 IQ points. The overall impact of mercury on the IQ of children in the general population is small, less than one-thousandth of a normal IQ (IQ=100). Using a value of $8,800 income loss per IQ point (foregone earnings over a lifetime discounted at 3%), EPA estimates a cost impact of $2.6MM to the exposed population. The CAMR benefit is an avoidance of IQ loss of 0.0006 points, amounting to $5.28 per child over his or her lifetime.

The findings of this report may be interpreted in several ways by the regulatory agencies. In response to the finding that the implementation of CAIR and CAMR appear to have a relatively small benefit to a relatively small sector of the overall population, the states may be more willing to push the development of mercury TMDLs into the future. On the other hand, the limited reductions that appear to be brought about by the implementation of these regulations may motivate the states to press harder on control of mercury from point sources dischargers.

3.5 References

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4
GUIDANCE FOR DEALING WITH MERCURY TMDLS AT INDIVIDUAL POWER PLANTS

This section provides guidance for individual power plants facing the possibility of regulation via mercury TMDLs. The guidance is divided into two major portions, the first dealing with 303(d) listing and delisting issues, and the second dealing with mercury TMDLs. The thrust of the 303(d) listing/delisting section is the collection and analysis of fish and water samples and the presentation of the resulting data to best influence the listing/delisting process. The thrust of the TMDL section is to focus on ways the TMDL process can be influenced to mitigate the potential regulatory burden. It considers TMDL targets, collection, analysis and presentation of plant influent and effluent data, the establishment of the current load, load reduction and load allocation, the NPDES permitting process, and closes with a discussion of alternatives to TMDLs.

4.1 Navigating the 303(d) Listing Process

Every two years, the states are obligated to produce a list of waters that are fully, partially, or not supporting their assigned beneficial uses. These “integrated” lists combine what were formerly known as the 305(b) and 303(d) lists, named for the sections of the CWA that require them. While development and format of these lists were largely left up to the states in past years, EPA has moved towards a greater degree of formality and consistency with regard to their production. The most recent guidance can be found in USEPA (2005) and it is recommended that anyone interested in challenging a listing or pursuing a delisting of an impaired waterbody be familiar with this guidance. Equally important is familiarity with the state’s assessment methodology; the description of the particular process by which the state makes listing decisions. It provides the rationale for listing waters of the state as impaired for mercury and must be provided to EPA along with the state’s integrated list. However, prior to the submission of the integrated report, each state should provide the public with an opportunity to review and comment on the methodology, as part of its Continuing Planning Process (CPP).

4.1.1 Listing/Delisting

The Code of Federal Regulations (40 CFR 130.7(b)(5)) requires that each state “assemble and evaluate all existing and readily available water quality related data and information to develop the [303(d)] list”. EPA encourages the states to solicit information from various organizations, including NPDES permittees. States may have a “cutoff” date for considering information for a given listing cycle, so it is important that interested parties be aware of any such deadlines and plan accordingly. Obviously, an active dialogue with responsible state officials regarding the minimum standards for data and data submittals would be beneficial. Because most states have already categorized waters that may be impaired by mercury, this discussion will place more emphasis on the delisting, rather than the listing process.

States may delist (i.e. remove waters from Category 5) when one of the following occurs:

- an assessment and interpretation of more recent or more accurate data demonstrate that the applicable WQS is being met;
- the results of a more sophisticated water quality model demonstrate that the applicable WQS is being met;
- flaws in the original analysis led to the segment being incorrectly listed or
- a demonstration that effluent limitations have been implemented which will result in attainment of the WQS.

For purposes of this discussion, it is most likely that an assessment of new data or a reevaluation of previously utilized data would provide cause for a delisting.

4.1.2 Obligation of Agencies to Use New Information

It is important to emphasize that agencies are required to use *all* relevant information. Therefore, collection, analysis and presentation of data by a permittee, particularly if done in consultation with the regulatory agency, may be very beneficial, especially where it is suspected that new information might lead to a delisting. Delisting, where possible, is much preferred to dealing with the TMDL process.

4.1.3 Collecting and Analyzing Fish Tissue for Comparison to Human Health Criteria

Most states have relied on fish consumption advisories for listing waters as impaired for mercury. As discussed in Section 1.5.2.1, however, fish collections done for the purpose of screening waterbodies for public notification may have focused on older, larger fish, as residues in these fish tend to be higher (see USEPA 2000, Section 6.1.1.6). These fish may not be representative of those caught and consumed by anglers. For instance, residue levels that exceed the listing threshold in a single species composite may have resulted in the listing. Use of these tissue residues to compare to the WQS may result in a biased comparison. It is therefore important that interested parties be thoroughly familiar with the details of the data used to list the waterbody of interest. This data is in the public domain and should be readily available by contacting the state health services or natural resource agency.

Note that if the water has been listed using a criterion that is protective of piscivorous wildlife, either avians (e.g. bald eagles) or mammals (e.g. mink, otter), then the fish collection procedures may be much different.

To the extent that a given state has only a narrative standard for mercury in fish tissue and the fish consumption advisory is being used as an interpretation of the narrative standard, collecting new fish tissue data may not be beneficial. If the state has recently adopted a numerical, tissue-based WQS, however, the introduction of new data may prove useful. When collecting new samples, it is important to know the typical size and species harvested. This is best determined through the use of creel surveys.

4.1.3.1 Creel Surveys

Results of a typical creel survey are shown in Table 4-1. These data are for the freshwater section of the Savannah River. Numbers of individuals harvested by species are shown along with the percentage of the total harvest. Average weight of individuals caught is also shown by species. An underlying assumption, of course, is that the fish caught are consumed. As such, the creel survey represents an upper limit on the quantity of a given species consumed, as fish that are not caught cannot be consumed. The state game and fish of the state natural resource agency should be contacted to determine if a recent creel survey exists for the waterbody of interest[41]. If a creel survey is not available, interested parties may consider completing one, especially if it is suspected that the species used by the agency to list the waterbody are not frequently caught and consumed.

4.1.3.2 Target Species

In any new collection[42], it would be prudent to sample the more popular species identified in the creel survey and to target individuals of the typical size caught. For instance, based on the survey data presented above, the species representing at least 5% of the harvest by weight are, as follows:

- bluegill;
- redbreast sunfish;
- largemouth bass;
- crappie, channel catfish,
- bullhead; and
- shad.

Taken together, these seven species represent almost 70% of the harvest. It is important that trophic level 3 fish be included because they will tend to have lower body burdens of mercury than the more piscivorous, trophic level 4 fish. To the extent that they are consumed, trophic level 2 fish like shad, mullet, and carp are also important to include. These species will tend

[41] Emphasis should be placed on recent information as fish populations can change over time. For instance, a dominant species of sunfish in the Lower Altamaha River in Georgia almost disappeared over a ten year period due to an invasion by flathead catfish, a species that up until that time had not been present.

[42] Interested parties should be aware that valid collection permits are required for fish sampling. Permits and applications are available through the fish and wildlife management division of the state natural resource agency.

to have lower body burdens of mercury as well since they are primarily herbivorous. Data in USEPA (2000) show that average tissue concentrations in national studies of largemouth bass (TL-4), white crappie (TL-3/4), and carp were 0.46 mg kg^{-1}, 0.22 mg kg^{-1}, and 0.11 mg kg^{-1}, respectively. In general, including lower trophic level fish will bring down average tissue concentrations calculated from the collection.

Table 4-1
Savannah River Creel Survey Three Year Average Estimates of Harvest and Average Weight (Adapted from Schmitt and Hornsby, 1985)

Species	Number	Percent Total	Weight, kg	Percent Total	Average Weight, kg
Striped bass	633	0.2	2,663	3.9	4.21
Striped x white	842	0.3	1,414	2.1	1.68
Bluegill	73,624	24.1	9,298	13.6	0.13
Redbreast	83,277	27.2	11,088	16.2	0.13
Warmouth	22,191	7.3	3,286	4.8	0.15
Redear sunfish	13,534	4.4	2,645	3.9	0.20
Spotted sunfish	3,221	1.1	288	0.4	0.09
Largemouth	9,825	3.2	5,680	8.3	0.58
Crappie spp.	24,467	8.0	4,942	7.2	0.20
Yellow perch	9,188	3.0	1,309	1.9	0.14
Channel catfish	12,804	4.2	4,143	6.1	0.32
White catfish	6,327	2.1	2,086	3.1	0.33
Bullhead spp.	25,067	8.2	3,754	5.5	0.15
Shad	5,253	1.7	7,480	11	1.42
Chain pickerel	2,880	0.9	1,239	1.8	0.43
Others	12,644	4.1	6,955	10.2	0.55
Total	**305,778**	**100.0**	**68,270**	**100.0**	**0.22**

Some species collected and used by state agencies to list the waterbody may not be well-represented in the creel survey. For instance, bowfin (included in the “other” category in Figure 4-1) represents only 0.8 % of the harvest by number[43]. However, bowfin and similar species (e.g. suckers, smallmouth buffalo) are frequently sampled by the regulatory agency as indicators of pollution because they are relatively large bottom feeders and tend to have higher tissue levels of mercury. Some such species may also be targeted because they are thought to be more often caught and consumed by lower income anglers. Unless they are strongly represented in the creel, detrivores (bottom feeding fish) should be excluded as they tend to be in contact

[43] Percentage by weight was not available.

with and ingest sediment, which may have elevated mercury concentrations, and therefore exhibit higher mercury tissue levels.

While the relative importance placed on sampling these species may not be commensurate with their popularity in the creel, interested parties would do well to give them, as well as angler demographics, consideration when designing a data collection program. The creel survey for the Savannah River (Schmitt and Hornsby 1985) also identified species caught by "bank" versus "boat" anglers. Boat anglers caught almost twice the number of fish per hour of effort and twice the weight per hour of effort than bank anglers. The mix of species differed as well. Such considerations are important when designing a representative data collection program.

4.1.3.3 Fish Size and Age

Size of fish collected is important as there is at least a nominal relationship between fish size (as measured by weight, length, or age) and mercury in tissue. Length or weight is easily recorded in the field and should be documented for each fish taken. If tissues from multiple fish are to be composited for analysis, the size of each individual is still important to record, along with the average size of fish in the composite. Composite samples are relevant to a study of this type as the average exposure to the consuming population is of interest, rather than the concentrations in individual fish. Compositing also cuts down on the analytical costs. Three to five fish are normally included in a composite sample with the smallest being no less than 75% of the size of the largest fish in the composite. Individual states may have guidance on preparing composite samples. If not, guidance is available in USEPA (2000). Consultation with the state is advisable before data collection begins, if possible. Standardized procedures should be followed whenever possible unless they would obviously bias or negatively impact the study goals and results.

4.1.3.3.1 Relationship between Fish Size and Mercury in Fish Tissue

As mentioned earlier, a study performed for the purpose of delisting a water body should focus on the size of fish caught and consumed by anglers. In general, the larger the fish, the higher will be the mercury concentrations in tissue. Figure 4-1 shows a typical relationship between weight and methylmercury in tissue in largemouth bass collected from Tuckahoe Reservoir, MD. The R^2 value of the regression line indicates that about 42 percent of the variability in tissue concentration can be explained by fish weight. The slope of the regression line is about 0.28 mg kg^{-1} kg^{-1}, so for every kilogram of fish weight, the tissue concentration tends to increase by 0.28 ppm. However, it is of interest to note the scatter in the data. Several composites of fish less than 1 kg in weight have concentrations as high as composites of fish in the >1.5 kg weight range. Thus collection of fish in the range of those normally caught and consumed does not guarantee that lower concentrations will result. However, if several composites are taken in this size range, the results should average out at lower levels. Additional information on the relationship of fish size to mercury tissue levels can be found in EPRI (2003).

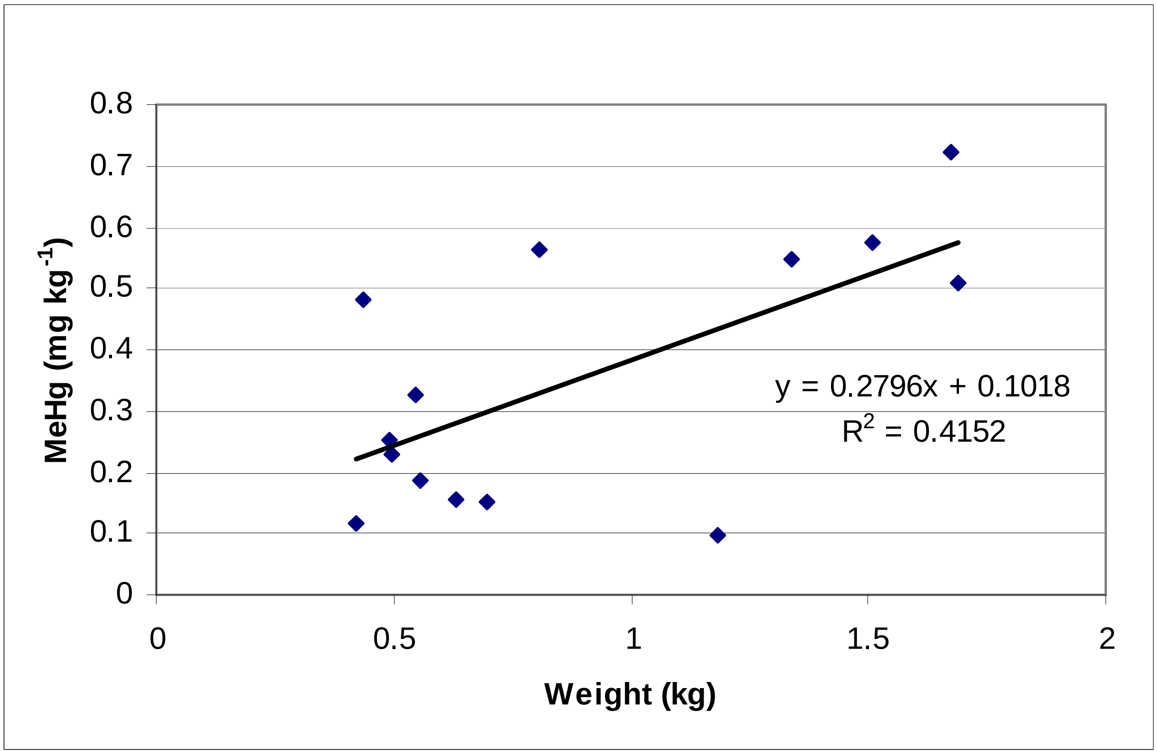

Figure 4-1
Relationship between Fish Weight and Methylmercury in Fish Tissue, Tuckahoe Lake, Caroline County, MD

4.1.3.4 Sample Size

The preceding observation leads naturally to a discussion of the number of samples required in a data collection program. Sample size depends on the variability in the parameter being measured among other considerations. The formula is:

$$n = [\, z_{\alpha/2}\,\sigma / d\,]^2$$ **Equation 4-1**

where:

n is the number of samples required,

$z_{\alpha/2}$ is the standard normal deviate at probability level α (for a two sided test),

σ is the standard deviation of the measured parameter, and

d is the error tolerance.

For instance, if 90% confidence that the sample results for 0.5 kg largemouth bass are within 20% of the true population mean (say, 0.4 mg kg^{-1}) is desired and the standard deviation for the fish tissue data is 0.25 mg kg^{-1}, then

$z_{(\alpha/2 = .05)} = 1.645$

$\sigma = 0.25$

d = 0.2(0.4) = 0.08, and

$n = [1.645(0.25)/0.04]^2 = 26$

Therefore, 26 tissue sample measurements would be required. If one desires to be within 10% tolerance of the population mean, all other factors being the same, the number of required samples rises to over 100. Obviously, variability in the data and the tolerance one is willing to accept are important, as the number of samples varies with the square of this ratio. Therefore, a discussion of the typical variability of mercury levels in fish tissue is warranted.

4.1.3.4.1 Variability of Fish Tissue Mercury Levels

An overview of variability of mercury in fish tissue samples is provided in EPRI (2003). Typically, coefficients of variation (CV)[44] for mercury in fish tissue range from 50 to 100%. Higher CVs tend to result when different species are sampled over multiple locations, seasons, and size ranges in a given water body. When sampling is more focused, for instance, by species and by location, CVs typically are lower and may be as low as 25%. In nine Maryland lakes, CVs for largemouth bass ranged from 33% to 60%[45], however, the fish sampled cover a large range of sizes. It has also been observed that lower CV tend to be associated with higher means (see EPRI 2003, Section 4.2.3.4), probably due to the fact that measurement of mercury in fish tissue close to detection levels tends to be more variable. Thus, CVs in species that tend to bioaccumulate less mercury may tend to be slightly higher. To be realistic, a CV of 30% is not unreasonable if the sampling is focused on a single location, species, and size class of fish. In the example provided above, the CV was 62% (i.e. 0.25(100)/0.4). Using a CV of 30% in the above example with a 20% error tolerance would result in a sample size of 7 rather than 26. Thus, 7 measurements would be made for a single species in the creel at one location in the waterbody to attain this level of confidence in the result. Thus, if tissue concentrations were to be measured on 5 species at three locations, the total number of sample measurements would be 105 (7 x 5 x 3).

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[44] CV is the ratio of the standard deviation in a data set to the mean, expressed as a percentage.

[45] Data was taken from TMDL documents for nine Maryland lakes identified in Section 3. Document citations may be found in Appendix A.

4.1.3.5 Seasonal Considerations

There is little data showing the effect of season on fish tissue concentration. However, because fish accumulate mercury they tend to integrate seasonal variations in concentration. There appears to be some speculation that fish tissue concentrations may be tend to be seasonally higher when methylmercury concentrations are higher in the water column. However, data available to this researcher does not bear this out. In 2000 and 2001, fish and water chemistry data were collected from six blackwater rivers in South Georgia by EPA Region 4[46]. The year 2000 samples were collected in the fall under low flow conditions while the year 2001 samples were collected during the spring during a relatively high flow period. The fact that different fish having different body weights complicates the analysis. In order to remove the variation in fish size, average total mercury concentrations in the tissue samples were normalized by dividing the tissue concentrations by the average weight of fish collected in respective seasons. The results are shown in Table 4-2.

Table 4-2
Comparison of Weight-Normalized Average Total Mercury Concentrations in Largemouth Bass Tissue between Summer, 2000 and Spring, 2001 in Three South Georgia Rivers

2000 (2001)	Satilla	St. Mary's	Alapaha
Average Tissue Concentration, mg kg^{-1}	1.13 (1.35)	0.98 (1.18)	1.19 (0.99)
Average Weight, kg	0.62 (1.17)	0.68 (0.99)	0.50 (0.40)
Weight-normalized Tissue Concentration, mg kg^{-1} kg^{-1}	1.84 (1.15)	1.44 (1.19)	2.38 (2.45)
Water Column MeHg, ng L^{-1}	0.91 (2.56)	0.61 (1.40)	1.01 (2.40)

Results of this analysis show that the weight-normalized concentrations in the St. Mary's and the Alapaha Rivers stayed about the same between seasons. However, weight normalized concentrations went down from 2000 to 2001 in the Satilla River. The data also reveal that the normalized tissue concentrations have little relationship to the ambient water column concentration of methylmercury. Despite the fact that water column concentration increased by a factor of nearly 3 in the Satilla River, the normalized concentration decreased. In the St. Mary's and Alapaha Rivers, although the methyl mercury concentrations increased by a factor of roughly 2 between the summer of 2000 and the spring of 2001, the normalized fish tissue concentrations stayed about the same.

Although this analysis is far from conclusive due to the small number of samples involved, it does appear to indicate a lack of relationship between seasonal changes in methylmercury in the water column and fish tissue concentrations. Given this, it does not appear that sampling in late summer/early fall would unduly bias the fish tissue results. Flows and water levels typically are lower during this season, which logistically simplifies sampling. If a particular

[46] Data was taken from TMDL documents for the Alapaha, Satilla, and St. Mary's Rivers. Document citations may be found in Appendix A.

species is only present or harvested during certain times of the year, this must be given obvious precedence in the sampling plan.

4.1.3.6 Sampling Locations

Sampling locations should be selected to be representative of the aquatic system being investigated and where commercial or recreational harvesting for the species of concern normally occurs. The biggest consideration is waterbody type, as sampling locations will be chosen by different criteria for rivers, lakes and estuaries. After consideration of waterbody type, the next major factor is habitat and the natural history of the species of interest. Fish are more likely to be collected from habitats in which they spend a greater proportion of their time. In rivers, near-bank habitat and backwater areas are likely to be preferred. In lakes, consideration should be given to deep and shallow water preferences as well as near-bank habitat. In estuaries, depth and salinity are important factors as species composition will change dramatically along salinity gradients. Migration patterns and time of year must be taken into account for migratory species and anadromous fish. In addition to the representativeness of habitat and likelihood of obtaining the species of interest, access is important. However, sampling locations should not be immediately downstream of or in the mixing zones of obvious point sources, including stormwater outfalls. Locations should be chosen so that they are accessible in both low and higher water conditions. If the state has collected in known locations, some consideration should be given to collocating new collections in the same areas. Sampling locations should be marked with a Global Positioning System (GPS) so that they can be easily found again.

4.1.3.7 Sampling Methods

Standardized sampling methods should be followed whenever possible. Typically states have written protocols that should be followed. If not, methods should adhere as closely as possible to those in USEPA (2000) and sound scientific practice. Detailed discussion of procedures is beyond the scope of this document.

4.1.3.8 Sample Handling, Preparation and Preservation

Since mercury tends to accumulate in muscle tissue, edible filets, rather than whole fish, should be analyzed when collecting for comparison to human health criteria. There has been considerable debate over whether to leave the skin on when preparing filets. Leaving the skin on will tend to lower concentrations somewhat. However, it is argued that most consumers do not eat the skin. Because removing the skin will not substantially increase the resulting concentrations, it should be removed, eliminating the controversy. However, if the state analyzes tissues with skin on, it may be preferable to leave it, thereby providing a better comparison to previously collected data. Otherwise, standardized sampling methods should be followed whenever possible.

4.1.3.9 Analytical Methods

EPA Method 1631E (USEPA 2002) should be used for the analysis of fish tissue samples for total mercury. This method has the ability to detect mercury in fish tissue with detection limits ranging from 1.3 to 100 ppb and quantitation limits ranging from 2 to 10 ppb in fish tissue (USEPA 2000).

It is also possible to measure methylmercury in fish tissue. However, it is widely accepted that most (~95%) of the mercury in upper trophic level fish is in the methylated form (Watras et al. 1994, USEPA 1997). However, this percentage becomes lower as one moves down the food chain. Thus smaller fish may have proportionally lower percentages of organic mercury and higher percentages of inorganic mercury. This is important in risk evaluations for wildlife that may consume smaller fish, but less important where human health is the issue. Another critical consideration is that, to date, the EPA has not promulgated the draft Method 1630 for methylmercury. Since a delisting determination would have to be made using a method listed at 40 CFR 136.3, pursuant to Section 304(a) of the CWA, determinations would need to be made using 1631E, which is an approved method.

4.1.3.10 Analysis of Fish Tissue Data

Once fish tissue data are available, they need to be analyzed and presented in an acceptable way for delisting purposes. Hopefully, discussions on content and format of the data acceptable to the regulatory agency charged with making the decision have taken place. In the event that the regulatory agency cannot or does not provide such advice, this guidance provides a recommended format for data analysis and presentation.

The goal of this exercise is to convince the regulatory agency to remove the listed waterbody from the 303(d) list or Category 5 of an integrated list of waters. Recall that the most likely ways this may occur are the following:

- an assessment and interpretation of more recent more accurate data demonstrate that the applicable WQS is being met; or
- flaws in the original analysis led to the segment being incorrectly listed.

This guidance will focus on the first of these. However, existing or older data might also be subjected to the same analysis in order to demonstrate the latter. This guidance also assumes that there is a numerical water quality standard to which data comparisons can be made.

For delisting purposes, the interest is in determining if concentrations are less than the WQS. Because fish tissue concentrations are a random variable, and because the sample obtained represents only a few of the fish in the population, there will always be some uncertainty if all fish from the waterbody are below the WQS. For this reason, the agencies will likely want to rely on some statistical measure of the data to make this determination and make some inference about the *population* based on the collected sample.

The steps involved in making inferences about a population are the following:

- Identification of the appropriate probability model and the parameters about which the hypothesis is made;
- Formulation of the null hypothesis, H_0, and the alternative hypothesis H_1;
- Choice of the test statistic;
- Determination of the rejection region for a specified α; and
- Implementation of the test.

This discussion will assume that the sample size is small and that the data are normally distributed or can be transformed so that they are normally distributed. Since the observations form a random sample from a normal distribution $N(\mu,\sigma)$ with population mean μ and variance σ, the mean of the sampling distribution is a natural choice for a test statistic. In this case, the hypothesis to be tested is of the form:

H_0: $\mu \geq \mu_0$ vs H_1: $\mu < \mu_0$

That is, the null hypothesis is that the population mean μ is greater than or equal to the WQS, μ_0. The alternative hypothesis, what is desired to be proven, is that the population mean, μ, is less than the WQS, μ_0. A common test for making inferences of this type is the one-sided, one sample t-test.

The boundary of the rejection region must be selected from a specified tolerance of the Type I error probability[47]. Obviously, by relaxing the probability of making a Type 1 error, it is easier to reject the null hypothesis. Thus, it is easier to reject the null hypothesis if $\alpha = 0.1$ than if $\alpha = 0.01$. Recall that the number of samples collected also affects the ability to reject the null hypothesis in favor of the alternative. It is therefore important to decide on the Type I error probability before collecting data. Hopefully, this could be decided beforehand in consultation with the regulatory agency. In the absence of guidance from the regulatory body, a Type I error probability of 0.1 (10%) seems reasonable. If the null hypothesis is rejected with a Type I error probability of 0.1, then there is reasonable certainty that the correct inference about the population mean has been made.

Statistics that might be employed to test hypotheses about the data include percentile values (e.g. the 95th percentile) or measures of central tendency of the data, (e.g. the arithmetic mean, geometric mean, median). Obviously, it will be more difficult to delist the waterbody if the agency focuses on extreme rather than mean values; that is, the 95th percentile value of fish tissue will be much greater than the mean. However, there is underlying motivation to use a measure of central tendency rather then extreme values. This motivation is discussed in EPRI (2003)[48].

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[47] Type I error is the rejection of the null hypothesis in favor of the alternative when the null hypothesis is true. Type II error is the failure to reject the null hypothesis when the alternative is true.

[48] The reader is referred to Section 3.3 of EPRI (2003).

4.1.3.10.1 Measures of Central Tendency

The calculation of mean values for each species or of a trophic-weighted mean is central to making the delisting determination. A basic question is whether to use the arithmetic mean or some other measure of central tendency. A common alternative to the arithmetic mean is the geometric mean. The geometric mean is the n^{th} root of the product of all the observations, whereas the arithmetic mean is derived by summing the values and dividing by the total number of observations. The geometric mean is a better statistic of central tendency when there are a few very high values in the data set and the rest tend to be small. These high values unduly bias the arithmetic mean. The geometric mean deemphasizes these high values (Yevjevich 1972). The use of the geometric mean is justified when the logarithms of the observations show symmetry around their mean value (i.e. are normally distributed). This condition occurs frequently with environmental measurements. *It is desirable to use the geometric mean whenever it is justified, as the values of the geometric mean of a data set will always be less than or equal to the arithmetic mean when the data are skewed to the left.*

4.1.3.10.2 Tests for Normality

A good way to determine if the geometric mean will be appropriate to use is to make a frequency plot of the data. If they are skewed to the left (i.e. there are many low values with very high values in the upper tail of the distribution) then it is likely that the logarithms of the data will be more normally distributed than the observations themselves. Figures 4-2 and 4-3 show a relative frequency plot (or histogram)[49] of largemouth bass data collected by the Department of Energy (DOE) Savannah River Site from the Savannah River. There are 208 fish tissue values in this dataset covering a three year period from 1996 to 1998. Notice that the histogram of the untransformed data appears to be skewed to the left (Figure 4-2 as compared to the normal distribution with mean and variance calculated from the data). Figure 4-3 shows the natural logarithms of the data. This histogram appears to be a better "fit" to the lognormal distribution. There are two popular ways to test for normality of the data (or logarithms of the data); the Chi-square test and the Kolmogorov-Smirnoff test (Haan 1977). For grouped data such as those in Figure 4-2, the Chi-Square (X^2) test can be used to test for normality. "Goodness-of-fit" tests are shown in Table 4-3 for both the original and log-transformed data.

[49] The frequency histogram is constructed by setting up class intervals for the observations and counting the number of occurrences in each interval.

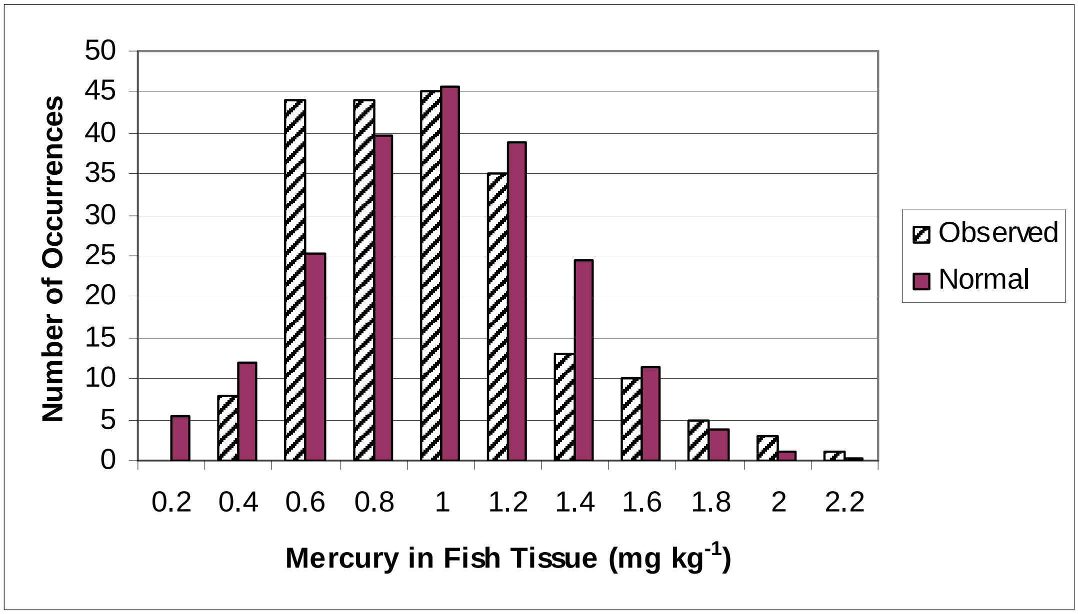

Figure 4-2
Frequency Histogram of Mercury in Largemouth Bass in the Savannah River.
Data Source (WSRC 1997, 1997a, 1998)

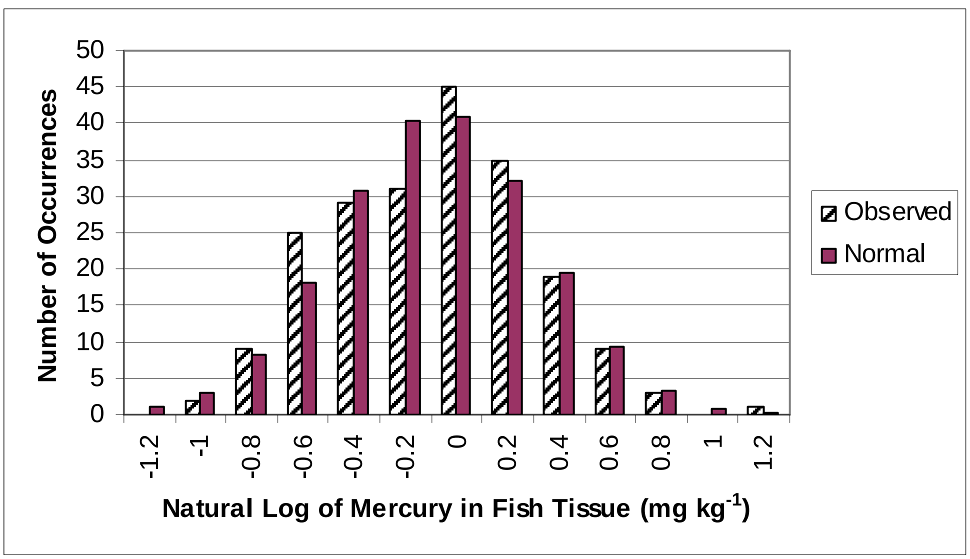

Figure 4-3
Frequency Histogram of the Natural Logarithms of Mercury in Largemouth Bass in the Savannah River. Data source (WSRC 1997, 1997a, 1998)

Focusing first on the upper portion of the table, the number of intervals for which the frequencies are to be determined are provided in Column 1[50]. These intervals are set up so that the number of occurrences in any given interval "n" are counted as the number of occurrences less than the entry in the nth row, minus the number of occurrences in the (n-1)th row (Column 2). For example, the number of occurrences in interval number 2 are those fish tissues values less than 0.4 mg kg^{-1} but greater than 0.2 mg kg^{-1}, as shown in Column 3. In column 4, the cumulative normal distribution function (CDF) is computed at the upper end of the class interval. In column 5, the difference in the cumulative probability between the nth and (n-1)th cell interval is multiplied by the total number of observations (208) to arrive at the expected interval frequency per the normal distribution. The difference between the observed (column 3) and expected (column 5) cell frequencies are then squared and divided by the expected interval frequency (column 6). The sum of the computations in column 6 over all intervals is the X^2 value for the test. The critical value is obtained in a look up table which can be found in any number of basic statistics texts. For the X^2 test, the critical value is found by entering the table with $1-\alpha$ and degrees of freedom equal to the number of intervals (k) minus the number of parameters (p) estimated for the normal distribution (μ, σ) minus 1, or

$$d.f. = k-p-1 \quad \text{Equation 4-2}$$

In this case, with k = 11 and p = 2, the d.f. is 8 and the critical X^2 is 13.4. Since the computed X^2 statistic (35.04) is greater than the critical value, the null hypothesis that the data are normally distributed is rejected.

When the data are log-transformed (lower portion of Table 4-3), the X^2 test shows that the computed statistic is less than the critical value. So the null hypothesis that the data are log-normally distributed cannot be rejected. In this case, then, the data can be assumed to be log-normally distributed and the geometric mean is a more appropriate statistic to represent the central tendency in the data.

When there are enough data that they can be organized into a frequency histogram, the X^2 test can be used to determine goodness-of-fit. However, when the data set is small, the Kolmogorov-Smirnoff test offers an attractive alternative.

Table 4-3
Chi-Square Test for Goodness-of-Fit for Largemouth Bass Data from the Savannah River and Tributaries, Original and Log-Transformed Data

(1) Interval Number	(2) Interval Upper Limit, mg kg^{-1}	(3) Number of Occurrences	(4) Cumulative Normal Distribution	(5) Probability Density Function	(6) $(O-E)^2/E$
Original Data					
1	0.2	0	0.026	5.496	5.496
2	0.4	8	0.084	12.001	1.334
3	0.6	44	0.206	25.398	13.625
4	0.8	44	0.397	39.667	0.473
5	1	45	0.617	45.725	0.012

[50] The number of intervals can be determined in a number of ways but the most basic is to take the range and divide it into a manageable number of intervals, about 10.

Table 4-3 (continued)
Chi-Square Test for Goodness-of-Fit for Largemouth Bass Data from the Savannah River and Tributaries, Original and Log-Transformed Data

(1) Interval Number	(2) Interval Upper Limit, mg kg^{-1}	(3) Number of Occurrences	(4) Cumulative Normal Distribution	(5) Probability Density Function	(6) $(O-E)^2/E$
Original Data					
6	1.2	35	0.804	38.904	0.392
7	1.4	13	0.921	24.430	5.348
8	1.6	10	0.976	11.322	0.154
9	1.8	5	0.994	3.871	0.329
10	2	3	0.999	0.976	4.194
11	2.2	1	1.000	0.182	3.687
				$\Sigma((O-E)^2/E)$ =	**35.04**
		Total = 208		**$X^2(0.9,8)$=**	**13.4**
Log-Transformed Data					
1	-1.2	0	0.005	1.017	1.017
2	-1	2	0.019	2.955	0.308
3	-0.8	9	0.059	8.327	0.054
4	-0.6	25	0.147	18.179	2.559
5	-0.4	29	0.294	30.745	0.099
6	-0.2	31	0.488	40.283	2.139
7	0	45	0.685	40.892	0.413
8	0.2	35	0.839	32.162	0.250
9	0.4	19	0.933	19.597	0.018
10	0.6	9	0.978	9.251	0.007
11	0.8	3	0.994	3.383	0.043
12	1	0	0.999	0.958	0.958
13	1.2	1	1.000	0.210	2.970
				$\Sigma((O-E)^2/E)$ =	**10.84**
		Total = 208		**X^2 (0.9,10) =**	**16.0**

Table 4-4 shows a set of methylmercury data in fish tissue from Liberty Reservoir, MD (column 1). To perform the K-S test on log-transformed data, the log values (column 2) are ranked (column 3). Using the ranks, a probability plotting position is assigned (column 4). A number of methods are available for assigning a plotting position. The Weibull plotting position formula (m/n+1), where m is the rank of the observation and n is the total number of observations, is used here. Values of the cumulative normal distribution for the m^{th} fish tissue value with a mean and standard deviation computed from the data are next computed (column 5). The absolute values of the differences between the plotting position and cumulative normal distribution are then calculated (Column 6), and the maximum deviation is determined (0.084). The value of the K-S test statistic is found by table lookup with the significance level and degrees of freedom (in this case equal to the number of data points)[51]. The value of the statistic (0.295) is then compared to the maximum deviation between the sample distribution and the normal distribution. If the maximum deviation is less than the value of the K-S statistic, then the hypothesis that the data are drawn from a log-normal distribution cannot be rejected, as is the case in this example.

Table 4-4
Example Application of the Kolmogorov-Smirnoff One Sample Test for Normality

(1) MeHg in Fish Tissue mg kg^{-1}	(2) Ln (MeHg in Fish Tissue) mg kg^{-1}	(3) Rank	(4) Plotting Position, S(x)	(5) Cumulative Normal Distribution, F(x)	(6) ABS[F(x) – S(x)]
0.314	-1.158	11	0.647	0.621	0.026
0.282	-1.266	9	0.529	0.551	0.021
0.298	-1.211	10	0.588	0.587	0.001
0.219	-1.519	6	0.353	0.383	0.030
0.126	-2.071	2	0.118	0.109	0.008
0.202	-1.599	5	0.294	0.332	0.038
0.503	-0.687	14	0.824	0.865	0.041
0.154	-1.871	3	0.176	0.186	0.010
0.198	-1.619	4	0.235	0.320	0.084
0.226	-1.487	8	0.471	0.403	0.068
0.224	-1.496	7	0.412	0.397	0.015
0.549	-0.600	15	0.882	0.894	0.012
0.709	-0.344	16	0.941	0.954	0.012
0.355	-1.036	12	0.706	0.697	0.009
0.449	-0.801	13	0.765	0.819	0.054
0.068	-2.696	1	0.059	0.011	0.048
Mean	**-1.341**			**Maximum**	**0.084**
Standard Deviation	**0.593**			**K-S(0.1,16)**	**0.295**

4.1.3.10.3 t-Test for Comparing Data to the WQS

Once the data have been judged to be normally distributed, the *t*-test can be conducted. The one sample t-test is performed, when the population variance is unknown, by calculating the test statistic as follows:

$t = (X - \mu_0) \sqrt{n} / s$ **Equation 4-3**

[51] Tables of critical values of the K-S test statistic can be found in Siegel (1956) or in most texts on non-parametric statistics.

where:

_X is the sample mean,

μ_0 is the WQS,

n is the number of fish tissue samples, and

s is the sample standard deviation.

Suppose it is desired to test whether the population fish tissue mean is less than 0.4 mg kg^{-1} using the fish tissue data from Liberty Reservoir, MD. The null hypothesis is that the mean is $\geq$ WQS and the alternative is that the mean is less than the WQS. The level of significance chosen is $\alpha = 0.1$. There are 16 fish tissue samples. The log sample mean and standard deviation from Table 4-3 above are -1.341 and 0.593, respectively. A one-sided test is used. In this case,

$t = (-1.341 - \ln(0.4))\,(4) / 0.593 = -2.86$

From a table of percentage points of the *t*-distribution, with a significance level of 0.1 and n-1 (or 15) degrees of freedom, the critical value is -1.341[52]. Since the *t*-statistic (-2.86) is greater than the critical value of -1.341, the hypothesis that the population mean is greater than or equal to the WQS is rejected in favor of the alternative hypothesis. Thus, in this case, it has been shown that the population mean is less than the WQS at the 0.1 significance level. Had the WQS in this case been 0.3 instead of 0.4, the value of the test statistic would have been -0.924, a value less than the critical value, and the null hypothesis could not have been rejected.

One can use inferences about the population mean in another way, to determine if the waterbody should have been listed in the first place. For instance, fish tissues may have been collected and the resulting sample mean concentration may have been above the standard. The question is whether the population mean is (or was) above the standard. In this case, the null hypothesis is that the mean tissue concentration is less than or equal to the standard, and the alternative hypothesis is that it is greater than the standard. Once again, the *t*-test would be used to determine if the population mean can be said to exceed the standard at a predetermined level of confidence.

4.1.3.10.4 Sampling Distribution of the Trophic-Weighted Mean

To conclude this section, let it be supposed that the agency is amenable to computing a trophic-weighted average for the fish tissue data. This is a desired outcome, especially if the WQS is based on trophic-weighted fish tissue residue values. As has been discussed earlier, the comparison of a single trophic level 4 species (e.g. walleye) residue values to a standard based on trophic-weighted residues values represents an overly conservative approach to judging the

[52] It is purely coincidence in this example that the log mean of the sample has the same numerical value as the critical value of the *t*-statistic. Percentage points for the *t* distribution can be found in almost any basic statistics text.

fishing impairment of waterbodies. If the agency is willing to compute a sample value of the trophic level mean and compare it to the standard without making an inference about the population trophic-weighted average (and it turns out to be below the standard), so much the better. However, if the agency wishes to make inference about the population trophic-weighted mean, then the sampling distribution of this mean needs to be defined.

Assuming the data collection has encompassed both trophic level three and four fish (perhaps even trophic level 2), the tissue residues from the trophic level 3 fish and the tissue residue values from the trophic level 4 fish represent two independent random variables. Furthermore, the statistics of these random variables (e.g. mean and variance) are themselves random variables (Haan 1977). This can easily be envisioned in the following way. Suppose that a sample of 10 fish is taken from a waterbody with a corresponding sample mean and variance. Suppose, then, that another sample of 10 fish is taken. This sample also has an associated mean and variance, and so forth. If enough samples were to be taken, the means and variances from each sampling would have a distribution of values. In fact, the distribution of the mean of a random variable is the *t*-distribution described above for small samples[53]. Thus if the sample mean and variance are known, the t-distribution can be use to make inferences about the population mean. This logic forms the basis of using the *t*-distribution to make inferences about the population mean based on the sample mean.

A crucial aspect of the means and variances of normal distributions central to this discussion is their reproductive properties. If X is a normal random variable $N(\mu, \sigma)$ then $Y = a + bX$ is also a random variable with mean $a + b\mu$ and variance $b^2\sigma^2$ (Haan 1977). Furthermore, if $Y = a + b_1X_1 + b_2X_2 + \ldots + b_nX_n$ then

$$\mu_Y = a + \Sigma\, b_i\mu_i \text{ and} \qquad \textbf{Equation 4-4}$$

$$\sigma_Y^2 = \Sigma\, b_i^2\sigma_i^2. \qquad \textbf{Equation 4-5}$$

Therefore, the mean and variance of the trophic-weighed mean can be calculated from the means and variances of the different trophic levels. Since the intercept in the trophic weighted mean is zero and b is equal to the consumption weighting for that trophic level, a new random variable (the trophic-weighted average, TWA) can be defined with a mean of

$$TWA = w_2(TRV_2) + w_3(TRV_3) + w_4(TRV_4) \qquad \textbf{Equation 4-6}$$

and a standard deviation of

$$s_{TWA} = \sqrt{(w_2s_2)^2 + (w_3s_3)^2 + (w_4s_4)^2} \qquad \textbf{Equation 4-7}$$

where TRV_2, TRV_3, TRV_4 are the mean tissue residue values in each trophic level and w_2, w_3, w_4 are the consumption weighting factors for each trophic level and the sample means and variances are estimates of the population means and variances.

[53] For large samples, the *t*-distribution approaches the normal distribution.

Suppose that through data collection it is determined that 5 trophic level 4 fish in a water body have a mean concentration of 0.45 mg kg^{-1} with a standard deviation of 0.2 mg kg^{-1}, 5 trophic level 3 fish have a mean of 0.25 mg kg^{-1} with a standard deviation of 0.08 mg kg^{-1} and 5 trophic level 2 fish have a mean of 0.15 mg kg^{-1} and a standard deviation of 0.04 mg kg^{-1}. Using the USEPA's national average consumption weights of 0.217 for TL-2, 0.457 for TL-3, and 0.326 for TL-4, the TWA is calculated to be 0.294 mg kg^{-1}. If the state has adopted EPA's standard of 0.3 mg kg^{-1} it might be concluded that the fishing use was being met on the basis of the sample mean and the waterbody might be delisted on that basis. However, if the state wishes to make an inference about the population TWA, the sample variance could be computed as above

$$s_{TWA} = \sqrt{(0.217(.2))^2 + (0.457(0.08)^2 + (0.326(.04))^2} = 0.046.$$

The *t*-statistic is calculated as

$$t = (0.293 – 0.3) \sqrt{15} / 0.046 = -0.58$$

The critical value of $t_{(0.9,\ 15\text{-}3)}$ = -1.36. Therefore, the null hypothesis cannot be rejected and it cannot be judged that the population mean is below the standard at $\alpha = 0.1$. Therefore, the waterbody should not be delisted. In this situation, all else being equal, the TWA would have to be less than 0.284 mg kg^{-1} in order for the waterbody to be delisted.

4.1.4 Collecting and Analyzing Ambient Water Samples for Comparison to Water Quality Standards

Assuming that the WQS is water column-based rather than tissue-based, water samples may need to be collected in order to delist a waterbody. In this exercise, it will be assumed that the waterbody has been listed for violation of a water quality standard, regardless of how that standard has been determined. For instance, had it been derived from a tissue-based standard by using a bioaccumulation factor (BAF) or other means, fish tissue could be collected and the comparison made of the collected samples to the standard. While this will be further discussed in Section 4.2.2.2, for the present the discussion will be confined to the collection and interpretation of ambient water quality measurements in the context of the delisting objective.

4.1.4.1 Total, Methyl, or Both?

One of the first considerations in sampling water is whether to sample for total mercury or for methylmercury. In terms of the delisting objective, the answer is trivial. If the WQS is for total mercury, then samples should be collected for total mercury. If the WQS is based on methylmercury, then samples should be analyzed for methylmercury in order to make direct comparisons to the methylmercury WQS. This statement is made with the caveat mentioned earlier that EPA does not have a 303(a) approved method for methylmercury in water, and as such cannot establish a WQS for methylmercury until an approved method for measuring it has been promulgated. Having said this, some WQTs in mercury TMDLs have been expressed in terms of methylmercury. At this time, EPA's schedule for promulgating Method 1630 (or an equivalent method) is not known.

Setting this legal issue aside, unless there is reason to investigate methylation of mercury in the waterbody, there is no reason to incur the expense of measuring methylmecury. Aside from this, methymercury levels typically are lower in the environment, much of the time at or near detection levels, sampling and analytical methods are less consistent, and results are less reproducible and more costly to obtain than for total mercury.

4.1.4.2 Sample Locations

The key factor in taking water samples for the purpose of delisting is to insure that they are representative of the waterbody and/or segments under consideration. Representativeness of sampling location will depend on the type of waterbody, that is, whether it is a river/stream or lake. Because this is such an important determinant, the discussion of sampling location is provided along these lines.

4.1.4.2.1 Sampling in Rivers

The key difference between the sampling strategy for rivers/streams and lakes is the hydraulic difference resulting from their geometry and movement of water. In rivers and streams there is normally a measurable horizontal velocity in the direction of flow, although this velocity may be negligible in areas off the main channel, such as in oxbows, backwaters, pools, or riparian wetlands.

Theoretically, there are four regimes of flow[54], which typically are characterized in open channel hydraulics by the computation of the Reynolds and Froude numbers. The Reynolds number characterizes the effects of inertial to viscous forces in water and the Froude number characterizes the effects of inertial to gravitational forces (Chow 1959). When the Froude number is less than 1, flow is said to be subcritical and gravitational forces rather than inertial forces dominate the flow regime. Otherwise, the flow is said to be supercritical. In a supercritical flow regime, it is unlikely that stratification, which would lead to vertical variations important in the sampling of lakes, would occur in a waterbody. When the Reynolds number is less than about 500, the flow is said to be laminar. Above a value of about 2000, the flow is classified as turbulent. Under supercritical turbulent flow, the river or stream is certain to be well-mixed.

The Froude number is calculated as

$$\mathbf{F} = V / \sqrt{gL} \qquad \textbf{Equation 4-8}$$

where

V is the mean flow velocity in ft sec^{-1},

[54] Laminar-subcritical; laminar-supercritical, turbulent-subcritical, and turbulent-supercritical.

L is a characteristic length (in ft, usually taken to be the hydraulic depth; that is, the channel cross-sectional area normal to flow divided by the top width), and

g is the acceleration of gravity (ft sec^{-2}).

The Reynolds number is calculated as

$$\mathbf{R} = V\ L\ /\ \nu \qquad \textbf{Equation 4-9}$$

where

ν is the kinematic viscosity of water in ft sec^{-2}.

The length used in the computation of the Reynolds number is usually taken to be the hydraulic radius; that is the cross-sectional area normal to flow divided by the wetted perimeter. The kinematic viscosity of water ranges from 1.931×10^{-5} at 32 degrees-F and 0.826×10^{-5} at 90 degrees-F. In this temperature range, the kinematic viscosity can be approximated by the following power function:

$$\nu = 34.219 \times 10^{-5}\ (°F)^{-0.8211} \qquad \textbf{Equation 4-10}$$

where

°F is the Fahrenheit temperature of the waterbody.

Practically, to compute the Reynolds or Froude numbers, one would need to estimate or measure channel velocities and geometries. To obtain a mean channel velocity, one would need to measure velocities at varying depths over the width of the channel. Given this necessity, one might coincidentally measure the temperature profile of the stream at the sampling location. If the temperature is fairly uniform with depth, the stream is well-mixed and the sample may be taken from any depth. In this case, the midpoint of the channel is appropriate. Measurement near the bottom may bring into play the effects of more reduced (lower oxygen) conditions and higher suspended sediment concentrations (both of which would tend to increase mercury levels) while measurement immediately at the surface may bring into play photo enhanced demethylation and volatilization of dissolved gaseous mercury. Measurement at mid-depth should mitigate against these possibilities in channels of reasonable depth.

Spatially locating samples depends on other factors. Aside from the caveats to avoid point sources, the samples should be taken from locations "characteristic" of the waterbody. Spatially, stream channels may exhibit a wide variety of configurations. They can be straight with regular cross-sectional geometries, in the case of engineered channels, to meandering with irregular sections in the case of natural channels. With higher gradient streams, deposition of sediment may lead to "braiding"; that is the formation of islands and sand bars in the stream channel. With lower gradient streams, meandering streams may create oxbows and have extensive adjacent riparian wetlands. Practically, the term "representative" applies to any heterogeneities that may affect the concentration of total or methylmercury in the water column. These include variations in flow, geometry, temperature, water chemistry, and biology.

Total mercury in the water column is probably influenced more by suspended particulates (including inorganic sediments and particulate organic carbon) and dissolved organic carbon concentration than by any other single factors. Both divalent mercury and methylmercury are strongly adsorbed by both organic and inorganic particulates. In addition, suspended algae and zooplankton may bioconcentrate both divalent and methylmercury. Mercury is also attracted to organic sulfur groups in dissolved organic carbon. Suspended inorganic sediment concentrations are likely to be higher in open, shallow water where wind and boat traffic can resuspend sediments. Organic particulates are likely to be encountered at higher concentrations where nutrients are available, water temperatures are higher, and other conditions conducive to the growth of free-floating algae are found. DOC is likely to be higher in low flow, shallow areas (like adjacent wetlands) where there is an abundance of biodegradable organic matter. Such areas should be avoided unless, of course, they are truly representative of the waterbody.

Data from the Willamette River, OR collected by the Oregon Department of Environmental Quality (ODEQ) from 7 locations in the mainstem and reveal some interesting spatial patterns. While total filtered and unfiltered mercury, and dissolved methylmercury, appeared to be more or less consistent along the length of the river during all seasons, total methylmercury showed a definite trend from upstream 0.067 ng L^{-1}) to downstream (0.707 ng L^{-1}) during the summer sampling (r = -0.78). This may be due in part to the physical characteristics of the river, with slower velocities and warmer temperatures occurring in the lower reaches.

4.1.4.2.2 Sampling in Lakes

Sampling in lakes represents a special challenge due to the potential vertical variations in flow, temperature, and water chemistry. In typical North American lakes, the thermal expansion of water at temperatures above and below its maximum density of 4°C (39°F) leads to both spring and fall periods of uniform temperature when vertical circulation occurs. During the fall, declining temperatures and insolation cause surface waters to cool. These denser surface waters settle away from the surface, replaced by warmer water from below. When surface waters approach their maximum density at 4°C, they sink to the bottom. At this time, the entire lake is replenished with oxygen from the surface waters, which mix with waters of a different chemical character that have accumulated near the bottom during summer stratification.

From spring through summer, the opposite occurs. Surface waters warm and become less dense and form a layer known as the epilimnion. Below this is a thermocline in which water temperature rapidly declines and density rapidly increases. The thermocline forms an effective barrier for mass transport between the epilimnion and the hypolimnion, the waters beneath the thermocline. At full development, the thermocline is recognized during sampling by a temperature gradient on the order of 1°F per foot. If the lake is deep and clean, the chemical character of the water in the hypolimnion may stay relatively unchanged throughout the summer. However, if the lake is shallow or has a significant oxygen demand exerted by bottom sediments, oxygen may be depleted, leading to the reduction of sulfur and thence to the methlyation of mercury under weakly reducing conditions. Reducing conditions also lead to the dissolution of iron and manganese precipitates that may release divalent or methylmercury, which may have been adsorbed to there mineral surfaces, into the water column. Upward mass transfer of mercury and other dissolved solids is likely limited by diffusion since warm waters flowing into the lake or reservoir seek regions of like density and preferentially flow into the epilimnion, above the thermocline. Groundwater inflows are likely cooler than the epilimion and favor the denser waters near the bottom. Thus mercury released into the hypolimnion tends to stay there without the benefit of mixing with the overlying epilimnion. If reservoir managers release cool, hypolimnetic waters during summer droughts to maintain downstream minimum flows, such releases could affect downstream mercury levels.

Since waters near the bottom and near the surface of lakes may have a quite different chemical character, the question becomes whether to sample the epilimnion or hypolimnion (or both) to characterize a lake for the purposes of comparing to a water quality target or standard. With regard to bioaccumulation, the question is probably best addressed by an assessment of where the resident fish spend their time and the concentrations to which they are thus exposed. Barring a thorough examination of this issue (which would undoubtedly be subject to debate) it is probably best to sample the epilimnion. If the agency insists, then depth integrated sampling or collection of multiple samples with depth is warranted. However, sampling of the hypolimnion alone should be avoided as well as near bottom samples within the hypolimnion, as this would bias the sample results toward the worst case.

Much of the fishing pressure in the summer in reservoirs and lakes is concentrated in shallow coves, inlets and embayments as fish migrate into these warm, productive areas to feed. Unless these waters are deep, they will tend to exhibit characteristics of the epilimnion. Access is good, which tends to make them good potential sampling locations. If these are areas where inflows to the lake occur, care should be taken. In developed watersheds, these can be areas that receive excess nutrients in runoff, which may tend to make them more eutrophic. In developed areas, incoming water may also have elevated mercury levels from highway runoff and from other impermeable surfaces. Other developed areas, such as marinas should obviously be avoided. All in all, it is probably best to avoid near shore areas and collect samples from deeper, open areas near the center of the lake. Areas downstream of bridges or causeways that may be affected by highway runoff should likewise be avoided.

Sampling of the reservoir outlet to characterize reservoir waters for total mercury is not advised. As discussed above, reservoir outflow may consist primarily of hypolimnetic waters in the summer, depending on reservoir operations. Outlet concentrations were higher than other locations in two lakes sampled in California (Tetra Tech 2005). This may be less an issue in natural lakes, where the outlet is more likely to consist of epilimnetic waters during stratification.

4.1.4.2.3 Collocating Water and Biota Samples

If sampling of both fish tissue and water is not required, sampling of fish tissue alone is advised for delisting purposes. Two motivations recommend this. First, fish tissue are less variable than water samples and fewer samples will likely be required to provide an adequate sample size for statistical tests. Second, collocated samples will inevitably be used to calculate BAFs. Unless this is a requirement of the data collection, it is not advisable to collect data that can be used to calculate BAFs; the reason being that the use of BAFs to translate fish tissue levels to water column concentrations is not recommended (EPRI 2003).

However, if both are required, then water and fish samples should definitely be collocated. This represents a challenge since ideal areas to sample fish may not be ideal areas for taking representative samples of the water body. Since the success of biological collection will dictate the sampling sites, ideal water sampling criteria will likely be compromised. Ideally, multiple water and fish samples (minimum of 1 sampling event per quarter) should be collected over the course of at least one year. More than one year's data is desirable. Sample size and seasonal considerations are discussed in the following sections.

4.1.4.3 Number of Samples

As with fish tissue samples, the number of samples required is a function of the variability of the measurement and allowable error in the statistical test used to compare the data to the standard. As previously mentioned, the variability in the measurement of total and methylmercury in the water column is substantially higher than the variability associated with fish tissue measurements. It was reported in EPRI (2003) that CVs for total mercury were about 50% for data collected from the same locations in the East Fork Poplar Creek, TN and 60% when data was averaged over different locations. The CVs for time- and spatially-averaged data for dissolved total mercury were about 50% and 150%, respectively. CVs for total and dissolved methylmercury were about 50% and 70% when averaged over time and space. In the Willamette River, OR, there was also a difference in CVs when the data were averaged over time and across locations. Time-averaged CVs for total mercury and methylmercury (filtered and unfiltered) ranged from 53 to 76%. Location-averaged CVs for the same four parameters ranged from 62 to 130%. For the most part, the CVs from the Willamette River were in the same ranges as those from the East Fork Poplar River, TN.

As with fish tissue data, it is important to verify that the data are normally distributed prior to computing test statistics. Often, data that are bounded by zero with many measurements close to the detection limits will exhibit a leftward (positive) skew (i.e. there are a few high values while most values are low). With data of this type, a log normal transformation will often provide a more accurate test of the central tendency of the data relative to the standard.

Suppose it is desired to know how many samples would be required to be 90% confident of being within 20% of the value of the population water column total methylmercury mean for the East Fork Poplar River. In a previous sampling, the sample mean was 0.332 ng L^{-1}. To be conservative, the CV is estimated to be 90%.

Recall that the formula for determining the number of samples is:

$$n = [\, z_{\alpha/2}\, \sigma / d \,]^2$$

where

n is the number of samples required,

$z_{\alpha/2}$ is the standard normal deviate at probability level α (for a two sided test),

σ is the standard deviation of the measured total methyl mercury in water, and d is the error tolerance around the standard.

In this case,

$z_{(\alpha/2 = .05)} = 1.645$

$\sigma = 0.298$ (recall that the standard deviation is the CV expressed as a fraction times the mean)

$d = 0.2(0.332) = 0.066$, and

$n = [1.645(0.298)/0.066]^2 = 56$.

Therefore, 56 samples would be required.

4.1.4.4 Seasonal Considerations

Seasonal considerations are more important when sampling the water column than when sampling fish tissue. As discussed in Section 4.1.3.5, fish tissue does not appear to vary a great deal seasonally. However, water column measurements can vary widely with season. Total mercury variation is probably more properly attributed to variations with flow than with season. Total mercury tends to be higher when suspended sediment concentrations are higher and higher suspended sediment concentrations typically are correlated with higher flows. However, in many parts of the country, higher flows are associated with late winter and spring conditions. Thus it may be observed that total mercury will be lower in typically low flow season (late summer, early fall) and will be higher in late winter/early spring.

As reported in EPRI (2003), samples collected during spring high flows in six South Georgia Rivers had higher total mercury concentrations than samples taken at the same locations during summer, low flow conditions. Tetra Tech (2005) observed that total mercury levels were higher in two California lakes in the spring and were associated with higher suspended sediment levels. Rolfhus et al. (2003) found higher total mercury concentrations in Lake Superior in April than in August, which was attributed to tributary inputs during spring snowmelt. Data from the Oregon DEQ for the mainstem of the Willamette River, OR[55] show that total mercury (filtered and unfiltered) where lowest in the fall (0.47, 0.31 ng L^{-1}), increased to their highest levels in winter (3.99, 1.60 ng L^{-1}), and declined gradually back to the fall levels over the spring (1.21, 0.69 ng L^{-1}) and summer (0.69, 0.30 ng L^{-1}) seasons.

Methylmercury varies seasonally as well, probably to a greater extent than total mercury. Superimposed upon the effects of associations with suspended sediments is the observation that methylmercury increases in the hypolimnion of lakes as summer stratification advances and conditions become more reducing (Tetra Tech 2005). Similarly, methylmercury concentrations increase in wetlands during the summer, when higher temperatures and lower DO levels favor methylation. Interestingly, as reported in EPRI (2003) however, methylmercury levels can be higher in the spring in rivers. Presumably, this is a consequence of methylmercury being produced in wetlands in the summer and fall during low flows but being flushed into stream channels during higher flows occurring in winter and spring. Similarly, methylmercury

[55] Geometric means of 7 locations.

concentrations may be lower in the epilimnion of lakes during the summer, but higher after fall turnover when mercury released into the hypolimnion during stratification is redistributed throughout the lake profile. Total (filtered and unfiltered) methylmercury in the Willamette River exhibited its highest levels in the summer (0.146, 0.038 ng L^{-1}) and fall (0.082, 0.071 ng L^{-1}), declining gradually over the course of the winter (0.069, 0.019 ng L^{-1}) and spring (0.040, 0.017 ng L^{-1}).

Given this seasonality, it is reasonable that total and/or methylmercury measurements should be made over the period of a year with samples taken each quarter to characterize the concentrations in either a stream or lake. At each location selected, a number of samples necessary to make statistical inferences should be collected over the period of a year. If 56 samples (as in the example above) are required, 14 should be made at each location during the collection. Ideally, these 14 would not be collected at exactly same location on the exact same day. In this case, they would be equivalent to field duplicates. Collecting 2 per day at each location over a period of a week would probably inspire greater confidence in the results.

Alternatively, fewer samples can be collected at each location if the samples are to be pooled across locations in the analysis of the data. However, if this is the case, the number of samples should be estimated using inflated CVs as pooling data will increase the variability of the results. To illustrate, if the CV for methylmercury increased to 120% from 90% due to spatial averaging, the number of samples estimated in 4.1.4.3 above would go from 56 to 98. If 56 samples were collected at each of three locations, the total number of samples would be 56 x 3 or 168. In this case, pooling the data spatially would lead to a more efficient sampling program, with the total number of samples reduced from 168 to 98. If 98 samples were collected in each of four seasons at each of three locations, then 8 samples rather than 14 could be collected at each location each quarter.

Data presented in EPRI (2003) for the East Fork Poplar River, TN show that for total mercury, total methylmercury, and dissolved methylmercury, CVs for spatially averaged data were 25% higher than for time-averaged data. In the case of dissolved total mercury, CV for spatially averaged data was 273% higher than for the time-averaged data. CVs for time averaged data were on the order of 50%. In the Willamette River, time-averaged CVs for the same four parameters averaged 65% with the location averaged CVs being on average about 40% higher. Therefore, it is reasonable to assume a slightly (~30 to 40%) higher CV with the intent of spatially averaging the collected data.

4.1.4.5 Sampling Methods – Method 1669

Once the sampling strategy has been decided, sampling methods must be detailed and samplers trained in the methods before collection takes place. Method 1631E states that EPA Method 1669 will be used for sample collection. Therefore, in order to follow the analytical method, this sampling protocol must be used. The method provides for the collection of “clean” samples in the field consistent with the level of care taken to eliminate contamination of samples in the laboratory. Contaminating water samples when low level measurements of mercury are involved is easy to do and great care must be taken to avoid it.

It is difficult to identify the most common ways that samples may be contaminated. However, if has been noted that the breath of individuals with mercury amalgam dental fillings contains trace levels of mercury (Patterson et al. 1985) and breathing on water samples may be a frequent problem. Mercury in the saliva of subjects with mercury amalgam fillings typically ranged from 11 to 38 $\mu g\ L^{-1}$, with 6 of 108 subjects having levels of over 100 $\mu g\ L^{-1}$ (WHO 2003). These levels are 1,000 to 10,000 times higher than those typical of ambient surface water. Smoking should be avoided both before and duting sampling as tobacco smoke contains trace levels of mercury[56] (Arista Laboratories 2003) and elevated levels may be present in the exhaled air of smokers. Since mercury is strongly associated with suspended matter, disturbance of sediments or the presence of naturally elevated levels of suspended particulate matter may be a frequent means of contamination. Rainwater may also contain higher levels of dissolved mercury than surface waters, due to the biogeochemical interactions to which surface waters have been subjected that rainwater has not been. This is could be important during wet-weather sampling. Airborne dust or particulates could also be a problem, albeit more rare, since such conditions would likely be noticeable during sampling.

4.1.4.6 Sampling Handling and Preservation

Sampling handling and preservation for metals is covered in Method 1669 and is not recounted in detail here. The USGS (2004)[57] provides a very detailed set of protocols that it follows when acquiring low-level mercury samples and review of this document is recommended prior to establishing one’s own field sampling methodology.

Samples for methylmercury require special attention. It is important to stop the biological processes responsible for methylation from continuing in the sample bottle. Therefore, samples collected for methylmercury should be cooled to between 0 and 4 degrees centigrade as soon as possible and shipped to the analytical laboratory. These samples are preserved by the addition of HCl[58]. In general, the analytical laboratory should be queried as to any special preservation requirements and these procedures should be followed.

4.1.4.7 Filtered versus Non-Filtered Samples

Filtering involves the removal of particulate matter from the sample prior to preservation. As alluded to above, the decision to filter is an important one because the presence of suspended particulate matter in the sample can affect reported concentrations. Once the sample is acidified, any mercury associated with particulates will be released into solution.

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[56] Data reported show that between <0.25 to 4.3 ng of mercury per cigarette were present in the smoke of 25 cigarette brands. Subsequent calculations by this researcher suggest that concentration in smoke is in the low part per billion range.

[57] Available online at http://pubs.water.usgs.gov/twri9A.

[58] It is important to note that samples collected for total mercury may be preserved with either HCl or BrCl. If BrCl has been added to a sample bottle as a preservative, it cannot be used for methylmercury analysis.

In order to address the delisting issue with water samples, the collection should involve data of the same type used to list the waterbody or that has been identified in a TMDL analysis. Thus, if the data or standard for the waterbody is total filtered mercury, then total filtered mercury samples should be collected for comparative purposes. If the exact type of the data used for listing and/or developed as the TMDL target is unclear, the regulatory agency should be asked to clarify. If the agency declines to give advice, then filtration is desirable as it will usually lower the result.

Filtering typically is performed using a 0.45 micron filter, although smaller filters, down to 0.1 microns, may be used[59]. In the case of smaller filters, water may have to be placed under pressure (or vacuum) to aid the filtration process. In either case, the filters should be prepared so that they are free of background mercury. Because the filtration step requires extra time in the field and introduces the potential for contamination, filtration is sometimes deferred to the analytical laboratory. Note, however, that Method 1669 requires field acidification for total metals. Thus, laboratory filtration would compromise the method. If samples are analyzed within a reasonable time frame, however, this should not be a problem. If laboratory filtration is desired, it should be discussed with the laboratory.

4.1.4.8 Analytical Methods

Method 1631E is the currently approved method for low level analysis of total mercury in water. Method 1630 for methylmercury has been proposed, but as of this writing, had not been adopted as an approved 303(a) method (see also Section 4.1.3.9). The fundamental difference in these methods is that in method 1631, mercury in solution is oxidized to divalent mercury by the addition of BrCl, then reduced to elemental mercury Hg(0) by the addition $SnCl_2$, whereupon the volatile elemental mercury is purged and collected on a gold trap, desorbed, and analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS). In Method 1630, methylmercury in the sample is ethylated by the addition of sodium tetraethyl borate, whereupon the methylethyl mercury is separated from the solution using a graphitic carbon trap, thermally desorbed, converted to Hg^0 and then analyzed by CVAFS.

4.1.4.9 Ancillary Measurements

Ancillary measurements are often useful in the interpretation of analytical results for mercury. Measurements of suspended solids, organic carbon, sulfur and sulfur species may be particularly helpful in this regard.

4.1.4.9.1 Suspended Solids

The importance of suspended solids was mentioned in Section 4.1.4.4. Measurement of total suspended solids (TSS) is a useful diagnostic when elevated levels of mercury are observed in water samples. The chief advantage of making this measurement is that is it inexpensive

[59] Method 1631E requires the use of a 0.45 micron filter. The Method also requires that an equipment (filter) blank be provided with filtered samples.

compared to analyzing filtered and unfiltered samples for mercury or analyzing filtered water and filtered solids. The chief disadvantage is that it does not prove conclusively that elevated mercury samples are due to levels in suspended solids, as would the alternatives mentioned above. Because it can be inexpensively measured, it is recommended that suspended solids be included in the analytical suite.

Although correlation to TSS may help explain elevated concentrations in unfiltered water samples, it is not sufficient to argue that this mercury is not bioavailable. Even with measurements showing the quantity of mercury associated with solids, this argument cannot be made conclusively without some knowledge of the mercury species present in the solid phase. It is of utmost importance to know whether the mercury is simply adsorbed to the solid matrix or has precipitated out of solution in the form of a mercury mineral, such as cinnabar (HgS). While such determinations can be made, the procedures are experimental and subject to interpretation. It is unlikely that they would be conclusive in terms of a delisting decision.

4.1.4.9.2 Total and Dissolved Organic Carbon

It has been observed that mercury levels are elevated in surface waters in the presence of dissolved organic carbon (DOC). This is due to the fact that mercury has a strong affinity for organic sulfur groups in this material. As with TSS, DOC is recommended as a diagnostic measurement which may serve to explain elevated concentrations in water samples. If there is particulate organic material in the sample, it may be useful to measure total organic carbon (TOC) as well. TOC is measured by filtering the sample and measuring the loss (of weight) of ignition (LOI) of the solids.

Because of the strong affinity for DOC, it has been argued that DOC-bound mercury is not bioavailable. This is debatable due to the fact that in rivers with high DOC, fish tend to accumulate mercury to levels as great, or greater, than in rivers with lower DOC levels. It has also been shown that DOC inhibits the precipitation of cinnabar at levels of a few parts per million, which may serve to keep more mercury in solution.

4.1.4.9.3 Sulfur and Sulfur Species

The affinity of mercury for sulfur has a profound influence on its environmental chemistry. It is generally assumed that mercury precipitated as cinnabar is not available for biological uptake. On the other hand, microbes that reduce sulfur in low oxygen environments are largely responsible for the production of methylmercury. Of the sulfur species, it is probably most important to know the sulfide concentration. Sulfides provide an indication of the redox state of the system. Sulfates are converted to sulfides at Eh[60] of -150 mv. Eh levels on this order (that is, mildly reducing conditions) are conducive to the formation of methylmercury. Under more strongly reducing conditions (-200 mv), the formation of cinnabar is favored.

Due to the nature of the equipment required to measure sulfides accurately in the field, it is best measured by a commercial laboratory. Care must be taken that the sample is not exposed to oxygen during sampling. Sample bottles must be filled beneath the water surface and filled

[60] Eh is a measure of the reduction/oxidation (redox) status of the system. Eh values in natural systems range from about +700 mv (miilivolts) to -250 mv. Redox potential may also be expressed in units of p*e*, the negative log of the electron activity, a unit similar to and compatible with pH.

completely to avoid the introduction of oxygen into the sample. Some commercial meters are also available to measure sulfides.

4.1.4.9.4 Manganese and Iron

Along with sulfur, nitrogen, manganese and iron can be measured as indicators of the redox status of an aquatic system. As Eh decreases, one of the first reactions to occur is the reduction of nitrate to N_2O or N_2, which occurs at about +220 mv. At +200 mv, manganese is transformed from manganic (+4) to manganous (+2) compounds and at +120 mv, iron is converted from ferric (+3) to ferrous (+2) forms. The reduction of manganese and iron is important because of the solubility of the reduced forms. Precipitated iron and manganese minerals provide adsorption sites for mercury. When these minerals go into solution, they release adsorbed cations like mercury into solution. Therefore, measurement of iron and manganese provides a means not only of diagnosing elevated mercury levels in water samples, but also of interpreting the redox state of the system. As with sulfur, sample bottles for dissolved iron and manganese must be completely filled under water to avoid the introduction of oxygen into the sample.

4.1.4.9.5 Other Parameters

Other parameters discussed below can provide diagnostics for elevated levels of mercury in water samples. These can easily be made in the field and as such should be considered routine when taking mercury samples.

Dissolved oxygen (DO) is an indicator the oxidation/reduction date of an aquatic system and is important to diagnosing elevated mercury levels. Low DO (below 1 - 2 ppm) is indicative of the onset of reducing conditions. As long as free oxygen is present in the water column, redox potential (Eh) will be in the +400 to +700 mv range. When free oxygen disappears, Eh will quickly decrease. When this occurs, other transformations important to mercury will occur, as discussed above.

Dissolved oxygen and water temperature can be measured using any number of commercial meters.

Redox is an important determinant of the concentration and species of mercury in solution in a water sample (refer to the discussion in the preceding sections). In lieu of measurements of dissolved manganese, iron, and sulfides as indicators of redox, measurements of redox can be made directly using a commercial meter.

pH is also important to the environmental chemistry of mercury and other metals. Lindsay (1979) shows that in soils a strong demarcation exists at a pH+ p*e* value of 3.71, at which sulfate reduction rapidly occurs. At pH+ p*e* of about 5.5, Hg^0 achieves its maximum solubility in water. Thus pH and redox are important determinants of both the levels and speciation of mercury in solution. pH is easily measured in the field with a commercial meter.

4.1.5 Data Analysis

The analysis and presentation of data is important to successfully completing the delisting process. It is best to provide both visual as well as statistical evidence. Examples are provided below. Both parametric and non-parametric inference concerning the population means derive from sampling is discussed. The methods are similar to those discussed in Section 4.1.3.10 for the analysis of fish tissue data.

4.1.5.1 Determining Normality of the Sampling Distribution

In making a comparison of the mean of sample data to a numerical water quality standard to infer whether it is less than the standard, the first step is to be assured that the data is normally distributed. One hundred seventeen values of total methylmercury collected from the East Fork Poplar Creek near the Department of Energy's Oak Ridge National Laboratory (ORNL) from July 12, 1995 to December 18, 1998 were available to use as an example. The first obvious step is to plot the data, which are shown in Figure 4-4. As expected with data of this type, they do not appear to be normally distributed.

If the data do not appear to be normally distributed, the next step is to determine if some type of transformation will render them approximately normal. Many such environmental data are log normally distributed. In this case, the data appear to be skewed more than one would expect with a lognormal distribution, with many values in the lowest frequency class. In addition, there is an extended distribution tail with a few values much higher than the others in the dataset[61]. However, given the ease of manipulating the data for a lognormal analysis, it is worth trying.

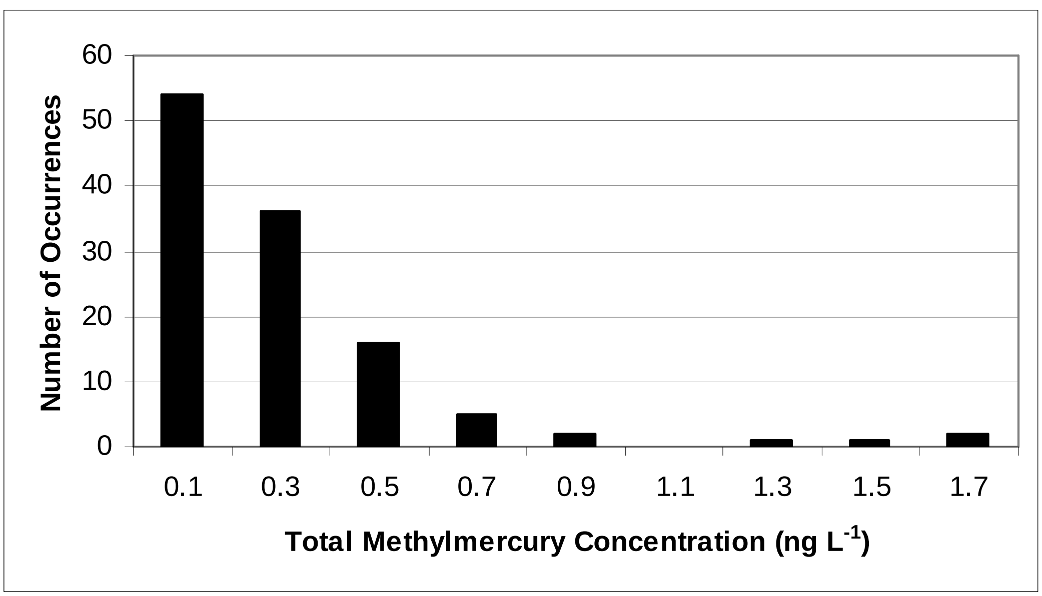

Figure 4-4
Histogram of Total Methylmercury for East Fork Poplar Creek, TN

[61] The x-axis labels in Figure 4-4 refer to the midpoint of the cell.

A plot of the frequency of the logarithms of the data versus the lognormal distribution is plotted in Figure 4-5. It is evident from visual observation that the log transformation provides a reasonable and perhaps adequate transformation for the data. To determine the adequacy of the transformation, a Chi-Square test can be used. Recall from Section 4.1.3.10.2 that the Chi-Square statistic (X^2) is calculated as:

$$X^2 = \Sigma(O-E)^2/E$$ **Equation 4-11**

where O is the observed frequency in a given cell and E is the expected frequency from (in this case) the lognormal distribution. For convenience, a table is constructed and the calculations are made as shown in Table 4-5.

Since the Chi-square statistic (35.0) exceeds the critical value of 14.7[62] at $\alpha = 0.1$, the null hypothesis that the sample data are drawn from a lognormal distribution is rejected. An inspection of the table shows that the reason is the cell frequency in the first interval, which shows a relatively large deviation from the lognormal distribution (20.19).

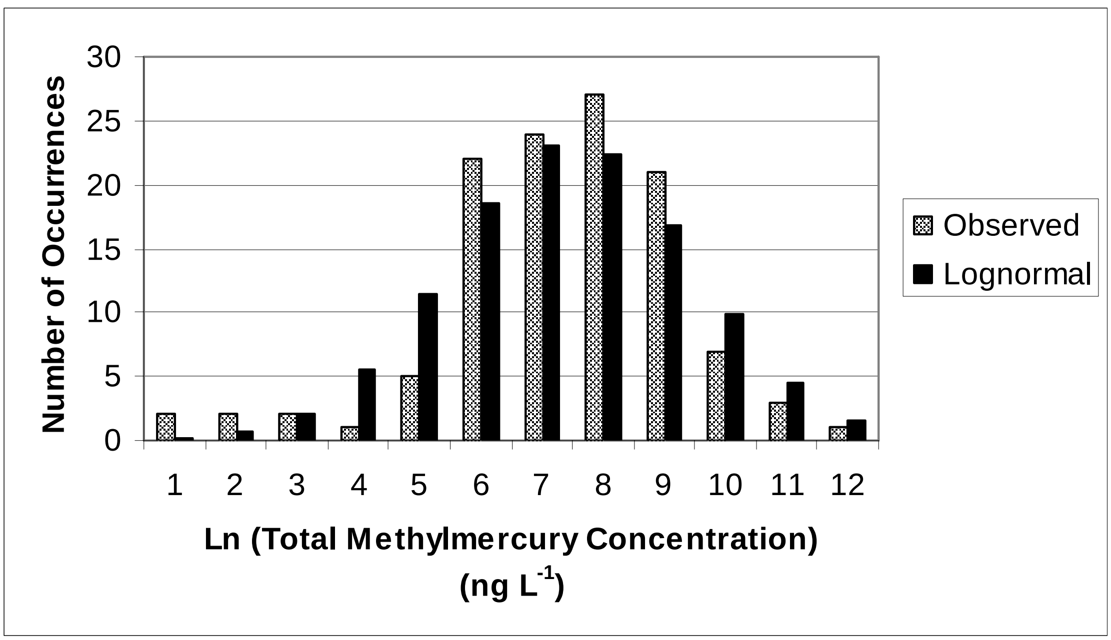

Figure 4-5
Histogram of Total Methylmercury Logarithms in East Fork Poplar Creek, TN Compared to the Lognormal Distribution

Otherwise, the fit seems to be reasonably good (note that deviations in other cells are quite a bit lower). This example points out a problem with the Chi-square test in that it is very sensitive in the tails where one observation in a cell with a low expected value can lead to the rejection of the test (Haan, 1977).

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[62] Recall that the degrees of freedom for the Chi-square test is d.f = k-p-1 where k is the number of cells in the histogram and p is the number of parameters of the distribution (in this case 2, the mean and standard deviation of the lognormal distribution.

In this case, one might choose to use the Kolmogorov-Smirnoff non-parametric test. Recall from Section 4.1.3.10.2 that all 117 values are ranked and assigned a plotting position. This plotting position is then compared to the cumulative normal distribution with mean and standard deviation of the sample data by taking the absolute difference between the plotting position value and the cumulative normal probability. The maximum difference is then selected and in this case it is 0.092. The critical value of the K-S test may not be found in standard tables due to the large number of degrees of freedom (117). In this case, the asymptotic formula is used to compute the critical value, which is

$$K\text{-}S_{(0.9,\ 118)} = 1.22/\sqrt{n} = 1.22/\sqrt{118} = 0.112. \qquad \textbf{Equation 4-12}$$

Since the test statistic value of 0.092 is less than the critical value, the null hypothesis is not rejected. Thus the K-S test does not, as the Chi-square test does in this case, reject the hypothesis that the data were drawn from a lognormal distribution. While this result is inconsistent, it must be pointed out that the KS test is not very discriminating; that is, the test is prone to accept the hypothesis when in fact it is false, especially with small sample sizes. In this case, since the sample size is larger, the result of the KS test is reasonable, especially in light of the Chi-square rejection based on the deviation in one cell.

Table 4-5
Chi-Square Test for Goodness-of-Fit for Total Methylmercury Data from the East Fork Poplar Creek, TN, Log-Transformed Data

(1) Interval Number	(2) Interval Upper Limit, mg kg^{-1}	(3) Number of Occurrences	(4) Cumulative Normal Distribution[63]	(5) Probability Density Function	(6) $(O-E)^2/E$
Log-Transformed Data					
1	-4.5	2	0.001	0.17	20.19
2	-4	2	0.007	0.61	3.16
3	-3.5	2	0.025	2.09	0.00
4	-3	1	0.072	5.57	3.75
5	-2.5	5	0.171	11.51	3.69
6	-2	22	0.329	18.48	0.67
7	-1.5	24	0.526	23.05	0.04
8	-1	27	0.716	22.33	0.98
9	-0.5	21	0.860	16.80	1.05
10	0	7	0.944	9.82	0.81
11	0.5	3	0.982	4.46	0.48
12	1	1	0.995	1.57	0.21
				$\Sigma((O-E)^2/E)$ =	**35.0**
		Total = 117		**X^2 (0.9,9) =**	**14.7**

[63] In this case the mean and standard deviation of the logarithms of the data are -1.56 and 0.984, respectively.

4.1.5.2 Parametric Methods for Comparing to a Standard

Suppose that in the cited case of methylmercury measurements in the East Fork Poplar River, it is desired to compare them to a hypothetical standard of 0.3 ng L^{-1}. Since the logarithms of the data have been subjected to a normality test and found to be approximately lognormal, the t-test can be used to test whether the log mean of the population is less than the standard within an allowable error. The test statistic is given by:

$$t = (\overline{X} - \mu_0)\sqrt{n} / s$$ **Equation 4-13**

where:

$\overline{X}$ is the sample mean,

μ_0 is the WQS,

n is the number of water column samples, and

s is the sample standard deviation.

The null hypothesis is that the mean is $\geq$ WQS and the alternative is that the mean is less than the WQS. The level of significance chosen is $\alpha = 0.1$. There are 118 water column samples for total methylmercury. A one-sided test is used. In this case,

$t = (-1.56 - (-1.20)) (10.9) / 0.984 = -3.98$

From a table of percentage points of the *t*-distribution, with a significance level of 0.1 and n-1 (or 118) degrees of freedom, the critical value ($t_{0.9,116}$) is approximately -1.29. Since the *t*-statistic (-3.98) is greater than the critical value of -1.29, the hypothesis that the population mean is greater than or equal to the WQS is rejected in favor of the alternative hypothesis. Thus, in this case, it can be said that the population mean is less than the WQS at the 0.1 significance level and the water body should be delisted.

4.1.6 Laboratory Bias

Laboratory bias has been shown to be a significant problem when measuring mercury at very low levels. This is exemplified using the results of split samples for total and methylmercury sent to two independent laboratories when water data was being collected on the Savannah River by the U.S. EPA from a regulated entity. While differences, perhaps large differences, are to be expected when making measurements of such minute quantities, consistently low or high results relative to another laboratory is a problem, especially when the objective is to compare to an absolute standard. Table 4-6 shows that the RPD between these two laboratories ranged from about 2 percent to over 25% for total mercury and from around 20% to almost 40% for methylmercury[64]. Obviously, selecting a laboratory that reports consistently high results is

[64] Note that bias also occurred in some, but not all, split fish tissue samples.

problematic. Therefore, it is recommended that anyone undertaking a study of low level mercury in water should qualify a laboratory they wish to use prior to initiating the study. It is recommended that at least six ambient water samples be collected and sent to a minimum of two laboratories. If there is a suspected bias, then the study sponsor should ask the laboratories to analyze a reference material. The laboratory reporting results closest to the reference material should be retained.

Table 4-6
Example of Bias in Total and Methylmercury Results for Waters of the Savannah River, GA

Location	Laboratory A		Laboratory B		RPD	
	Total	MeHg	Total	MeHg	Total	MeHg
1	5.68	0.17	7.36	0.25	-25.77	-39.23
2	2.43	0.13	2.63	0.16	-7.91	-26.39
3	3.27	0.07	3.45	0.09	-5.36	-33.82
4	9.5	0.06	9.65	0.07	-1.57	-21.36

In the example shown in Table 4-6, there is obvious bias because the sign of the difference (or the RPD) is always negative. However, suppose that the difference was of the same sign in only 6 of the 8 samples. Bias can be statistically tested by using the binomial test. If there is no bias, the results should be like the flip of a coin, with one laboratory being higher or lower than the other with equal probability. The binomial test rejects the null hypothesis that there is no bias if there one laboratory has too many results that are too high or too low. Interested parties are referred to Siegel (1956) or any number of texts on nonparametric statistics for the details of the test.

4.2 Navigating the TMDL Process

This section, in contrast to the previous section which focused on 303(d) delisting, will focus on dealing with the TMDL process. The section is organized in much the same way that a TMDL document would be, and addresses the issues associated with each step of the process. The major steps include:

- Identification or development of applicable standards or TMDL targets;
- Assessment of mercury sources;
- Performance of the linkage analysis (of mercury loads to water, fish or sediment concentrations);
- TMDL development, load allocations, and wasteload allocations; and
- Margins of safety, seasonal variations and critical conditions.

Of these topics, the bulk of the scientific issues are within the scope of the first three steps and consequently a greater portion of the guidance is devoted to them. In addition, however, implementation issues, with special emphasis on NPDES permitting will be covered, along with other miscellaneous topics including alternatives to TMDLs.

4.2.1 Stakeholder Involvement

As a preface to this guidance, it is very important to stress that stakeholders be involved in each aspect of the TMDL, from the listing process onward. This will hopefully give ample opportunity, to the extent possible, to influence various issues. Having said this, many states have been observed to have a very open process in this regard, while others have tended to be quite covert. States have an obligation to include shareholders in this process, however. Beyond this, many states see shareholder involvement as a way to resolve issues as they arise. In some states were lawsuits have mandated very tight timeframes for developing TMDLs, the states simply have not had the time or resources to adequately involve the public. In this case, it is the stakeholder's right and obligation to get and remain involved.

As mentioned in Section 4.1, states produce a list of impaired waters every two years. In each of these lists, waterbodies requiring TMDLs are ranked and a schedule is prepared for those TMDLs that will be developed over the ensuing two years. Stakeholders should inspect this list carefully. If schedules are unclear, the agency should be contacted for clarification. Once it is evident that a TMDL will be done for mercury on a waterbody of interest, the stakeholder should contact the state's TMDL coordinator, inquire about the stakeholder process, and express interest in being involved. The stakeholder should ask for ongoing communications concerning meetings and be consistently and timely informed of each opportunity to interact with the agency during the development of the TMDL.

Where formal stakeholder groups already exist in a watershed and have adequate scientific expertise and resources, they may petition the agency to self-perform the TMDL. Many state agencies are open to this, especially where the agencies are not obligated by lawsuit settlements to perform the TMDLs themselves and where agency resources are limited.

4.2.2 Applicable Standards/TMDL Targets

The first step in the establishment of a TMDL for a specific waterbody is to identify or develop the applicable standards or TMDL target. This is a hugely important issue as the target will determine the extent to which load reductions are necessary. Since point sources, except in certain cases, do not discharge significant quantities of mercury, there may be little that can be done within the watershed to limit mercury loads to the waterbody. Thus the setting of the target will determine how long it will take to attain compliance with the standard and perhaps with the overall success of the TMDL process. Targets will be either fish tissue-, water column-, or sediment-based. These various types of targets and the issue associated with each are discussed in the following subsections.

4.2.3 Fish Tissue-Based Targets

Most states rely on their narrative standards to list waterbodies for mercury impairment and most rely on fish consumption advisories as the means of judging impairment. Following the development of the methylmercury criterion in fish tissue by the U.S. EPA in 2001, fish tissue-based targets have emerged as the most popular in TMDLs. Tissue-based targets are consistent with the listing process and provide a reasonable means of measuring progress toward attainment of the standard. In most cases the states will make policy decisions concerning the targets, and targets set in one waterbody create precedents for those that follow. States may or may not have adopted EPA's methylmercury criterion or a similarly derived tissue-based criterion. If they have not, the targets are yet more open to interpretation and creativity.

4.2.3.1 Site-Specific Adjustments to the Methylmercury Criterion

Some states have adopted the methylmercury criterion or have plans to do so. Where this adoption has occurred, decisions will have been made concerning site-specific adjustments to the criterion. The most popular is to make an adjustment for fish tissue consumption. EPA based its methylmercury criterion on a consumption rate of 17.5 grams day^{-1}. Many states are considering or electing to raise the consumption rate. This will have the effect of lowering the tissue-based criterion by an equivalent amount. For instance, if the consumption rate is raised to 30 grams from 17.5, the tissue based target will decrease from 0.3 mg kg^{-1} to 0.175 mg kg^{-1}. Many states have not yet adopted the methylmercury criterion because they are still awaiting implementation guidance from EPA. Thus, stakeholders in many states will still have the opportunity to be involved in the standards setting process during the triennial review process. Guidance on modifying the methylmercury criterion can be found in Chapter 2 of EPRI (2003) and is not dealt with further in this document.

If states have not yet adopted the methylmercury or similar criterion, targets are "created" in the TMDL. Most of these variants are based on protection of human health. However, as discussed in Section 3, some states have begun to incorporate wildlife protection and/or protection for threatened and endangered species into the targets. In general, this results in a lower criterion than would otherwise have been used. In some cases, TMDL authors make additional assumptions regarding the application of the standard, which has the effect of further reducing the target. For instance, an often made assumption is that the criterion is applied to trophic level four fish rather than a weighted average of all fish caught and consumed. Additionally, in some cases, specific species and sizes of fish are specified for application of the target. These modifications are discussed in the following section.

4.2.3.2 Reference Species and Sizes

If tissue levels in a trophic level four species (e.g. walleye, largemouth bass) are used to compare to a target, then the target should be based on tissue residue levels appropriate to that species. If tissue levels in trophic level four species are being compared to the methylmercury criterion, or a similar consumption-weighted criterion, then the target is inappropriate and will lead to an unwarranted level of protection.

To illustrate this point, using fish tissue data from the Savannah River and tributaries draining the Department of Energy's Savannah River Site (SRS) from 1996 to 1998 (a total of 396 fish tissue samples), the trophic weighted average fish tissue concentration (using EPA's consumption weighting factors) is 0.59 mg kg^{-1}. Using the commonly invoked "Principle of Proportionality", the percent reduction in mercury loads to achieve a fish tissue concentration of 0.3 mg kg^{-1} is 47%. If trophic level four fish only (largemouth bass and bowfin) are used in place of the trophic-weighted average, the tissue concentration is 0.8 mg kg^{-1} and the % reduction increases to 62%. If largemouth bass data only are used (average tissue concentration = 0.89 mg kg^{-1}), the percent reduction increases to 66%. If the 90^{th} percentile largemouth bass is used (average tissue concentration = 1.33 mg kg^{-1}), the percent reduction increases to 77%. Finally, if the standard is lowered by adjusting the fish consumption rate to less than 0.3 mg kg^{-1}, say 0.2 mg kg^{-1}, the % reduction increases to 85%.

The use of a percent reduction calculation actually masks the magnitude of these encroachments on EPA's AWQC methodology and methylmercury standard because the current fish tissue value is used in the denominator of the calculation. The actual margins of safety (MOS) above the reduction required in the base case are 72%, 103%, 248%, and 282% [65]. As adequate factors of safety are already built into the methylmercury reference dose, the singling out of certain trophic level four species to compare to the standard, the use of high percentile values of fish tissue data, and the further lowering of the methylmercury standard to pad the required load reduction is excessive and unnecessary.

The use of a reference size fish may be beneficial, depending upon the statistic used to characterize the size class. In the Savannah River, the average size largemouth bass caught is 0.58 kg. Using the SRS data alluded to above, the mean tissue concentration in the weight class from 0.5 kg to 0.7 kg is 0.74 mg kg^{-1}, which is lower than the average tissue concentration for all largemouth bass of 0.89 mg kg^{-1}, but still higher than the trophic weighted average of 0.59 mg kg^{-1}. However, if the 90^{th} percentile tissue concentration in this size class is used, the value is 1.17 mg kg^{-1} (compare to 1.33 mg kg^{-1} from the analysis above). In this case, the use of a reference size fish close to that typically caught and consumed lowers the mean largemouth bass tissue concentration by about 17% and lowers the 90^{th} percentile value by about 12%. However, it increases in the tissue concentration relative to the trophic weighted mean by about 25% and by about 98% relative to the 90^{th} percentile value.

4.2.4 Water Column-Based Targets

In some TMDLs, tissue based targets are eschewed in favor of water-column-based targets. In some cases the target is the statutory water quality criteria (most likely 12 ng L^{-1}, but in some cases 51 ng L^{-1} or higher). In many cases, however, a water column-based target is derived in the TMDL as an interpretation of the narrative standard. Normally, the derivation of a water column-based target will involve the calculation and use of a BAF to translate from a tissue-based to a water column-based target.

[65] The margin of safety is calculated as the ratio of the fish tissue concentration minus the standard, to the fish tissue concentration in the base case minus the standard (0.59 - 0.3 mg kg^{-1} = 0.29).

4.2.4.1 Calculation and Use of BAFs

The BAF is defined a multiplier used to estimate the extent of bioacumulation in fish tissue. It is developed much in the same way that a partition coefficient is established to estimate concentrations of a chemical in sediment given its concentration in water and there is an assumption of equilibrium between the concentrations in tissue and in water. The BAF is inherently empirical, as the dominant pathway for bioaccumulation of mercury in fish tissue is through the ingestion of prey, and not as an equilibrium bioconcentration phenomenon. As a result, it encompasses many complexities including the intricacies of the food web and the biogeochemistry of the waterbody. A number of issues associated with the assumptions, calculation, and use of bioaccumulation factors are reviewed in EPRI (2003).

EPA's draft guidance suggests three approaches to establishing and using BAFs, as follows:

- derivation of site-specific methylmercury BAFs;
- use of a scientifically defensible bioaccumulation model; and
- use of EPA's empirically-derived BAFs.

Of these three, the first represents the only viable option. With regard to the second option, there are no models that reliably predict bioaccumulation from loads (see Section 4.2.4.2, below); therefore, there are no models that reliably predict BAFs[66]. In terms of the third option, the complexities of the biogeochemistry and food web in any given water body preclude the application of BAFs developed in one water body to another.

The empirical bioaccumulation factor for methylmercury is calculated by:

$$BAF = C_b / C_w \qquad \textbf{Equation 4-14}$$

where

C_b is the methylmercury concentration in the biota (fish tissue) in mg kg^{-1}, and

C_w is the methylmercury concentration in the water column.

From the outset, there are two immediately obvious issues with this calculation.

The first is that the mercury burden in fish tissue may not all be in the methylmercury form. It has been observed that in larger predatory fish most of the mercury tissue burden is in the methylmercury form. However, this may not always be the case. Data from Tuckahoe Lake, MD (MDOE 2002), show that although methylmercury averaged 88% of total mercury in largemouth bass, methylmercury in individual fish ranged from as low as 18% to as high as 225% of total mercury in the sample. These data indicate a high degree of variability in

[66] EPA admits in its draft guidance that the available "bioaccumulation models" use BAFs as an input. Therefore, the use of any of these models to derive a BAF or a water column-based standard would predetermine the answer.

methylmercury measurements in fish tissue and it is not clear whether the variability is a result of natural processes, the inability of the method to precisely measure it in fish tissue, or the inability of the particular laboratory used to make accurate measurements. Regardless of the source of the variability, the assumption that all the mercury in fish tissue is in the methylmercury form introduces a "margin of safety" on the order of 10 to 20%. It is not specifically known if the percent methylmercury in tissue changes from species to species and the diligent reviewer of a mercury TMDL would do well to point this out.

In lower trophic levels in the food chain, the ratio of total to methylmercury typically is lower so that the assumption that all the mercury is in the methyl form is far from valid. This should be taken into account when BAFs are calculated by using only that portion of the total mercury that is methylmercury in the calculation of equation 4-14. If so, it might lead to substantially lower BAFs (and therefore higher water column targets). Conversely, not taking this into account leads to inflated BAFs, lower water column targets, and higher margins of safety.

The second issue is that of the methylmercury measurement in the water column. The variability and potential bias associated with making measurements of a very low concentration of methylmercury in the water column have already been discussed, and it has also been pointed out, that Part 136 is not an approved method for methylmercury. There is also the issue of filtered versus unfiltered samples. The use of filtered versus unfiltered samples will give an obviously different result. Reference to the Oak Ridge data presented in EPRI (2003) suggests that this could be as great as a factor of two, with higher BAFs calculated from dissolved versus total methylmercury. Comparability of BAFs across waterbodies is hampered in many cases by the lack of reporting the details of methylmercury analysis used in the calculation. An additional issue with the use of methylmercury data in this calculation is that the reported values are often below the method detection limit for total mercury in water by Method 1631 (0.5 ng L^{-1}). Where lower values are reported and used, the reviewer of the TMDL would do well to request documentation that a specific detection limit study was done by the laboratory and that the reported values are reliable.

A variation of the calculation of the BAF is to weight the fish tissue concentrations using the trophic level consumption factors, discussed in Section 4.1.3.10.4. Use of the consumption-weighted BAF,

$$BAF = \Sigma \, (C_{b,i} \, w_i) \, / \, C_w \qquad \textbf{Equation 4-15}$$

in which

$C_{b,i}$ is the tissue concentration in the i^{th} trophic level, and

w_i is the consumption-based weight for the i^{th} trophic level,

is sanctioned by EPA in its draft guidance document and was essentially used to derive the methylmercury criterion. It will generally result in a lower BAF (than that derived from use of the highest trophic level fish alone), due to the lower tissue concentrations in lower trophic level fish, and a higher water quality target. An example for calculating a weighted BAF is given in Appendix B of EPRI (2003).

The impacts of location, season, and year-to-year influences on the concentration of methymercury in the water column have been previously discussed. The same concerns apply in this case where methylmercury sampling results may be used to calculate BAFs. The importance of having representative methylmercury measurements cannot be overstated. However, in many cases, one or two values from one location are used to derive BAFs. The use of such a limited number of values is unjustifiable and scientifically indefensible. In view of the variability of fish tissue versus water column sampling results, it is easy to see that more water than fish samples are required to produce a defensible result. The obvious notwithstanding, the situation is usually reversed, with more fish tissue than water samples available to the analyst.

Another variation on the calculation of BAFs is to calculate BAFs for individual fish and produce a distribution of BAFs based on the results. From such a distribution, percentile values for BAFs can be estimated. It should be pointed out, however, that the uncertainty in extreme values of distributions is even greater than the uncertainty in the calculation of the mean. Agencies should be steered away from such an approach if at all possible. EPA points out in its draft guidance that the mean is preferred and that choosing distribution extremes may introduce an "unacceptable level of uncertainty into the CWA goal of protecting public health". Another significant drawback of using extreme values of fish tissue or water column measurements to set the WQT (other than the fact that their use will result in higher BAFs and lower WQTs) is that, to this researcher's knowledge, there are no statistical tests to make population inferences concerning percentile values of a sampling distribution as there are with the mean. How then, will the agency determine when an extreme (e.g. 95^{th} percentile) value has been achieved in the population of methylmercury levels in a waterbody and its beneficial use has been reestablished?

Due to the technical, legal and cost issues involved in establishing a methylmercury WQT, most agencies have chosen to establish a WQT for total mercury instead. The use of total mercury is also in keeping with the requirement of most NPDES permits that permitees measure total mercury. In order to so this, BAFs must either be calculated using total mercury measurements in the BAF calculation or by using what is referred to as a "methylation translator".

The methylation translator is simply the ratio of methyl to total mercury in the water column. Once the WQT is calculated in terms of methylmercury, the translator is used to convert methyl to total mercury. The normal approach is to calculate the mean or geometric mean of the each form and divide the means. As with the BAF, it is possible to calculate this ratio with paired samples and construct a distribution of values, although this is rarely done due to the paucity water column data. It is unfortunate that EPA, in its draft guidance document, has provided the states with quartile values for the methylation translator. The use of a percentile value, based on observations made from nationwide data, is clearly inappropriate for use in any given waterbody without serious caveat.

Among the troubling assumptions concerning the methylation translator are that:

- it is a constant, and
- it is proportional to the total mercury concentration in the waterbody.

Given the previous discussion regarding the seasonal and year-to-year variability in both methyl and total mercury in water, it is easy to imagine that the first assumption does not hold true. However, given enough samples at representative locations and times, a reasonably accurate value might be estimated. If this assumption is to be challenged in a TMDL, a reasonable approach would be to show the variability in methyl and total mercury measurements and the variability in the resulting translator values.

The second assumption is more troublesome. It leads inexorably to the conclusion that if total mercury (load/concentration) is reduced in a waterbody that methylmercury levels in water and in fish tissue will also drop by proportional amounts. At this time there is little evidence to support that the reductions will be proportional. While it has been pointed out that mercury levels in fish have dropped with decreases in deposition in the Everglades (FDEP 2003), it is not yet possible to establish whether these decreases are either proportional or linear with respect to the decrease in deposition. In another study, Engstrom and Swain (1997) presented data from lake sediment cores indicating that deposition had decreased in northeastern Minnesota, yet Swain and Hedwig (1989) showed that fish mercury concentrations had increased during the same time periods. Porcella (1994) pointed out that a ten-fold variation in mercury in fish of similar size in a lake where inputs were relatively uniform does not suggest a linear relation with loading. Validation of this assumption must await further measurements over time as deposition continues to decrease.

There are also abundant observations that methylmercury concentrations in water are not well predicted by total mercury. For instance, in the Willamette River, ODEQ used the ratio (Ω) between THg and dissolved MeHg in the water column as a translator to establish interim water column guidance values. To investigate this relationship for the Willamette River this researcher calculated coefficients of determination (R^2) for regressions of dissolved MeHg concentrations on total mercury (THg) concentrations. The R^2 values are provided in Table 4-7.

Table 4-7
Seasonal Analysis of the Relationship between Water Column Total and Methylmercury in the Willamette River, OR

Sampling Period	Regression Coefficient (R^2)	
	THg (unfiltered) vs. MeHg	THg (filtered) vs. MeHg
1st Quarter	0.13	0.25
2nd Quarter	0.21	0.23
3rd Quarter	0.47	0.52
4th Quarter	0.004	0.23
All Data	0.001	0.10

As the table demonstrates, little of the variance in dissolved MeHg concentrations is explained by THg. Methylmercury (total) at the various sampling locations constituted from 0.8% to 15.5% (average of 5.2%) of the total mercury in the water column, suggesting that total mercury concentration is not limiting methylation.

The lack of correlation between total mercury and methylmercury concentrations is not unique to the Willamette River. Total mercury concentrations account for almost none of the variance in methylmercury concentrations (R^2 = 0.007, N = 38) in various streams in the Experimental Lakes Area in Northwestern Ontario, and sites with one of the highest total mercury concentration also had the lowest average methylmercury concentration (Kelly et al., 1995). Based on this observation, Kelly et al (1995) concluded that, "*total mercury concentration is not a good predictor of methylmercury concentration in stream water or in lakes*". Other examples come from recent mercury TMDLs in Georgia, where the EPA collected total mercury and methylmercury samples of water, sediments, and fish. No significant relationship was found between these two parameters in the Savannah River water column data (R^2 = 0.003) or in water column data from South Georgia rivers (R^2 = 0.28). The absence of this relationship has been observed between total mercury and methylmercury in a number of other studies as well (Cope et al., 1990; Monson and Brezonik, 1998; Gilmour et al., 1998). The conclusion is further supported by the data from the nationwide study conducted by Krabbenhoft et al (1999), where sub-basins with mining operations that had the highest total mercury concentrations in sediment and water had low methylation rates, whereas methylation rates were highest in basins with the more wetlands. Gilmour et al (1991) concluded that, "*in general, the percentage of methylmercury does not appear to be a function of total mercury, i.e. contaminated systems do not have consistently higher or lower % methylmercury than pristine waters*".

Several studies have even indicated that the proportion of total mercury present as methylmercury is *inversely* related to the total mercury concentration in the water column. Data analyzed by Schaefer et al (2004) shows an *inverse relationship* between total mercury in water and percent methylmercury. The authors hypothesized that this "methylmercury accumulation paradox" is a result of abundance of certain bacteria that demethylate methylmercury in waters contaminated with mercury. As pointed out by Ullrich et al. (2001), despite the vast body of literature on the subject (348 publications cited in Ullrich et al., 2001), we are still unable to predict mercury methylation rates or the likely effects of reducing mercury loadings to the environment on methylmercury production.

In closing this section, a comment is warranted on a methodology presented by EPA in its draft guidance document for estimating the methylation translator. It is based on EPA's methodology for estimating dissolved metals from total metals concentrations in water (the so-called metals translator). The methodology makes two assumptions. The first is that the methylation translator (from dissolved methylmercury to total mercury) is a linear function of the total suspended solids concentration in water. To this researcher's knowledge, there has been no demonstration in the literature that this assumption is valid. Inherent in this assumption is that the biological process that converts inorganic mercury to methylmercury can be described by a constant, the same problematic assumption alluded to in previous paragraphs. Stakeholders in a TMDL in which this methodology is utilized should point out that it is both untried and unproven.

In EPRI (2003) the authors argued that the development of water column based targets was premature, given the state of the science. This recommendation is still valid and will remain so until methylation and bioaccumulation are better understood and are predictable in a variety of waterbodies under a range of environmental conditions.

4.2.4.2 Stochastic Analysis (Food Web Model)

An alternative pursued in at least one TMDL is the use of a stochastic (probabilistic) analysis to determine BAFs and the WQT from fish tissue data. In the Willamette River mercury TMDL, the Oregon DEQ used a food web model (Hope 2003) with uncertainty analysis to accomplish this.

The advantage of such an analysis is that, if the system and its input parameters can be adequately described, it provides a more robust analysis than one based on mean values alone. In particular, it provides information about the distributions of the outputs and better estimates of percentile values than those based on small data samples. Such output ideally provides information that risk managers can use to make informed decisions. For instance, it can readily be appreciated that "conservative" or "worst case" assumptions give answers that are "in the tail" of the output distribution. The question is, where in the tail? Is the answer obtained at the 90th or the 99th percentile of the population? Uncertainty analysis answers this question by generating the distribution of the output variable of interest.

However, the drawbacks of such an approach are manifold. First, the science cannot be manufactured by the model. What is not known is not known and, as with any other model, the output is only as good as the information used to mathematically describe the real-world system and to estimate inputs. Second, distributions must be estimated (as opposed to mean values) for the input. For many parameters, little enough information is available to estimate a mean value, much less so the type and parameters of its probability distribution function (PDF). Because the data (e.g. methylmercury in water) has a high variability, the pdf will have a large variance. This uncertainty is propagated through the model calculations and may result in an output distribution that has far greater uncertainty that any of the inputs - the PDF of the output has a higher variance that it should have, the tails of the distribution are too thick, and the percentile estimates are inflated. Finally, correlations that exist between the input variables should be taken into account. If two variables are random, high values of one are associated equally with high and low values of the other and vice versa; whereas, if the variables are positively correlated, high values of one are more often associated with high values of the other and vice versa. This has a dramatic effect on the output distribution obtained from the analysis.

In the ODEQ analysis, the model was run in a forecasting mode to estimate fish tissue concentrations given methylmercury concentrations in water. When this was done, many of the generated CDFs underestimated bioaccumulation in the observed data. Calibration was then performed that involved minimizing the differences in the observed and predicted distributions, particularly at the median values. The trophic level 4 northern pike minnow was chosen as the species on which to base the calculation of the WQT. Using a median tissue value for this species of 0.6 mg kg^{-1} and a BAF determined from the analysis, the corresponding WQT was estimated to be 0.92 ng L^{-1}, requiring a 26% reduction in the currently estimated total mercury concentration in the Willamette.

In essence, observed fish tissue data were used to calculate the BAFs ultimately used in the model calculations for the WQT. The BAFs for the individual fish species could have as easily been calculated by dividing the median fish tissue concentration for a given species by the median methylmercury concentration in water. In fact, if one uses the mercury concentration (0.6 mg kg^{-1}) in northern pikeminnow from the Willamette River and computes the WQT using median values of MeHg (0.0469 ng L^{-1}) and methylation translator (0.025) from ODEQ's water database, the calculated target level would be 0.94 ng L^{-1}, a value nearly identical to that obtained using the model predictions.

In post-calibration runs, the median concentrations matched the observed concentrations reasonably well; however the tails of the distributions did not match the data well, overestimating the 95th percentile values for most species. In the cases of northern pikeminnow, largemouth bass, and smallmouth bass, the 95th percentile tissue concentration was overestimated by approximately a factor of 2. In addition to the base "stochastic" analysis, an "uncertainty analysis" was performed in which mean values of the input distributions were allowed to vary. The results of this analysis provided confidence bands about the predicted percentile values. The model estimated 95th upper confidence band on the 95th percentile value was 5.12 mg kg^{-1} and should correspond to the 99.75th percentile value. However, it is much larger than the 99.75th percentile value from the observed data distribution of 2.38 mg kg^{-1} (assuming the northern pikeminnow tissue data are log-normally distributed with a mean of 0.6 and a standard of 0.31) and demonstrates how much the tail probabilities are inflated in the analysis.

The way in which the information resulting from such an analysis using a food web model (or other model used in an uncertainty analysis) would be used in the regulatory context is of particular concern. As long as the policy decision is to use the median values of the distributions, then the estimates of uncertainty are of little consequence. As is demonstrated above, the use of median methylmercury concentrations, BAFs, and methylation translators gives a result similar to that produced by the model, without resorting to its use. However, once these output fish tissue distributions have been generated, there exists the real possibility that someone will think it a good idea to use them. This is could be a considerable problem for the regulated community. For instance, if the 95% confidence value for northern pikeminnow from ODEQ's analysis were used to calculate the target level rather than the median, a WQT of 0.03 ng L^{-1} would result. This would require a 98% reduction in mercury load to the Willamette; a target that is probably unachievable and unjustifiable.

Two important questions need to be answered if stochastic analysis with food web models are to be useful as a rule. First, which variables tend to have the greatest effect on the variability of the estimates about the median value, and second, how can the uncertainty in these parameters be reduced? ODEQ anticipated this and presented a sensitivity analysis that showing the contribution of various parameters to the variance in fish tissue concentrations. The variables with the greatest impact on variance tended to be MeHg assimilation efficiency, MeHg elimination rates, and the bioconcentration factor. Of these three, only bioconcentration factors and elimination rates can be readily measured or calculated from readily measured data. A considerable amount of work needs to be performed, probably in controlled microcosms, in advance of using models of this type in a regulatory framework.

4.2.4.3 Effect of Variability and Correlation of Water Column Mercury and Fish Tissue Mercury on Calculated BAFs and Water Quality Targets

Variability in the input variables in an equation, algorithm, or model affects the variability of the output variables. For simple mathematical operations, the propagation of error can be calculated directly but for more complex operations, the estimation of uncertainty in outputs given uncertainty in inputs is less straightforward. To demonstrate the effect and to provide a real world example of its importance, an error analysis of the computation of a WQT from fish tissue concentration, methylmercury concentration in water, and methylmercury translator was performed.

In virtually every TMDL it is assumed that:

- THg and MeHg concentrations in water are proportional; and
- mercury in fish and MeHg concentrations in water are proportional.

This implies that there is a positive correlation between total mercury and methylmercury in water and there is a positive correlation between methylmercury in water and mercury in fish tissue.

The function

$$WQT = 0.3*BAF^{-1}*\Omega^{-1}$$ **Equation 4-16**

where

BAF is the bioaccumulation factor, and

Ω is the methylation translator (ratio of MeHg to THg)

is used to calculate the target level. In the stochastic analysis, correlation between the random variables BAF and Ω should be preserved in the analysis if the values are related. Neglecting the correlation (more specifically, the covariance) between these two variables results in a product with a greater variance than would otherwise result from the calculation. This can be demonstrated by a simple example.

On the left-hand side of the spreadsheet of Table 4-8 100 independent (uncorrelated) random values of x = water column MeHg, y = Fish Tissue Hg, and z = water column total Hg were generated (for presentation purposes, only 70 values are shown in the table). Note that the means and standard deviations of these variables mimic, to a reasonable degree, the values for these variables observed in many waterbodies and that y and z are uncorrelated with x. The BAF and Ω functions (BAF = a y x^{-1} and $\Omega = x z^{-1}$) are calculated along with the WQT. Also note that although x, y, and z are uncorrelated, the BAF and Ω variables (Q1, Q2) are *negatively* correlated because they are respectively functions of x^{-1} and x. This will always be the case. In this example, the mean value of WQT is 1.36 ng L^{-1} and its variance (expressed as a coefficient of variation, CV) is 104.6% (shaded outlined box, left-hand side).

On the right-hand side of the spreadsheet of Table 4-8, 100 correlated values of x = water column MeHg, y = Fish Tissue Hg, and z = water column total Hg were generated. Notice that the means and standard deviations still approximately mimic the values for these uncorrelated variables but in this case, x is correlated with y and z. The BAF and Ω variables are again calculated along with WQT. This time, the BAF and Ω functions (Q1, Q2) are more strongly negatively correlated because they themselves are correlated to x^{-1} and x. This stronger negative correlation causes the overall variance between the BAF and Ω functions to be reduced when they are multiplied to yield the target level, WQT. Again, this will always be the case[67]. In this example, the mean value of WQT is 0.96 ng L^{-1} and its variance (expressed as a coefficient of variation, CV) is 36.5% (shaded outlined box, right-hand side). The degree of the reduction of the variance in the result, WQT, depends on the strength of the negative correlation of BAF and Ω. Therefore, when the correlation structure between the BAF and Ω variables is not preserved, the result is a WQT with greater variance than it should have.

[67] Taylor (1982) shows why. The variance of a function q of two random variables u and v is given by:

$$\sigma_q^2 = \left(\frac{\partial q}{\partial u}\right)^2 \sigma_u^2 + \left(\frac{\partial q}{\partial v}\right)^2 \sigma_v^2 + 2\left(\frac{\partial q}{\partial u}\right)\left(\frac{\partial q}{\partial v}\right)\sigma_{uv}\,.$$

In this case $q = a\,u^{-1}\,v^{-1}$, therefore the partial derivatives of q with respect to x and y are identical in sign. Because the covariance of u and v is always negative (since they are negatively correlated) the third term on the RHS is always negative. Therefore the variance of q is always less than it would be if u and v were independent (i.e. uncorrelated).

Table 4-8
Demonstration of the Effect of Covariance on the Expected Value and Variance of the Mercury Water Quality Target

	Uncorrelated MeHg, Fish Tissue, THg							Correlated MeHg, Fish Tissue, THg					
	MeHg	Fish Tiss	THg	BAF	Omega	WQT		MeHg	Fish Tiss	THg	BAF	Omega	WQT
	x	y	z	Q1	Q2	Q3		x	y	z	Q1	Q2	Q3
Mean	0.07	0.43	1.40	1.16E+08	0.10	1.36	**Mean**	0.07	0.48	1.58	4.87E+07	0.04	0.96
Std Dev	0.06	0.21	0.90	6.71E+08	0.15623	1.4268118	**Std Dev**	0.06	0.23	0.93	2.45E+08	0.01717	0.351274
	Covariance	0.00	0.00	-7813903.2	0.00339	-1.04E+07		Covariance	0.01	0.05	-2987200.2	0.00065	-1.57E+06
	Correlation	-0.02	0.00	-0.21	0.40	-0.10		Correlation	0.96	0.94	-0.22	0.70	-0.38
	Coefficient	y:z	z:x	Q1:x	Q2:x	Q1:Q2		Coefficient	y:z	z:x	Q1:x	Q2:x	Q1:Q2
					CV=	**104.6**						**CV=**	**36.5**

	MeHg	Fish Tiss	THg	BAF	Omega	WQT	MeHg	Fish Tiss	THg	BAF	Omega	WQT
	x	y	z	Q1	Q2	Q3	x	y	z	Q1	Q2	Q3
1	0.00	0.42	0.73	1.25E+08	0.00	0.52	0.00	0.16	0.13	4.78E+07	0.03	0.23
2	0.02	0.27	2.86	1.17E+07	0.01	3.21	0.02	0.21	1.23	9.05E+06	0.02	1.78
3	0.16	0.66	0.45	4.01E+06	0.37	0.20	0.16	0.79	3.19	4.81E+06	0.05	1.22
4	0.16	0.54	1.33	3.41E+06	0.12	0.74	0.16	0.77	3.36	4.84E+06	0.05	1.31
5	0.12	0.23	0.96	1.97E+06	0.12	1.26	0.12	0.73	2.61	6.26E+06	0.04	1.07
6	0.03	0.12	2.61	3.60E+06	0.01	6.35	0.03	0.36	1.35	1.06E+07	0.03	1.11
7	0.03	0.40	0.45	1.25E+07	0.07	0.34	0.03	0.38	0.90	1.21E+07	0.04	0.70
8	0.05	0.63	0.13	1.20E+07	0.39	0.06	0.05	0.43	0.87	8.14E+06	0.06	0.61
9	0.10	0.15	1.13	1.44E+06	0.09	2.27	0.10	0.56	1.65	5.35E+06	0.06	0.89
10	0.08	0.52	0.95	6.36E+06	0.09	0.55	0.08	0.57	1.97	6.92E+06	0.04	1.04
11	0.10	0.68	1.39	6.81E+06	0.07	0.61	0.10	0.63	1.84	6.29E+06	0.05	0.88
12	0.07	0.78	0.31	1.08E+07	0.24	0.12	0.07	0.41	2.06	5.67E+06	0.04	1.50
13	0.08	0.53	0.56	6.25E+06	0.15	0.32	0.08	0.56	1.38	6.57E+06	0.06	0.74
14	0.15	0.32	1.34	2.15E+06	0.11	1.26	0.15	0.70	3.03	4.75E+06	0.05	1.29
15	0.06	0.67	0.46	1.13E+07	0.13	0.21	0.06	0.35	1.50	5.93E+06	0.04	1.27
16	0.08	0.70	2.03	8.65E+06	0.04	0.87	0.08	0.47	1.99	5.83E+06	0.04	1.27
17	0.07	0.32	2.77	4.34E+06	0.03	2.56	0.07	0.48	1.68	6.48E+06	0.04	1.04
18	0.01	0.68	2.68	5.66E+07	0.00	1.18	0.01	0.19	0.75	1.59E+07	0.02	1.19
19	0.10	0.24	2.23	2.34E+06	0.05	2.82	0.10	0.67	2.07	6.61E+06	0.05	0.92
20	0.13	0.13	0.88	1.00E+06	0.15	2.03	0.13	0.77	2.35	5.95E+06	0.05	0.92
21	0.09	0.12	0.57	1.38E+06	0.15	1.41	0.09	0.50	2.20	5.68E+06	0.04	1.33
22	0.02	0.38	0.26	1.69E+07	0.09	0.21	0.02	0.36	0.63	1.61E+07	0.04	0.53
23	0.10	0.20	1.39	2.04E+06	0.07	2.04	0.10	0.58	1.88	5.84E+06	0.05	0.97
24	0.00	0.12	0.18	2.32E+08	0.00	0.46	0.00	0.29	0.33	5.73E+08	0.00	0.34
25	0.01	0.43	1.09	4.79E+07	0.01	0.76	0.01	0.17	0.21	1.87E+07	0.04	0.38
26	0.13	0.67	1.92	5.29E+06	0.07	0.87	0.13	0.65	1.92	5.18E+06	0.07	0.88
27	0.02	0.14	0.44	7.08E+06	0.04	0.95	0.02	0.22	0.95	1.14E+07	0.02	1.27
28	0.03	0.43	2.23	1.59E+07	0.01	1.55	0.03	0.30	0.86	1.11E+07	0.03	0.86
29	0.09	0.76	1.72	8.69E+06	0.05	0.68	0.09	0.52	1.86	6.00E+06	0.05	1.06
30	0.02	0.50	1.32	2.87E+07	0.01	0.79	0.02	0.20	0.75	1.12E+07	0.02	1.15
31	0.20	0.34	2.10	1.74E+06	0.09	1.85	0.20	1.00	3.13	5.11E+06	0.06	0.94
32	0.01	0.52	0.54	5.45E+07	0.02	0.31	0.01	0.14	0.86	1.49E+07	0.01	1.81
33	0.07	0.45	1.31	6.04E+06	0.06	0.88	0.07	0.52	1.26	6.99E+06	0.06	0.73
34	0.10	0.66	1.61	6.30E+06	0.06	0.74	0.10	0.57	1.95	5.47E+06	0.05	1.03
35	0.01	0.25	0.41	3.45E+07	0.02	0.49	0.01	0.30	0.90	4.09E+07	0.01	0.90
36	0.00	0.38	2.75	1.17E+08	0.00	2.17	0.00	0.18	0.60	5.38E+07	0.01	1.02
37	0.05	0.15	2.87	2.75E+06	0.02	5.78	0.05	0.36	1.74	6.65E+06	0.03	1.45
38	0.03	0.12	2.89	3.58E+06	0.01	7.26	0.03	0.27	1.40	8.17E+06	0.02	1.54
39	0.15	0.68	2.65	4.57E+06	0.06	1.16	0.15	0.78	2.97	5.23E+06	0.05	1.14
40	0.12	0.68	2.72	5.86E+06	0.04	1.20	0.12	0.76	2.70	6.52E+06	0.04	1.06
41	0.04	0.51	3.00	1.43E+07	0.01	1.76	0.04	0.40	1.13	1.13E+07	0.03	0.84
42	0.01	0.68	0.31	1.31E+08	0.02	0.14	0.01	0.13	0.24	2.55E+07	0.02	0.53
43	0.06	0.13	2.07	2.06E+06	0.03	4.72	0.06	0.47	1.67	7.37E+06	0.04	1.06
44	0.06	0.29	2.16	4.58E+06	0.03	2.23	0.06	0.37	1.87	5.85E+06	0.03	1.51
45	0.02	0.75	2.41	3.18E+07	0.01	0.96	0.02	0.27	1.25	1.13E+07	0.02	1.41
46	0.02	0.71	0.91	3.03E+07	0.03	0.38	0.02	0.39	0.46	1.64E+07	0.05	0.36
47	0.02	0.53	0.80	2.25E+07	0.03	0.45	0.02	0.20	1.26	8.61E+06	0.02	1.84
48	0.09	0.25	0.67	2.62E+06	0.14	0.82	0.09	0.63	1.46	6.64E+06	0.06	0.70
49	0.12	0.48	1.89	4.19E+06	0.06	1.18	0.12	0.63	2.39	5.51E+06	0.05	1.13
50	0.11	0.19	1.44	1.67E+06	0.08	2.27	0.11	0.74	2.40	6.50E+06	0.05	0.97
51	0.11	0.29	1.30	2.73E+06	0.08	1.35	0.11	0.64	1.67	6.05E+06	0.06	0.78
52	0.06	0.58	1.05	9.80E+06	0.06	0.54	0.06	0.34	1.38	5.73E+06	0.04	1.22
53	0.19	0.38	0.36	2.00E+06	0.53	0.28	0.19	0.93	3.85	4.86E+06	0.05	1.24
54	0.03	0.15	2.29	4.64E+06	0.01	4.56	0.03	0.37	0.56	1.14E+07	0.06	0.45
55	0.00	0.24	0.27	1.59E+08	0.01	0.34	0.00	0.26	0.90	1.70E+08	0.00	1.05
56	0.07	0.45	1.60	6.21E+06	0.05	1.07	0.07	0.51	1.40	6.96E+06	0.05	0.83
57	0.07	0.17	1.74	2.36E+06	0.04	2.98	0.07	0.52	1.66	7.01E+06	0.04	0.96
58	0.18	0.63	0.21	3.46E+06	0.86	0.10	0.18	1.00	3.24	5.51E+06	0.06	0.97
59	0.02	0.40	2.79	2.52E+07	0.01	2.08	0.02	0.17	0.33	1.03E+07	0.05	0.59
60	0.18	0.40	0.90	2.22E+06	0.20	0.68	0.18	0.85	3.08	4.78E+06	0.06	1.09
61	0.10	0.23	0.90	2.32E+06	0.11	1.16	0.10	0.63	1.93	6.33E+06	0.05	0.91
62	0.04	0.34	0.08	8.23E+06	0.52	0.07	0.04	0.45	0.66	1.07E+07	0.06	0.44
63	0.05	0.45	1.04	8.52E+06	0.05	0.68	0.05	0.33	1.79	6.19E+06	0.03	1.63
64	0.05	0.22	0.44	4.79E+06	0.10	0.61	0.05	0.35	1.35	7.75E+06	0.03	1.15
65	0.01	0.54	0.62	5.11E+07	0.02	0.35	0.01	0.34	0.73	3.20E+07	0.01	0.64
66	0.18	0.46	0.39	2.61E+06	0.46	0.25	0.18	0.99	3.37	5.57E+06	0.05	1.02
67	0.14	0.19	2.05	1.38E+06	0.07	3.29	0.14	0.77	2.80	5.65E+06	0.05	1.09
68	0.01	0.61	2.34	5.32E+07	0.00	1.15	0.01	0.35	0.96	3.02E+07	0.01	0.83
69	0.11	0.43	1.77	4.02E+06	0.06	1.23	0.11	0.67	2.09	6.25E+06	0.05	0.94
70	0.16	0.37	1.18	2.25E+06	0.14	0.96	0.16	0.78	2.53	4.79E+06	0.06	0.97

Due to the negative correlation of the BAF and Ω functions, the *mean* value of WQT is *also* lower than it would be if BAF and Ω were uncorrelated, not an opportune outcome for the regulated community. If, at some future time, the WQT were to be selected based on the tails of the distribution rather than the median, reducing the variance in the WQT value could become important (i.e. the WQT value at the lower 5th or 10th percentile, uncorrelated, could be lower than the corresponding percentile value of the WQT, correlated. In the above example, the 25th percentile WQT (uncorrelated) would be 0.40 ng L^{-1}, whereas the 25th percentile WQT (correlated) would be 0.72 ng L^{-1}, a more favorable result. The difference between the WQTs gets larger as one moves further out on the distribution tails (e.g. at the 5th or 10th percentile levels).

The fact that a calculated WQT is not a single number, but is a random variable with an associated variance, has implications for judging whether the water quality standard is being met. In particular, *t*-tests used to decide whether the mean of sampling data are below or above the WQT could take the uncertainty in the WQT into account. Just as the estimates of variance of the mean of water samples would improve with a greater number of samples, so the estimates of the variance of the standard would improve with a greater number of data points involved in its calculation.

4.2.5 Sediment-Based Targets

Sediment-based targets are not the rule in mercury TMDLs but they have been developed in some. Most of these are in the western U.S. where contaminated sediments from mining operations are a key issue. Most notably, in the San Francisco Bay TMDL, a sediment-based target was judged to be most relevant because most of the mercury mass in the Bay resides in the sediment. In this case, reduction in the load was determined from the difference in current fish tissue levels versus a fish tissue target of 0.2 mg kg^{-1} and reductions of 50% of the current load were deemed necessary. The sediment target was postulated by assuming linearity between the needed reductions and the current sediment concentrations, and a target of 0.2 mg kg^{-1}, was established. In several TMDL studies, however, it has been noted that fish tissue mercury does not appear to be correlated with sediment mercury. Additional information on sediment bioaccumulation factors (SBAFs) is available in EPRI (2003).

Obviously, the sediment target is very dependent on where the samples are collected, the texture of the sediment, its chemical composition, and a host of other influences. Perhaps most importantly, efficacy of a sediment-based target would be dependent upon the way in which mercury is associated with the sediment particles. For example, if the mercury in sediments is present as insoluble mercuric sulfide (cinnabar) it is unlikely that reductions in sediment concentrations will have an impact on concentrations in biota due to its low bioavailability. If, on the other hand, it is present in a more bioavailable form, regulating sediment may have a meaningful impact.

There are several ways to estimate the bioavailability of mercury in sediment. One is to measure the dissolved mercury in the interstitial or pore water. Another method is to sequentially extract mercury using a spectrum of weak to strong acids, at each step more aggressively extracting mercury from the matrix. Each acid is chosen to dissolve certain species of mercury from the matrix and in this way, the speciation of mercury in the sediment matrix can be roughly determined. Another method would involve the use of bioaccumulation tests using sediment dwelling organisms. Animals are exposed to sediment for a standard period of time at known levels of mercury in sediment and at the conclusion of the test the animals are analyzed to quantity the mercury body burden. In this way, SBAFs can be determined directly.

As is the case with total mercury in water, total mercury in sediment is not a particularly meaningful target without some knowledge of the aquatic system involved. A methodology to develop a sediment criterion analogous to the way water column criteria are derived would be:

- Determine the necessary reduction required in fish or wildlife;
- Estimate biomagnification in the food chain to target fish or wildlife species from important benthic species in the aquatic system;
- Estimate an SBAF for the benthic species based on bioavailable mercury; and
- Estimate partition coefficients to translate from bioavailable to total mercury.

Approaches of this type have wide-spread acceptance in the development of cleanup targets at hazardous waste sites.

4.2.5.1 Calculation and Use of SBAFs

In some toxicological studies, SBAFs have been estimated to describe the relationship between sediment mercury concentrations and mercury concentrations in aquatic biota. The concept is the same as with other bioaccumulation factors. The SBAF is calculated by

$$SBAF = C_b / C_s \qquad \textbf{Equation 4-17}$$

where:

C_b is the concentration in the biota (mg kg^{-1}), and

C_s is the mercury concentration in the sediment (mg kg^{-1}).

Per the discussion above, “bioavailable” mercury or even “porewater” mercury may be a more meaningful representation of mercury in sediments than total mercury.

In the TMDLs reviewed for this project, none were found that used the SBAF as a tool for translating targets in biota to sediment targets. If they were to be in future TMDLs, the same issues relevant to the translation of tissue based criteria to water-column criteria would apply. While temporal variability may be of less concern, spatial variability would be of greater concern. The number of samples and sampling locations required to adequately characterize a waterbody with respect to mercury in sediment would likely be greater given that sediment concentrations may vary in space to a greater extent than water concentrations. The assumptions concerning linearity between reductions in sediment mercury and fish tissue would still be troublesome. Just as the WQT calculated from a set of water column data has a sampling distribution, so would a sediment quality target calculated from an SBAF and tissue data.

4.2.6 Dealing with Older Data

In many TMDL studies data in addition to or in lieu of those used for the listing are collected. If so, these data are generally provided in the report. In this case, fish and water samples are normally collected over roughly the same times and the same locations. There may be quality issues with older fish tissue and water samples.

In the event that water samples were collected prior to about 1995 when concerns over the contamination of low-level water samples became widely appreciated and prior to the advent of Method 1631, reported levels of mercury may be erroneously high. Ambient samples having reported levels greater than 200 ng L^{-1} using Method 245.1 should probably be eliminated. Samples analyzed using Method 1631 having reported levels of total mercury greater than 15 to 20 ng L^{-1} should be examined carefully. Methylmercury samples with values greater than 2-3 ng L^{-1} should also be carefully scrutinized.

There are generally several issues with older fish tissue data. First, the data themselves may not be provided in the TMDL. While locations are generally recorded even with older data, fish lengths, weights, and/or ages of fish may not have been recorded. If so, there is no way to determine if the tissue samples are from fish representative of the sizes caught and consumed in the waterbody of interest. Perhaps the most serious concern with older data is the dislocation in time of the fish tissue and water samples (assuming the water samples are more recent). If BAFs are computing using older fish data (when ambient levels of mercury may have been higher) and more recent water data, BAFs could be artificially inflated, leading to lower WQT levels. TMDL stakeholders should insist that these data be made available so that issues of concern with their use can be properly evaluated. If serious concerns arise over the use of this data, then stakeholders should petition the agency to eliminate it from consideration in developing the TMDL.

4.2.7 Use of Self-Generated Data

As pointed out in Section 4.1.2, agencies are obligated to use all available information. Therefore, data collected in accordance with accepted scientific protocols and/or in consultation with the regulatory agency must be considered in the TMDL process. If stakeholders are interested in providing data, they should determine the agency’s approach to establishing the TMDL. Data collection should be focused on areas and concern and in areas where quality data may provide the greatest benefit. One of these areas may well be the stakeholder’s own effluent. While the agencies may have the resources to collect ambient sample from a waterbody, they generally will not have sufficient resources to collect data from each discharger sufficient to characterize its effluent. Collection and analysis of effluent data are the subjects of the next section.

4.2.8 Source Assessments

In this portion of the TMDL, current mercury sources are identified and quantified. The purpose is to establish a baseline from which allocations for source load reductions can be made once the assimilative capacity for mercury in the waterbody is established. Mercury loadings should be assessed from all sources, including both point, nonpoint, and atmospheric. Omitting sources contributes to uncertainty and may bias the outcome. The first three sections parts of this section (4.2.8.1 through 4.2.8.3) focus on the collection and analysis of samples and data from point sources. Nonpoint sources are discussed in 4.2.8.4.

4.2.8.1 Collecting and Analyzing Effluent Samples

Point discharges are an important consideration in the quantification of sources of mercury to a waterbody. In many TMDLs, it has been assumed or demonstrated that the point sources contribute a small or even *de minimis* quantity of mercury to the aquatic system. However, this does not diminish the importance of the TMDL to the individual discharger. The fact that currently discharged quantities are low is disadvantageous for two reasons. First, a small current discharge will translate to a small allocation in the TMDL. This may ultimately lead to a discharge limit that is restrictive and difficult to consistently meet. Second, dischargers of small quantities of mercury may find it more difficult to pinpoint and minimize mercury sources and bring about source reductions than those with higher and more obvious sources. Some states give consideration to those considered to be minor dischargers (usually based on quantity of flow) in the development of monitoring an minimization plans, but in general no point source will be exempt from at least minimal scrutiny. As power plants are large users of water they are likely to be of interest to the agency. Coal-fired plants are of special interest since coal itself is a major source of mercury.

4.2.8.1.1 Total, Methyl, or Both?

As with the sampling of ambient waters, dischargers wishing to characterize their own effluent will be faced with the decision of which mercury species to analyze. In general, power plants discharge divalent, inorganic mercury and total mercury is an obvious parameter to measure. Methylmercury may be produced in FGD sludge ponds, ash ponds, and other water handing facilities. However, methylmercury concentrations from the PISCES database show quite low levels, uniformly less than 0.1 ng L^{-1} and ranging from 0.4% to 2% of total mercury. These levels are in the same range as (or lower than) ambient samples and as such should raise no special concern for methylmercury in wastewater effluents from power plants. However, it is possible that the addition of sulfate in FGD wastewaters may stimulate methylmercury production in FGD sludge and ash ponds. The addition of ammonia from SCR and SNCR units may stimulate the growth of algae, leading to lower DO levels, which either alone or combined with higher sulfate levels may stimulate methylmercury production in ponds. Studies are currently being conducted by EPRI on these issues and their resolution awaits the outcome of this and other research. In the meanwhile, unless compelled to do so, or unless the TMDL is or will be established for methylmercury, there appears to be no regulatory motivation for power plants to measure methylmercury in their effluents.

4.2.8.1.2 Sample Locations

Location selection is an important issue when collecting samples from power plant environments. As with other sampling conducted with the intent of providing data to the regulatory agency preparing a TMDL, consultation with the agency is advisable in order to insure that they are optimally used to the benefit of the discharger.

Sampling of ash ponds and FGD ponds should be conducted as near (upstream of) the outlet as possible so that the samples are as representative of the plant's effluent as possible. If the discharge is from a weir or spillway, near-surface grab samples are most appropriate. It is advisable to collect low level samples for mercury analysis directly into the sampling bottle, below the water surface to avoid contamination. Discharge from pipes, pumps, and other conveyances where possible contamination of the sample may occur should be avoided.

Direct discharges other than ash pond effluents may also be of interest. Although they may be of a lower volume than ash pond discharges, they may contain higher levels of mercury and thus contribute an equivalent load to the receiving waterbody. These include wastewater treatment plants, landfill leachates, stormwater runoff, and the like. Wastewater samples may be taken from the final clarifier stage prior to discharge. Care must be taken that the wastewater treatment plant is operating efficiently and that solids concentrations are at optimal levels, otherwise, total mercury concentrations could be elevated. Other non-point sources such as stormwater runoff and landfill leachate should be sampled if possible from detention or treatment facilities prior to discharge. Opportunities to take samples from or downstream of solids settling facilities should be used to advantage, provided that that samples collected are representative of actual plant discharges.

4.2.8.1.3 Sample Size

As with ambient samples and as presented in Section 4.1.3.4, sample size should be determined using estimates of the variability of the parameter being measured. Recall that the expression is

$$n = [\, z_{\alpha/2}\, \sigma / d \,]^2$$

where:

n is the number of samples required,

$z_{\alpha/2}$ is the standard normal deviate at probability level α (for a two sided test),

σ is the standard deviation of the measured parameter, and

d is the error tolerance,

assuming the measured variable (in this case total mercury) is normally distributed. Tests to determine the sampling distribution are described in Section 4.1.3.10.2.

As pointed out in Section 2, CVs for total mercury in ash pond effluent samples from plants in the PISCES database ranged from 19% to 74%[68]. Three sets of discharge data were reported

[68] All of the data presented in this section (summarized from Section 2) are for coal-fired plants, unless other wise noted.

from Utility M, with CVs of 50, 101, and 104%. Fly ash pond effluent CVs for Utility N ranged from 14% to 85%. Ash pond effluent from Utility O (Discharge D-2), had a CV of 49%. Utility P had the highest CVs for discharges from ash ponds ranging from 121 to 168%. However, a personal communication with the person responsible for this data revealed that although the data were collected using "clean" techniques, the data were not analyzed in a "clean" laboratory facility, which may have led to the higher than normal variability in the samples. On the other hand, data in the PISCES database may have been collected with greater care than that which would normally be exercised at an operating plant, thus these CVs may be slightly lower than normal. Based on the above discussion, it would be safe to assume that a typical CV for total mercury in ash pond effluents is on the order of 100%.

Discharge D-1 from Utility O, which receives low volume waste, coal pile runoff, cooling tower blowdown, ash pit overflow, runoff from a sulfuric acid/caustic containment and unloading area, and non-chemical metal cleaning waste, had a CV of 28%. Leachate from an FGD sludge landfill provided by Utility N had a CV of 114%. Outfall 002 from a non-member utility in the Upper Midwest containing controlled cooling water blowdown and discharge from the waste treatment facility, with process wastes including ion exchange demineralizer regenerant, scrubber blowdown, and excess flow from the coal pile basin as well as floor drains from the boilder and scrubber buildings, had a CV of 92%. By comparison, a CV of 46% was characteristic of a discharge of once-through cooling water and other low volume wastes from a natural gas-fired power plant in the western U.S. The same plant discharging effluent believed to consist of water from the pretreatment system, treated by sedimentation and microstraining, and untreated water from the reverse osmosis building drains, had a CV of 78%. A petroleum coke-fired plant in the western U.S., with the longest record of any of the plants discovered in this project, had a CV of 49% in its discharge. Based on the foregoing discussion, it is safe to assume that CVs for miscellaneous power plant discharges will have a CV of at least 100%.

The only examples of methylmercury in power plant effluent data come from a limited number of samples in the PISCES database. Based on this sampling, CVs for the methyl mercury measurements are about the same as those for total mercury, ranging from 30% to 90%. Thus it would be safe to use a CV for methylmercury of 100% when planning for the number of samples to collect. As mentioned earlier, unless compelled to do so, sampling for methylmercury is not recommended.

4.2.8.1.4 Seasonal Considerations

Seasonal considerations are also important when sampling plant effluents. The settling of solids typically is less rapid at cooler water temperatures as the viscosity of water decreases at lower temperatures. Water is over twice as viscous at 32°F than at 80°F. Poorer settling of clarifiers is frequently observed in colder weather. In addition, solids levels in stormwater and other non-point source discharges during periods of higher natural rainfall and runoff may be observed. "First flush" effects, that is, elevated concentrations of mercury in runoff from areas that have not received rain in quite some time, or in the initial portions of runoff generated from storms due the accumulation of atmospherically deposited mercury, may also be observed. In ash ponds where thermoclines form in the summer, higher winter values may be associated with fall turnover of the pond.

Only two of the six facilities in the PISCES database exhibited a seasonal trend in total mercury concentrations from ash pond effluents, with winter/spring values being higher than summer/fall values. At three facilities, no consistent trend was observed and at the remaining facility there is no seasonal data to analyze.

Several sets of data from EPRI member companies had sufficient data to investigate seasonal variations. Lowest total mercury concentrations in discharges normally occurred in late summer/early fall and highest concentrations in late winter/early spring. In one plant the ratio between the highest and lowest seasonal values was about 3:1. At a second plant, the seasonal effect was much less pronounced. At a third plant, the ratio of highest to lowest quarterly means for leachate from an FGD landfill was about 2:1, with the highest mean occurring in the third quarter (late summer/early fall).

At a petroleum coke-fired plant in the western U.S. with a long-term discharge record, means of data from the third and fourth quarters of the year were lower than those for the first and second quarters, indicating a definite seasonal trend for total mercury data in the effluent of this plant. The ratio of the highest to the lowest quarter was 1.5:1.

Based on the data presented in this report, it is safe to assume that a seasonal component will be observed in effluent data from power plants. Total mercury levels will likely be highest in the winter and spring quarters, associated with higher runoff and cooler temperatures. Observed levels during this time period will likely be on the order of two to three times higher than during the summer and fall quarters. Obviously, mercury levels will also vary with coal source.

4.2.8.1.5 Sampling and Analytical Methods

Sampling and analytical methods have been covered earlier in this chapter and the reader is referred to Sections 4.1.4.5, 4.1.4.6 and 4.1.4.8. The only additional caveat is that power plant environments may present more opportunities for sample contamination than natural environments. Therefore, appropriate caution should be exercised to avoid such areas and to handle samples with the utmost care.

4.2.8.1.6 Filtered versus Non-Filtered Samples

Filtering samples may represent a significant opportunity to argue that the mercury of greatest concern is in the dissolved form and not otherwise bound to solids. The PISCES database offers the opportunity to demonstrate how great an advantage this may be. Analysis of the unfiltered and filtered paired samples for mercury reveal that dissolved total mercury was on average only about 18% of total unfiltered mercury. Filtering reduced methylmercury concentrations in paired samples as well, but not to the same degree, with filtered values being about 33% of the unfiltered values. If the argument were to be made that the portion of the total in solids is not bioavailable, then some additional knowledge concerning the nature of the mercury in the solids would be useful. However, these data demonstrate that much of the total mercury is associated with solids in some way.

4.2.8.1.7 Ancillary Parameters

Flow should always be measured when collecting with plant effluent (and intake) data. This is of utmost importance as it may be desirable to compare mercury loads (flow times concentration) across power plants rather than simply comparing concentrations.

The rationale for measuring other water quality parameters has been discussed in Section 4.1.4.9. Although this rationale is applied to ambient samples, the rationale for plant effluent samples is similar and is not recapitulated here. As with ambient samples, ancillary measurements provide an opportunity to diagnose why mercury appears to be higher or lower in plant effluent the plant and to learn how better to control mercury in the wastewater system. For instance, if higher total mercury is associated with high TSS, then an obvious mechanism for control is to better address the settling of solids. If redox is low when mercury levels are elevated, there may be opportunities to management oxygen levels in ash ponds so that reducing conditions do not develop.

4.2.8.2 Collecting and Analyzing Plant Intake Samples

The rationale for collecting plant intake samples is to demonstrate for purposes of compliance that mercury is not being added across the facility operations. However, this information may also be useful in the TMDL stage to avoid allocated reductions. Paired samples of intake/effluent are the most useful and provide an opportunity to analyze the data in several different ways. Often paired intake/effluent samples are taken close to the same time. However, there may be some value in assessing the residence time of water in the plant and attempting to sample the same water entering and exiting. If there are multiple intakes and outlet with differing residence times this may not be possible. However, if a typical residence time can be established, it would be reasonable to sample the effluent after sampling the intake in accordance with this time lag.

4.2.8.2.1 Makeup Water and Once Through Cooling Water

Cooling water is brought into a power plant to condense steam and cool equipment. It may be recycled or used once. It is generally cooled on the plant site in cooling towers and reused or discharged to cooling lakes to be recycled. Make up water is water brought in to a power plant to “make up” for evaporative losses in cooling towers. It may also refer to water that is pumped into a cooling lake to make up for evaporative losses from the lake. Make up water and once through cooling water represent true “background” to the power plant if they are not taken from a cooling pond or lake. At run-of-the-river plants, upstream water is true “background”. At power plants on large with large cooling lakes with natural inflows, there may be no separate makeup or cooling water source that is unaffected by the plant. Samples should be collected of the raw water, prior to any conditioning or pretreatment. The same ancillary parameters measured in the effluent should be collected in the intake.

4.2.8.2.2 Cooling Lakes

Samples of intakes from cooling lakes may be influenced by discharges and as such may not be true background samples. However, this may be the only option in some instances. In general, samples should be collected in consideration of the issues discussed in the sampling of lakes in Section 4.1.4.2.2. However, samples should be collected in close enough proximity to the intake that they are reasonably characteristic of the influent to the plant.

4.2.8.2.3 Total, Methyl, or Both?

Measured water quality parameters for intake water should be the same as those measured in the effluent. At this time, it is recommended that only total mercury measurements should be made (see Section 4.2.8.1.1).

4.2.8.2.4 Sample Locations

Cooling water intake structures come in a wide variety of designs, usually particular to the individual power plant. For the purposes of this discussion, however, they will broadly categorized as being either surface or subsurface (tunnel or pipe) intakes. Typically subsurface water intakes extend out into the body of a lake or other large water body and lie on or against the bottom. Surface water intakes are more often associated with flowing water and typically incorporate an intake canal or forebay to “still” the flow, allowing for the settling of solids prior to intake. Once the water has been brought into the facility, there may be another forebay (prior to or in the screenhouse), and a pump bay to provide a constant head basin for pumps. All of the features that hold and give access to water provide an opportunity for sample collection.

Sample locations should be carefully selected in order to provide a representative “background” sample for the plant. At plants with subsurface intakes, samples should be collected from a convenient location just as the water enters the plant. If screens are located in the plant, samples should be collected upstream of the screens, as biological tissues impinged on screens may affect mercury levels in water passing through them. At plants with surface intakes, samples should be collected from the intake canal near the intakes, but again, upstream of screens.

4.2.8.2.5 Sample Size

Calculation of the sample size required to make inferences about plant intake waters is the same as that provided earlier in this report (see Section 4.2.8.1.3). CVs for plant intake and once through cooling water appear to be similar to those for effluent samples.

CVs for once through cooling water in the PISCES database range from 10% to 81% and CVs for plant intake water range from 12% to 77%. Therefore, the use of a CV of 100% is advised to initially plan a sampling program.

Another way of calculating the number of samples required is by making use of the Student's *t*-test for comparing two treatments (e.g. to assess whether observed ash pond effluent concentrations are statistically greater than plant intake concentrations).

The test statistic is given by

$$t_{(\alpha,\, df)} = (\bar{X} - \bar{Y}) / (s_{pooled} \sqrt{1/n_X + 1/n_Y})$$ **Equation 4-18**

where:

$\bar{X}$ is the mean of the effluent concentrations,

$\bar{Y}$ is the mean of the influent concentrations,

s_{pooled} is the pooled standard deviation of the two means given by

$$\sqrt{[(n_X-1)\, s_X^2 + (n_Y-1)\, s_Y^2] / (n_X + n_Y - 2)} \qquad (3)$$

in which:

n_X is the number of samples of ash pond effluent,

s_X^2 is the variance of the ash pond effluent data,

n_Y is the number of samples of plant influent,

s_Y^2 is the variance of the plant intake data, and

d.f. is the number of degrees of freedom = $(n_1 + n_2 - 2)$.

For the purposes of this analysis it will be assumed that the effluent and intake samples are paired so that $n_1 = n_2$. Thus the equation for the t-statistic reduces to:

$$t_{(\alpha,\, df)} = (\bar{X} - \bar{Y}) / (s_{pooled} \sqrt{2/n})$$ **Equation 4-19**

and s_{pooled} is simply the square root of the average of the two variances.

Rearranging equation (4),

$$n = t^2 (s_X^2 + s_Y^2) / (\bar{X} - \bar{Y})^2$$ **Equation 4-20**

As an example, for Facility B reported in Section 2:

$\bar{X} = 4.66$, $CV_X = 74\%$, (therefore $s_X = 3.45$, $s_X^2 = 11.89$)

$\bar{Y} = 3.61$, $CV_Y = 77\%$, (therefore $s_Y = 2.78$, $s_Y^2 = 7.73$).

If 90% confidence (using a one-sided test) is desired that the effluent mean is greater than the intake mean, then the *t*-statistic (guessing that the number of samples will be about 20 or d.f = 20 + 20 - 2 = 38) is 1.303. Substituting these values into Equation 5 yields

$n = (1.303)^2 (11.89+7.73) / (4.66-3.61)^2 = 30$[69].

4.2.8.2.6 Seasonal Considerations

Plant intake levels will exhibit seasonal variation generally in accordance with the factors discussed in Section 4.1.4.4 that affect mercury levels in ambient water samples, with higher levels typically occurring in winter and spring and lower levels in the summer and fall. The reader is referred to this section for more detail.

4.2.8.2.7 Sampling and Analytical Methods

The same considerations apply as those for sampling and analyzing ambient samples, as discussed in Sections 4.2.4.5, 4.1.4.6, and 4.1.4.8.

4.2.8.2.8 Filtered versus Non-Filtered Samples

The same considerations apply as those for sampling and analyzing ambient samples, as discussed in Section 4.2.4.7.

4.2.8.2.9 Ancillary Parameters

The reader is referred to Section 4.1.4.9, which discusses the selection of ancillary parameters for ambient water quality monitoring. As with effluent samples, flow should always be measured when collecting plant intake samples.

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[69] The analyst may wish to make a new guess at the number of samples (and look up a new value of the *t*-statistic) to verify that the number of samples is indeed 30. Since the statistic is asymptotic to a value of 1.282 at $\alpha = 0.1$, however, there is not much error associated with the initial guess of t = 1.303. In this case, if the guess is 30 (and d.f = 30+30-2 = 58), t is 1.297, and the calculated n is still 30.

4.2.8.3 Data Analysis

Once plant effluent or plant effluent and intake data have been collected, there are at least two ways in which it may be used. One is to compare the effluent mean to TMDL target. This problem (i.e. the comparison of a sample mean to a standard) has been previously discussed in Section 4.2.5 and will not be repeated here. The second way in which this data may be used is to compare effluent data to intake data to determine whether there has been a net gain of mercury across the facility. In doing so, a number of statistical tests may be used. They are of two types. Parametric tests assume an underlying distribution of the variables involved and the assumptions of those tests should be confirmed as part of the analysis. The second type is a nonparametric test, in which assumptions concerning the underlying distributions of the data are not required. Examples will be given for each type of test and guidance will be provided on when it is best to use each type.

First, however, the issue of comparing loads versus concentrations will be discussed.

4.2.8.3.1 Concentrations Versus Loads

Because evaporative losses may occur across a power plant, concentrations of mercury in the effluent may be higher than concentrations in the intake. If this is observed, the analyst would do well to check the effluent loads against the intake load to determine if there has been a net mercury addition across the facility. The load is simply the concentration (in this case in ng L^{-1}) times the flow rate in L day^{-1} giving a result in ng day^{-1}. If the effluent flow rate from the facility is lower than the intake flow, it may more than offset any increase in mercury concentrations. A simple way to check this is to compare the ratio of mean effluent to intake concentrations to the ratio of average intake flow to effluent flow. If the ratio of the flows is greater than the ratio of the concentrations, then it may be worthwhile to focus the analysis on loads rather than concentrations.

The statistical tests to compare loads are no different than the tests to compare concentrations. However, the variability in the loads rather than the variability in the concentrations (which has been dealt with solely thus far) must be known to conduct some of the tests. The best way to estimate the sampling distribution parameters for the loads are to multiply each paired flow and concentration data point, check the distribution of these products, transform the data if necessary, and then estimate the mean and standard deviation of the sample data.

4.2.8.3.2 Parametric Tests for Comparing Effluent and Intake Samples

The most common way to compare two treatments is to use the two sample *t*-test. If X represents the concentrations (or loads) of mercury in the effluent and Y represents the concentrations (or loads) of mercury in the intake, then the two sample *t*-test can be used to determine if the mean of X is statistically greater than the mean of Y. The test statistic is:

$$t_{(\alpha,\, df)} = (\overline{X} - \overline{Y}) / (s_{pooled} \sqrt{1/n_X + 1/n_Y}) \qquad \textbf{Equation 4-21}$$

where s_{pooled} has been previously defined (See Section 4.2.8.2.5). Notice that the number of samples in the intake and effluent data sets may be different and that the effluent and intake values need not have been collected as paired observations. In using a *t*-test with two independent data sets, there are 2n – 2 degrees of freedom.

Paired comparisons can be used if paired samples of effluent and intake have been consistently made. The *t*-test is once more used but it focuses on the difference between effluent and intake rather than treating them as separate variables. To use it first define a new variable D_i as the difference between the paired effluent and intake concentrations (or loads)

$$D_i = X_i - Y_i, \qquad \textbf{Equation 4-22}$$

where:

X_i is the effluent sample of the i^{th} data pair, and

Y_i is the intake sample of the i^{th} data pair.

The mean and standard deviation of the differences are then calculated as for any other variable. The *t*-test is now used to test the one sided hypothesis that the difference is greater than zero. The test statistic, which has n-1 degrees of freedom, is:

$$t = \bar{D}\,\sqrt{n} \,/\, s_D \qquad \textbf{Equation 4-23}$$

in which:

$\bar{D}$ is the mean of the differences of the paired samples, and

s_D is the standard deviation of the difference between the paired samples.

The question may arise whether to collect (or analyze) paired samples or to collect independent samples of effluent and influent data. In answering this question, there are two important considerations. The first is that using paired samples results in a loss of degrees of freedom (and power) in the test. It has already been noted that when comparing to independent samples, there are 2n – 2 degrees of freedom, whereas when comparing paired samples, there are n – 1 degrees of freedom. For example, if there are 11 samples of intake and effluent measurements, the t statistic for $\alpha = 0.1$ and d.f. = 10 is 1.372. If the samples are analyzed as independent observations, the t statistic for $\alpha = 0.1$ and d.f. = 20 is 1.325. Thus, it is easier to reject the null hypothesis that the means of the effluent and intake samples are no different using the independent test than the paired test. However, there is a second consideration. The principle reason for pairing samples is to reduce the variability in the samples. If effluent samples tend to be higher when intake samples tend to higher and vice versa, then there is a *positive* covariance between X and Y, which reduces the standard deviation of the difference between the variables. If the pairing is effective, the reduction of variance due to pairing normally more than compensates for the loss of degrees of freedom. Thus sample pairing is preferable when an appreciable reduction in variance is anticipated.

Consider an example from Utility M where 20 paired samples were available for the inlet to the cooling lake and plant effluent. At first glance the data do not appear to covary positively. In fact, the correlation coefficient between the cooling lake inlet and the plant effluent is -0.43, indicating that the covariance between the two datasets is negative. The standard deviation of the paired data is 9.5 ng L^{-1} whereas the pooled standard deviation of the two data sets is 8.6 ng L^{-1}. The negative correlation (or covariance) between the inlet and outlet results in a larger standard deviation for the paired samples than for the independent samples. In this case, it would be best to the analyze the samples independently. If the analyst is unsure which test to use, then analyzing the data both ways and selecting the most favorable result would be prudent. In some cases, neither method may give an advantage.

4.2.8.3.3 Non-Parametric Tests for Comparing Effluent and Intake Samples

The use of non-parametric test is warranted under certain conditions. Recall that non-parametric tests are those that do not require any assumptions about the underlying distribution of the data. Thus they are appropriate when the distribution of the data is uncertain or where an appropriate transform cannot be found to normalize the data. Non- parametric tests are generally preferred when the sample size is small and the underlying distribution of the data is simply not known. Another advantage of the non-parametric methods is that they are also generally easy to understand and use.

In this section, two non-parametric tests to compare two sample datasets are discussed:

- Mann-Whitney U test; and
- Kolmogorov-Smirnoff two sample test.

The Mann-Whitney U test is used to determine whether two samples have been drawn from the same population. It is one of the most powerful of the non-parametric tests and is a useful alternative to the *t*-test (Siegel, 1956). To use the test, the two groups of data (e.g. intake and effluent data) are combined and all of the data are ranked, keeping track of the group to which a given value belongs. The value of U (the test statistic) is calculated by observing the number of times that a measurement from one of the groups of data precedes a value from the other group. One can easily imagine that if the group values are intermingled then the chance that they are drawn from the same distribution is greater than if the values from the two datasets tend to be clustered at opposite ends of the ranking. For larger datasets, it may be tedious to count the number of times that one groups' value is preceded by the other. In this case, the value of the test statistic can be computed using

$$U = n_1 n_2 + n_1 (n_1 + 1)/2 - R_1$$ **Equation 4-24**

or alternatively

$$U = n_1 n_2 + n_2 (n_2 + 1)/2 - R_2$$ **Equation 4-25**

where:

n_1 is the number of values in one of the data sets

n_2 is the number of measurements in the other,

R_1 is the sum of the ranks of values assigned to group 1, and

R_2 is the sum of the ranks of the values assigned to group 2.

The two formulas above yield a different U and the smaller of the two is the test statistic. The critical value of the test statistic is looked up in a table for small samples (where the number of samples in the largest group is 20 or fewer). For large samples, the sampling distribution of U approaches the normal distribution with mean

$$\bar{U} = n_1 n_2 / 2$$ **Equation 4-26**

and standard deviation

$$s_U = \sqrt{n_1 n_2 (n_1 + n_2 + 1)/12}.$$ **Equation 4-27**

The significance of an observed value of U is established by computing the value of a standard normal deviate of U by

$$z = (\bar{U} - U) / s_U$$ **Equation 4-28**

and observing if it exceeds the value of z at the chosen α in a table of standard normal probabilities.

As an example of the Mann-Whitney U test, eleven paired intake and effluent samples from Facility B in the PISCES database are shown in Table 4-9. The test statistic is easily computed in an EXCEL® spreadsheet by collecting the effluent data, followed by the influent data, in a column and using the RANK function to identify the rank of a specific value relative to the entire column of values. The sums of ranks for the effluent data and influent data are then found and the test statistic computed. In this example, the sums of the ranks are 151 and 102 and the U's are computed to be 36 and 85. U = 36 is the desired value (n_1 and n_2 are both equal to 11). The critical value of U for a one tailed test with $\alpha = 0.05$ is 34. Therefore, the calculated value of U exceeds the critical value and the null hypothesis, that the two datasets are drawn from the same population is rejected. Thus in this case, it appears that concentrations of mercury in the effluent samples are higher than those in the intake with 95% certainty. Tables of critical values for the Mann-Whitney U test can be found in Siegel, 1956 or other textbooks on non-parametric statistics.

Like the Mann-Whitney U test, the Kolmogorov-Smirnov two sample test also tests whether two samples are drawn from the same or from different populations. In this test, a cumulative distribution function is made using each set of data. The largest deviation between the two distributions in any class interval is then compared to the critical value. The test is demonstrated in Table 4-10 using data from a gas-fired power plant in the western U.S.

The largest difference, D, between the two cumulative sampling distributions Sn_1 and Sn_2 is 2, shown in bold in Table 4-10. The critical value at n= 17 and $\alpha = 0.05$ is 8. Therefore, the null hypothesis is not rejected using this test, and the values of the effluent cannot be said to be drawn from a different distribution than the intake values.

Table 4-9
Effluent and Intake Concentrations from Facility B in the PISCES Database Demonstrating the Use of the Mann-Whitney U Test

	Total Mercury ng L^{-1}	Rank of Combined Concentrations
Effluent Data	0.002619	13
	0.001988	8
	0.002733	14
	0.00205	9
	0.002234	11
	0.003574	16
	0.00393	17
	0.00404	18
	0.001446	2
	0.01356	22
	0.00703	21
Sum of Effluent Ranks		151
Intake Data	0.004412	19
	0.00467	20
	0.002216	10
	0.00319	15
	0.002368	12
	0.001331	1
	0.00162	3
	0.001789	4
	0.001973	7
	0.00188	6
	0.00186	5
Sum of Intake Ranks		102

Table 4-10
Effluent and Intake Concentrations from a Western Gas-Fired Power Plant Demonstrating the Use of the Kolmogorov-Smirnov Two Sample Test

Effluent Total Mercury ng L^{-1}	Data Class Interval	Sn_1	Sn_2	D $\lvert Sn_1 - Sn_2 \rvert$
0.00810	.0000 - .002	2	1	1
0.01300	.0021 - .004	2	2	0
0.00575	.0041 - .006	6	4	2
0.00050	.0061 - .008	9	7	2
0.00820	.0081 - .010	13	11	2
0.00712	.0101 - .012	14	13	1
0.00776	.0121 - .014	16	15	1
0.00516	.0141 - .016	17	16	1
<0.004	.0161 - .018	17	16	1
0.01360	.0181 - .020	17	16	1
0.00676	.0201 - .022	17	16	1
0.01440	.0221 - .024	17	16	1
0.00479	.0241 - .026	17	16	1
0.01060	.0261 - .028	17	17	0
0.00916				
0.00404				
0.00802				
Intake Total Mercury ng L^{-1}		Sn_2		
0.00750	.0000 - .002	1		
0.00570	.0021 - .004	2		
0.02780	.0041 - .006	4		
0.00060	.0061 - .008	7		
0.00725	.0081 - .010	11		
0.01350	.0101 - .012	13		
0.01230	.0121 - .014	15		
0.00606	.0141 - .016	16		
0.00400	.0161 - .018	16		
0.00964	.0181 - .020	16		
0.00860	.0201 - .022	16		
0.01480	.0221 - .024	16		
0.01040	.0241 - .026	16		
0.00845	.0261 - .028	17		
0.01030				
0.00481				
0.00978				

4.2.8.4 Nonpoint Sources

Quantification of nonpoint sources represents a special challenge in the case of mercury. Nonpoint sources are driven by hydrologic events where the two factors of greatest importance are the supply of mercury in watershed soils and on watershed surfaces available to be transported, and the magnitude and frequency of runoff events that provide the driving force for transport by erosion, washoff, and runoff. It is beyond the scope of this report to provide a comprehensive discussion of the physical, chemical and biological processes which affect the fate and transport of mercury in watersheds. It is of utmost importance, however, to impart to the reader the fundamental inability of current watershed models to address these processes in a quantifiable way.

The two issues for an individual power plant in terms of the TMDL are the nonpoint sources associated with the power plant itself and those that come from other sources. Of the nonpoint sources associated with a power plant, stormwater is the greatest concern in the TMDL process.

4.2.8.4.1 Stormwater

Stormwater originating from power plants may contain trace levels of mercury. This is primarily due to the fact that coal, which contains mercury in low part per billion levels, is stored and combusted on site. Runoff which contacts coal piles may contain elevated levels of both dissolved mercury and mercury bound to coal particles. Runoff that has contacted surfaces where particulate matter from the coal combustion process have been deposited may also contain low levels of mercury. Aside from loads directly attributable to the facility however, nonpoint source runoff contains mercury derived from wet and dry atmospheric deposition, part of which is due to anthropogenic sources other than the power plant itself, and other “natural” or “background” sources (e.g. soil particles, decomposed or decomposing plant matter, leaves, etc).

An important note with regard to rainfall is that it generally contains total mercury levels that are higher than those in runoff. This occurs because mercury in precipitation has few solids to interact with and is at or near equilibrium with gaseous mercury in the atmosphere. Once rainfall contacts surfaces where it comes into contact with solids and other elements with which it may interact, it partitions to and interacts with these materials. To the extent that these solids settle out of the runoff water, the total mercury concentration that was initially in precipitation is lowered, which amounts to a substantial reduction. Rainfall may contain on the order of 15 ng L^{-1} of mercury, whereas runoff may contain on the order of 5 ng L^{-1}.

Thus, when the issue of stormwater loads from the plant arises, a point that stakeholders should emphasize is the credit that one should get for mercury in rainfall. In this regard it would advisable to collect periodic samples of rainfall (perhaps quarterly) to establish the levels of mercury in precipitation. This, multiplied by the total amount of precipitation and the drainage area of the site, would establish the load of mercury incident to the site in precipitation. This load would then be subtracted from the stormwater (or combined stormwater and effluent load if stormwater and effluent are mixed), much in the way a credit would be given for plant intake credits in its raw water. Furthermore, facilities should be able to take credit for the treatment of atmospherically deposited mercury, including dry deposition, that can reasonably be attributed to other sources. In this regard, the facility may wish to monitor precipitation both on-site and off-site (preferably upwind of the normal wind direction) in order to establish that portion of the atmospheric load attributable to other sources.

An interesting topic recently arose in the State of Georgia associated with the promulgation of a new industrial general stormwater permit. The permit language states that *"if the TMDL establishes a specific numeric wasteload allocation that applies to an operator's discharge, or to storm water discharges associated with industrial activity in general, then the operator must incorporate that allocation into the facility's SWP3 and implement all necessary measures to meet that allocation."*

Thus, in the case of mercury TMDLs established in the State of Georgia, is appears that the stormwater load is considered part of the allocation assigned to regulated facilities. However, in establishing the current load, EPA only monitored effluent from facilities, and not necessarily stormwater. If the stormwater loads or concentrations must then be considered as part of the allocation assigned to the facility, then the facility may not be able to meet the allocation. Stakeholders should take care in future TMDLs that all sources from their industrial facility are identified and recognized in the TMDL.

4.2.8.4.2 Groundwater

Groundwater may also be a source of mercury to a power plant. Groundwater from wells may be used to supply potable or process water to the facility. To the extent that this occurs, credit should be available for mercury in well water, provided that groundwater has not been affected by the facility.

Another source of mercury to plant facilities may be the movement of shallow groundwater on-site that may contain mercury. To the extent that shallow groundwater may intersect ash ponds and other water detention facilities, this mercury may contribute a load to the effluent and credit should be available for it. Shallow groundwater may contain significant levels of mercury held in solution by DOC, especially in low lying areas where wetlands are commonplace. The data of Harvey, et al. (2002) show that mercury levels in shallow groundwater in the Everglades are typically about 1 ng L^{-1} but range up to 10 ng L^{-1}. While these levels are low, concentrations of this order may represent a substantial contribution to the mercury budget of an ash pond in communication with shallow groundwater, depending on local groundwater flow rates. The credit would be established by monitoring shallow groundwater up gradient of the facility (perhaps quarterly) and multiplying this concentration by the groundwater flow rate and the depth over which the intersection of the pond and shallow groundwater intersect.

4.2.8.4.3 Other Nonpoint Sources in Watersheds

Nonpoint sources of mercury in watersheds that would not be attributable to the power plant abound. As mentioned previously, the volatility of mercury makes it available for atmospheric transport of a global scale. Wet and dry deposition of mercury from the atmosphere assures that it is ubiquitously found in watershed soils and water. Loadings of mercury to waterbodies from watersheds occur during rainfall and runoff events and on a more continuous basis through the slow drainage of surface water from wetlands and the flow of shallow groundwater into streams and lakes.

In addition to the loadings of mercury that may result from the deposition and subsequent transport of atmospheric mercury into water bodies, other sources of mercury also contribute to the mercury loading of water bodies. A not uncommon source of elevated mercury in watersheds is the natural background in soils and geologic materials. For instance, in the mineralized rock formations of the Ouachita River basin, AR, that have historically been mined for mercury, mercury concentrations in rock ranges from 0.01 mg kg^{-1} to 0.25 mg kg^{-1} and from 0.02 mg kg^{-1} to 0.30 mg kg^{-1} in soils derived from the weathering of these formations (FTN Associates 2002). Calculated mercury concentrations in suspended sediments from the Guadalupe River (Tetra Tech 2005) range from 0.11 mg kg^{-1} to 0.58 mg kg^{-1} from areas unaffected by mercury mining activities, while concentrations in suspended sediments from mine-affected areas ranged from 0.63 mg kg^{-1} to 61.26 mg kg^{-1}. These values are as high as mercury levels found in coal (USGS 2001) and rival the levels reported in fly ash (See Section 2.2). Mercury concentrations in sediments in other areas may more typically be in the low part per billion range, as reported in EPRI (2003). Even at these low levels, the mercury associated with particulates is a thousand times or more higher than the typical concentrations in water (1 µg L^{-1} vs 1 ng L^{-1}) and can contribute substantially to concentrations in the water column.

Another nonpoint source of mercury to waterbodies is via transport of organic matter from the watershed. Plants bioaccumulate mercury to some degree, either from mercury in soils or from the assimilation of atmospheric gaseous and particulate mercury. For instance, tree leaves grown in mesocosms contained on the order of 150 ng g^{-1} (ppb) (Ericksen et al. 2003). Friedli et al. (2001) reported levels of coniferous and deciduous tree litter ranging from 13.9 ng g^{-1} to 71.3 ng g^{-1}. EPRI (2004) reports mercury concentrations in deciduous tree leaf litter ranging from 100 ng g^{-1} to 270 ng g^{-1} in south Georgia. When this plant material decomposes it can be transported to the waterbody in particulate form, carrying with it part per billion levels of mercury. An overlooked avenue of transport into waterbodies is the direct deposition of mercury via litter fall from overhanging trees. Balogh et al. (2002) attributed elevated October levels of methylmercury in Little Cobb River, MN to leaf litter deposited in the stream during autumn litter fall. These processes are either inadequately represented or not considered at all in current watershed mercury models.

Loss of mineral and particulate matter in soils can be aggravated by natural and anthropogenic activities. Forest fires have the affect of volatilizing much of the mercury in forest litter into the atmosphere (Fiedli et al. 2001). In addition, denuded soils lead to accelerated erosion. Clear cutting can also lead to enhanced mercury losses from forested areas (Porvari et al. 2003). Mercury losses were associated with total organic carbon and levels in runoff (27.9 ng L^{-1}), rival those found in runoff from mine sites in California (13.4 ng L^{-1} to 82.2 ng L^{-1}) (Tetra Tech 2005). It has been suggested by Dean et al. (2004) that land clearing in the early to mid-1800s in the southeastern United States may be responsible for the entry of much of the mercury currently found in aquatic ecosystems in this part of the country. Again, the models currently in use to characterize transport of mercury from watersheds deal with these topics insufficiently and are incapable of quantifying the mercury loading to aquatic systems from historical or ongoing catastrophic events.

Other potential nonpoint sources of mercury in watersheds become increasingly difficult to quantify. For instance, mercurial pesticides had many applications in agriculture including herbicides, fungicides, and seed treatments. Although they are no longer in use in the U.S., their introduction into watersheds associated with farming practices dating from the 1920s could represent a significant load in some cases. Aspelin (2003) indicates that about 13 million pounds of inorganic mercury was used as a fungicide in the period from 1930 to 1975. A list of commonly used mercury containing pesticides can be found in Appendix A of EPRI (2004).

4.2.9 Linkage Analysis

Once the current loads of mercury into the waterbody are estimated, the TMDL must establish the linkage from the load entering the waterbody to the tissue levels of mercury in fish. This is the point at which the TMDL process suffers a major setback. There are two major reasons for this. First, there are no adequate environmental markers for mercury. So, for instance, it is impossible to tell whether the mercury in a soil or water matrix came from an industrial process, a combustion process, was deposited by atmospheric means or originates from other natural sources. While it is possible to measure different stable isotopes of mercury added to a water body, such as in the METAALICUS study, there is no way to positively identify sources of mercury using isotopic methods at this time. Second, there is no clear relationship between the loading of mercury to a waterbody and the accumulation of mercury in fish tissue. This has been discussed in detail in EPRI (2003) and earlier in this report (see Section 4.2.4.1). Even so, the models currently available to estimate fish tissue concentrations from loads are linear with respect to total mercury, methylmercury production, and methylmercury bioaccumulation, and predictions of reductions in fish tissue given reductions in loads are artifacts of this formulation and assumption. A review of the currently available models and combinations of models for linkage of mercury loads to concentrations in fish tissue is provided in Appendix B.

The next few sections briefly highlight important facets concerning linkage analysis.

4.2.9.1 Point Sources and Mercury in Fish Tissue

Mercury discharged by a point source typically is in the divalent (inorganic) form. While there is some accumulation of divalent mercury in lower trophic level aquatic species, the methylation of mercury is essential for substantial bioaccumulation and for the expression of its predominant toxic effect. Predictable relationships among inorganic mercury, methylmercury and mercury in fish tissue have not been established between point sources and mercury in fish tissue. In fact, the opposite has been observed in at least one instance.

The Olin mercury cell chloralkali plant in Augusta, Georgia, has an NPDES permit that allows discharge at up to 11 parts per billon. Despite this relatively high discharge level relative to ambient concentrations, no gradients in total or methylmercury that would implicate Olin as a source were observed in the waters, sediments or fish tissue in the Savannah River downstream of the plant (U.S. EPA 2000a). Conversely, fish tissue concentrations and total mercury appeared to increase with distance downstream from the plant. Upstream to downstream, methylmercury remained more or less constant at a value of about 0.07 ng L^{-1}. There is no evidence that total mercury was limiting methylmercury production in the river as total and methylmercury were slightly negatively correlated ($r = -0.2$) and fish tissue mercury and methylmercury were uncorrelated ($r = 0.09$).

What does stand out in the data, however, is that methylmercury and fish tissue levels were higher in the tributaries (0.28 ng L^{-1}, 0.70 mg kg^{-1}, respectively) than in the river (0.08 ng L^{-1}, 0.35 mg kg^{-1}, respectively). It appears that methylation and bioaccumulation occur primarily in the tributaries, which consist of low gradient streams with extensive riparian wetlands. The source of the mercury in the tributaries could not have been aqueous discharges from the Olin plant, which operates on the mainstem. Thus, even with what could be considered a major mercury source, there was no evidence suggesting a relationship between Olin's discharges and fish tissue mercury in the Savannah River.

4.2.9.2 Methylation

Methylation is the process by which divalent mercury is transformed into methylmercury, the more bioaccumulative and toxic form. The primary mode of methylation is through the activity of sulfate reducing bacteria, although abiotic methylation is also thought to occur. Demethylation is primarily driven by photolytic reactions, which may contribute to higher methylmercury levels in waters with high DOC where light penetration is limited. A more detailed discussion of methylation can be found in EPRI (2003) and the reader is directed there for additional technical information. What is important to point out in this discussion is the lack of ability of current mercury science, and models constructed on the basis of the existing science, to predict the extent or magnitude of methylation in aquatic systems. For this reason, models must rely on empirical relationships between total and methylmercury in a given waterbody. The accurate characterization of this relationship is usually limited by the available data, which typically consist of a handful of observations.

4.2.9.3 Bioaccumulation

Bioaccumulation is the process by which methylmercury is taken into and concentrated in the tissues of higher trophic level organisms. This process is thought to occur mainly through ingestion of lower trophic level organisms with a corresponding and characteristic jump between trophic levels. Despite this knowledge, information on the food chain relationships between upper and lower level organisms are generally not well studied in any given system. More detailed information on bioaccumulation can be found in EPRI (2003).

Models to adequately simulate the bioaccumulation process are lacking. Instead, most TMDLs rely on another empirical constant that assumes linearity between methylmercury in the water column and methylmercury in fish tissue, the BAF. Despite the fact that the BAF is dependent on a host of site-specific factors, not the least of which is the complexity of the underlying foodchain, BAFs are widely compared between waterbodies. EPA's draft guidance document even provides a distribution of BAFs calculated nationwide. Few of the studies that form the basis of this distribution have been reviewed for comparability, mixing fish species, waterbody types, and seasons. If the BAF is to be used on a specific waterbody to characterize the relationship between methylmercury in water and methylmercury in fish, then it must be developed on a site-specific basis with enough data to accurately define the result. Recall that the

BAF is not a measurement. It is a random variable that is calculated as the quotient of two other random variables, both of which are characterized by significant uncertainty. The result is a constant whose value is highly uncertain, although it is treated in most TMDLs as a true constant.

What is salient to this discussion is that the BAF (along with the methylation translator) is often used in TMDLs to span the chasm between total mercury in the water columns and mercury in fish tissue based on a handful of observations. This will invariably result in regulation that misses the mark. Stakeholders should insist on, and probably assist with, the collection and analysis of sufficient data to reduce the uncertainties to reasonable levels.

4.2.9.4 *De Minimis* Status

In many TMDLs the point sources are considered *de minimis* contributors to mercury in a waterbody given the magnitude of other sources. In some ways this is beneficial, in that it takes dischargers out of the public spotlight. The downside is that little of the resources of the TMDL are spent characterizing point sources. As with other measurements made during the course of the TMDL study, they typically are inadequate to characterize the concentrations or load from a facility or group of facilities. The result is a small allocation (because the load is small) that may or may not be achievable if turned into a compliance requirement. Prudent stakeholders should take the time and effort to characterize their effluent and make sure that the agency has adequate information to make decisions concerning allocations, even though *de minimis* status appears to provide regulatory cover.

4.2.10 TMDL Development, Load Allocations, and Wasteload Allocations

A TMDL is supposed to establish the assimilative capacity of a waterbody for the pollutant of concern. In the case of mercury, given that increased (or decreased) loadings do not necessarily translate into higher (or lower) concentrations in fish tissue, this is a difficult, if not impossible task. In actuality it is the waterbody and its aquatic biogeochemical systems, that condition the response of the system.

4.2.10.1 Assessment of Loading Capacity

In the TMDL, it is a requirement that the maximum concentration or load based on the assimilative capacity or water body be established. This is done in several ways as discussed in Section 1.6.5.1. Loading assessments typically are separated into point and nonpoint. The nonpoint assessment is frequently divided into atmospheric sources and all others. However, the assessment of loading capacity is usually computed as a percentage of the current load based on a percentage reduction in the TMDL target. If a 30% reduction is calculated in fish tissue in order to move from current levels to the standard, then the same 30% will be applied to the load to estimate the required reduction. If a 50% reduction in the water column concentrations is calculated by comparing existing water column measurements to the WQT, then that 50% reduction will be applied to the loads. Thus, the way to impact the assessment of loading capcaity is to assure that the TMDL target and the assessment of current load are addressed in an appropriate way.

Stakeholders should carefully review information related to the setting of the TMDL target. The lower the target is set, the lower the allowable load to the water body will be. If the TMDL uses a water column-based target level for methylmercury, stakeholder should carefully review the assessment of the relationship between methylmercury in the water column and methylmercury in fish tissue; that is, the development of BAFs or equivalent factor. The higher the BAF, the lower will be the calculated water quality target. In addition, if the water column-based target is based on total mercury, the assessment of the relationship between methylmercury and total mercury; that is the methylation translator or equivalent factor, should be carefully reviewed. The higher the percentage of methylmercury to total mercury used, the lower will be the total mercury WQT.

As recommended in the previous section, the best way that stakeholders can affect the point source loading analysis and provide protection for themselves is to make sure that adequate information is available to the regulatory agency on their discharge and other point source discharges in the watershed. Given the limited financial and manpower resources of the agencies, stakeholders should collect this data and view the expenditure as they would a good “insurance policy”.

In reviewing the nonpoint source load assessment, stakeholders should look for overly conservative assumptions. Such assumptions lead to an inflated assessment of the current load. The difference between current load and assimilative load is therefore larger. When multiplied by the percent reductions required to meet the TMDL target, the resulting load reduction is larger and the allowable load becomes smaller, ultimately making compliance more difficult to achieve.

4.2.10.2 Development of Reductions by Source

Once the TMDL and the load reductions are established, allocations are made to the various sources; point and nonpoint, including atmospheric. This is normally done in one of several ways that may be found in EPA guidance for developing wasteload allocations (U.S. EPA 1991).

One way is to require that all sources achieve the same percentage reduction as the overall TMDL. This places an especially onerous burden on point source dischargers whose discharges may already be in the low part per trillion range. The best treatment processes available for mercury removal can only consistently treat effluent to the low part per billion range. If dischargers are required to reduce from, for instance, 10 ng L^{-1} to 5 ng L^{-1}, the treatment technology simply does not exist to do so.

Another method commonly employed is to require reductions based on the discharger’s percentage of contribution to the current load. Thus, if nonpoint sources currently are responsible for an estimated 80 % of the load and the load reduction is 30%, they would be required to reduce the overall load by 24%. If point sources were 20% of the load, they would be required to reduce the overall load by 6%.

While neither of these methods are founded in scientific or engineering principles (i.e. neither is based on effectiveness, feasibility or cost) the latter is more advantageous to point sources dischargers in most cases since their relative contribution is normally smaller. If point sources are categorized as *de minimis*, they may not be subject to load reductions at all. In such cases, they may be allowed to continue to discharge at current levels. In other cases, point sources have been offered the option to take an effluent concentration at the end-of-pipe equal to the WQT or to develop a mercury minimization plan. At a minimum, point source dischargers normally are asked to monitor their effluent using Method 1631.

Being capped at current discharge levels is the best outcome that a point source discharger could hope for in terms of an allocation. The next best outcome is being given the option to develop a minimization plan. Under this approach, the discharger is allowed to identify sources of mercury to its discharge and develop a plan for eliminating them, rather than taking an allocation that could become the basis of a permit limitation at a later time.

An approach that has been advocated by the Oregon Association of Clean Water Agencies (ORACWA 2005) in its comments to the Oregon DEQ on the Willamette River TMDL is to identify best management practices that would reduce mercury loads to the Willamette and rank them according to anticipated effectiveness and cost. The most cost-effective approaches would be implemented first, in an overall adaptive management framework, with additional measures implemented as the need is dictated by monitoring. Costs of implementation could be shared in an equitable way by all dischargers.

4.2.10.3 Major Versus Minor Sources

In some states, minor dischargers are exempted from the requirement to monitor, the thought being if they are not contributing much flow, they cannot be contributing much mercury. However, given their cooling water requirements, electric generating plants tend to be large volume dischargers. If non-contact cooling water were to be exempted, the argument might be made that a plant is a low volume discharger of wastewater.

4.2.10.4 Individual Waste Load Allocations

In some TMDLs, point source dischargers are given an individual waste load allocation. This can be either concentration based or load based. Concentration based allocations would normally be at the water quality TMDL target (or the water standard) and expressed in nanograms per liter (parts per trillion). Concentration based allocations may also be at the current measured discharge level.

Load based allocations are in mass per time units like mg day^{-1} or kg yr^{-1}. These allocations are normally developed by taking a concentration, as identified above, and multiplying by the average flow of the facility. In some case, they are developed using the design or permitted flow of the facility. Obviously, the larger the load allocation the better for compliance purposes. Load based allocations are preferred to concentration based allocations for the simple reason that it may be easier to reduce flows (and loads) by implementing water conservation measures than to identify and eliminate mercury sources or treat wastewater.

Currently, there appear to be few states with guidelines for permit writers to take TMDL allocations and develop permit limits. That is not to say it will not happen when the need arises. Stakeholders should lobby the agency for a “margin of safety” specific to the point source allocations. For instance, if the regulatory agency determines that the load for a discharger or group of dischargers is 1 kg yr^{-1}, then there should be a safety factor that allows for variation in this load. This type of analysis underlies the NPDES process, but is neglected in the TMDL process. It has already been shown that the concentrations in effluents have a sampling distribution around a mean. If the agency determines (based on the mean or even a single sample) that the concentration is ‘x’ and the mean annual discharge is ‘q’, then the allowable annual load is ‘xq’. The allowable load should then be a percentile (say the 90^{th}) of the loading distribution. On top of this, there should be a margin of safety to account for the fact that the agency may not have accounted for all the point sources in the watershed. If the point sources are designated as *de minimis*, then this argument carries yet more strength.

The typical application of a margin of safety in a TMDL results in just the opposite. The TMDL is established and allocations are made to point and nonpoint sources based on the required overall load reduction. Once this done, a margin of safety is applied to the entire TMDL and allowable loads become reduced by this factor. For instance, if the TMDL is 1 kg yr^{-1}, point sources are allocated 0.1 kg yr^{-1} and the nonpoint sources 0.9 kg yr^{-1}, the MOS (say of 20%) is applied to the entire TMDL and the point source allocations becomes 0.08 kg yr^{-1}. Were this allocation to result in a permit limit, the maximum allowable annual load would be 0.08 kg yr^{-1}, the discharger would already be forced to perform at a level below its current capability based on the mean, and substantially below its capability based on a percentile of its discharge.

4.2.10.5 Aggregate (Categorical) Waste Load Allocations

In the case that particular dischargers do not stand out as the targets of regulatory scrutiny, the TMDL may assign a group or aggregate allocation. Groups may include all point source dischargers, all major or minor dischargers. Groups are not normally defined based on industry type or geography. This also commonly done when the regulatory agency either does not have the depth of information to develop individual allocations or where the mercury load from the group is thought to be small compared to the overall mercury load. In this case, the group would be given a mass load, most likely in kg day^{-1} or kg yr^{-1} with the caveat that if as a group, the dischargers exceed the allocation, they may be subject to individual allocations at a future time. Presumably, someone in the agency would analyze the self-reported data from these facilities and make this determination. It is also presumed that the summed annual load would be the most relevant comparison.

All things considered, it is probably best to have an individual allocation, especially if the stakeholder has good information about its discharge and is uncertain about the information available for others.

4.2.11 Margin of Safety, Seasonal Variations, and Critical Conditions

In TMDLs for conventional pollutants and toxicants, critical conditions are normally considered. For instance, when permit limits are developed for the discharge of BOD or copper, the critical condition is low flow when mixing of the discharge with the receiving is minimal. For mercury, critical periods have not yet been defined (to the extent that they even exist) and typically the analysis is performed at the mean flow occurring in the system. The same is true for seasonal variations. Since it is not known to what extent seasonal highs or lows in methylmercury affect bioaccumulation, seasonality is normally not considered in mercury TMDLs. The fact that this language is a part of the TMDL process for mercury is an artifact of its anticipated use to address more conventional pollutants.

The margin of safety (MOS) is a factor, usually applied at the conclusion of the TMDL analysis, that further reduces the load allocation based on the agency's level of confidence in the answer. This type of MOS is explicit and is normally specified as a percentage of the overall TMDL load. The larger the explicit MOS, the lower will be the load allocations for any of the sources. Explicit MOS's as high as 50% have been used, although it is normal for the agency to tack on 10% to 20% of the total load as an additional reduction to account for uncertainty.

Explicit margins of safety in mercury TMDLs expressed as a percentage of the total load are not based on defensible scientific rationale. If there is a rationale, it is likely to simply be a policy decision by the agency.

Implicit margins of safety may also be used in the TMDL. An implicit margin of safety is unquantified (and largely unquantifiable). The typical TMDL language will state that "an implicit margin of safety is incorporated by the use of conservative assumptions in the analysis". The difficulty with this approach is that the agency doesn't know how conservative its assumptions are. In some cases, the agencies use both implicit and explicit margins of safety, which lead to even more restrictive loadings. In the case of the implicit MOS, the agency has no idea how conservative the assumptions are. In the case of the explicit MOS, the agency has no particular basis for selecting it.

Borsuk et al. (2002) reported on a probabilistic approach to incorporating uncertainty in water quality models used in TMDLs. The approach accounts for the residual error between observations and model predictions. The model plus randomly selected residual error is used to simulate time series values of the state variables, which are then statistically analyzed to determine the magnitude, frequency and duration of excursions above the water quality standard. Such an approach is feasible. However, as pointed out by the authors (and observed in the stochastic analysis using the Food Web Bioaccumulation Model to develop a mercury water quality target for the Willamette River), the consequence of performing this type of analysis is that the uncertainties in the data and the models lead to wide confidence bands on the answer, which would in turn translate to large margins of safety.

There are several problems with using a probabilistic approach for mercury TMDLs. First, models available to predict mercury bioaccumulation in fish tissue from atmospheric deposition are few and complex, and their predictive abilities are largely unproven. Even if adequate models were available for mercury that could predict fish tissue concentrations given loadings to a waterbody, the assumptions of linearity in these models and the lack of data to test them limits their ability to predict the impact of increased or decreased loadings with a definitive degree of certainty. Finally, the methodology to compare results to the standard is ill-defined. It lies outside of the agencies long-standing magnitude/frequency/duration paradigm based on acute and chronic toxicity principles. What do seasonal or year-to-year exceedances of a mercury water column-based target mean in the context of attaining the beneficial use?

For the present it would seem the best approach to advocate is a TMDL based on the use of mean values and an adaptive approach that recognizes the tentative nature of the analysis and accords an appropriate degree of leniency to dischargers.

4.2.12 NPDES Permitting

The “worst case scenario” for a point source discharger resulting from a mercury TMDL would be to receive a mercury limit in its permit. Unless the agency is amenable to developing limits which truly reflect the uncertainties in mercury concentrations in effluents, the resulting limits could be very difficult to achieve on a consistent basis. Since every discharger has some level of mercury in its discharge, a significant issue is at what concentration or load does mercury in an individual discharge become a public health or regulatory concern. In the normal regulatory framework, this question would be answered by doing a “reasonable potential” analysis. Such an analysis determines if the concentration in a dischargers effluent has the potential to exceed the water quality standard. There are several interesting challenges for the regulatory process in this regard:

- What is the mercury standard?
- What if the mercury standard is tissue based?
- Since the WQT has already been exceeded, does reasonable potential automatically exist for all dischargers?

This guidance will address these issues in the next few sections.

4.2.12.1 Reasonable Potential

The reasonable potential analysis is done by the regulatory agency to determine whether a discharger has the potential to exceed the water quality standard. In the case where there is a 303(d) listing on a waterbody and every discharger has the potential to contribute some level of mercury in its effluent, the agency certainly has and will likely exercise its authority to do a reasonable potential analysis. On the other hand, it may make a policy decision that all dischargers to a 303(d) listed stream automatically have reasonable potential to exceed the standard. The latter may occur especially in situations where data is lacking. But it may also be done to ease the work load for already overloaded permit writers and relieve the staff and management of making these difficult decisions on a case-by-case basis.

In the case where a TMDL has been established for a listed waterbody, it is assumed that the standard would be the WQT, if a water column-based target has been established. If not (if the stream is listed but there is not yet a TMDL) then the standard would presumably be the preexisting statewide standard. In some cases, there may only be a narrative standard. In many cases, however, the listing may be based on fish tissue and there may be no clear regulatory "path forward" for determining RP. Stakeholders should also be aware of specific permit writer's guidance for determining RP in their particular state, as they may differ from EPA's approach.

4.2.12.1.1 Tissue Based

In some states, RP may be established on the basis of mercury in fish tissue. The State of Idaho has developed guidance for its permit writers in this regard. The Idaho guidance simply states that if fish tissue mercury in a water body exceeds 0.24 mg kg^{-1}, the RP exists for any discharger to that waterbody. While the guidance is relatively straightforward, it may unduly place a burden on point source dischargers to the waterbody, regardless of whether they have significant potential to discharge mercury. The 1997 Draft Mercury Permitting Strategy (USEPA 1997a) proposed that a state's "permitting authority must find reasonable potential and impose a Water Quality-Based Effluent Limits (WQBEL) when the geometric mean of a pollutant in fish tissue samples exceed[s] the tissue basis for [human health] criteria, after consideration of the variability of the pollutants' bioconcentration and bioaccumulation in fish, and the facility discharges detectable levels of the pollutant." This statement suggests that RP should be established for dischargers with *detectable* quantities of mercury if fish tissue concentrations are above an adopted standard. The qualifier for "consideration of variability of the pollutant's bioconcentration and bioaccumulation in fish" leaves the door open albeit in an ill-defined way.

Other means of establishing RP based on the translation of a tissue-based mercury standard to a water column-based standard may be possible; however, to date, available information suggests that none of the states have adopted such an approach.

4.2.12.1.2 Water-Column Based

More typically in the regulatory process, the water quality standard is water column-based. EPA recommends finding that a permittee has RP if it cannot be demonstrated with a high degree of confidence that the upper bound of the distribution of the effluent data is below the water quality criteria at the specified flow condition. If data is limited, then the agency may use a statistical process to first establish the maximum confidence level based on a desired confidence level in the effluent data (U.S. EPA 1991). In such a case, the relationship

$$p_n = (1 - \text{confidence level})^{1/n} \qquad \textbf{Equation 4-29}$$

where

p_n is the percentile level of the highest value in the data, and

n is the number of samples.

For instance if there are 10 effluent samples, and the desired level of confidence is 95%, then

$p_n = (1 - 0.95)^{1/10} = 0.74$

which means that the largest value in the data is greater than the 74th percentile of the data. The second part of the analysis relates the percentile value calculated above to a selected upper bound of a lognormal distribution. The CV of the data is estimated and tables in U.S. EPA (1991) are used to select a “reasonable potential multiplying factor”. For instance, with a CV of 80%, n = 10 samples, at the 95% confidence level, the multiplier is 2.0. Therefore, the highest value from the effluent dataset would be multiplied by 2, and this concentration (the projected maximum receiving water concentration or RWC) would be compared to the WQS. So, if the highest value in the dataset is 5 ng L^{-1} and the multiplier is 2, a value of 10 ng L^{-1} would be compared to the WQS. EPA recommends that a state or a tribe find reasonable potential if the RWC exceeds the WQS (or in the case of a TMDL, the WQT). In a TMDL situation, the WQT would likely be exceeded by invoking this procedure.

In EPA’s guidance document the paradigm is, and a conservative assumption is made, that the permittee is discharging a toxic pollutant under low flow conditions with attendant deleterious impacts to aquatic life when this combination occurs. The high percentile effluent value and the low flow conditions in the receiving waterbody are assumed to be independent events. Furthermore, the objective is to assure that this “toxic” combination of high discharge effluent concentration and low flow in the receiving water rarely occurs.

With mercury, the scenario is quite different. First, the value of interest is the mean value in the effluent, rather than an arbitrarily selected high value in the distribution of discharge concentrations. This is the case because the concentration of interest is the long-term average based on human health and not toxicity to aquatic life. Next, the RWC may not be discharged at levels independent of the receiving water concentration. If fact, levels of mercury in background may be correlated with levels in the discharge. Therefore, the combination of higher effluent flow and average concentrations in ambient water does not constitute the “rare” and “lethal” event that EPA’s analysis presupposes. Finally, the most relevant comparison is the one that has been made consistently throughout this guidance document, that of the mean of the effluent to the mean value of the WQS. Stakeholders should try to impress upon the permitting authority that the RP analysis presented in its 1991 guidance document is inappropriate when the pollutant is mercury and the concern is the protection of human health. In this case, the RP procedure outlined in the U.S. EPA (1991) is overly conservative and would result in RP in almost every case.

If the discharger has collected sufficient data, it may want to supply the permitting authority with his own analysis based on mean values. In such an analysis, the assertion should be that if the population effluent mean cannot be said to be above the WQS or WQT, then RP should not exist. Even if this is the case, RP should not exist if the population effluent concentration mean cannot be judged to exceed the population mean of the influent concentrations.

In a recent permit issued in the southeastern U.S., the procedures recommended by the U.S. EPA, described above, where used to determine RP for the outfalls of a coal-fired power plant.

In this case, the discharger was spared the requirement of having permit limits because of the high statewide WQS (in this case 51 ng L^{-1}). If the standard had been 12 ng L^{-1} rather than 51 ng L^{-1}, most of the outfalls would have required permit limits based on the limited data available. Even though the use of this RP analysis did not result in permit limits for the discharger, a precedent has been set for the use of this procedure. When the WQS is revised downward (as it is likely to be), the application of this procedure will result in the requirement that many outfalls will have mercury limits where there is no need.

4.2.12.2 Permit Limits

Even if RP is determined by the permitting authority, there is no need to develop permit limits for point source dischargers, especially if the presumption is that the point sources are *de minimis*. Stakeholders should be aware of the regulatory agency's procedures, however, and be armed with the knowledge to challenge inappropriate procedures and or those that are inappropriately applied in the case of mercury. Stakeholders should also be aware of specific permit writer's guidance in their state, as they may differ from EPA's approach.

The U.S. EPA's recommended procedure for developing permit limits based on human health protection is to develop limits that will meet the WLA every month. These are developed by setting the average monthly limit (AML) to the WLA. The maximum daily limit (MDL) is then calculated from a procedure in its 1991 guidance document. The procedure involves estimating the CV of the data and then identifying multipliers from a table based on the number of effluent samples to be collected each month. If, for instance, one sample per month is to be collected and the CV is 80%, then the MDL would be 1.61 times the AML.

Note that these are concentration based limits. Some assumption concerning daily and monthly flow would have to be made by the permitting authority to translate between concentration and mass based limitations. Consideration should be given to the fact that variability in flow affects the variability in mass limits. Thus, daily or monthly limits should consider the CV of the mass load, rather than using the CV of the concentration data and assuming the flow is constant. This would result in a higher daily limit. For instance, if the CV of the mass load is 150% versus 80% (the assumed CV of the concentration data alone), the daily load based on the MDL would be 2.09 times the AML, rather than 1.61 times higher (based on Table 5-3 in U.S. EPA, 1991) as identified in the example in the previous paragraph, giving the discharger greater flexibility in meeting a daily load limit.

In the permit referred to in 4.2.12.1.2, procedures in US EPA (1991) were also used to establish monthly and daily permit limits for an outfall that had a previous mercury limit. In this case, the new AML was set at the statewide WQS and the daily limit was developed using a multiplier (1.46, assuming a CV of 60% and 1 sample per month at the 95% confidence level) on the AML. The permittee has been given a compliance schedule to comply with the new permit limit of 50 ng L^{-1} (the old permit limit being 400 ng L^{-1}). Again, the unfortunate outcome of this analysis is not the immediate result, but the fact that a precedent has been set by the permitting authority that will have unfavorable impacts at some future time.

In cases where the state provides the option for the discharger to develop a minimization plan, this often occurs in lieu of developing permit limits.

In California, GWF Power Systems recently submitted an "Infeasibility Analysis" to the San Francisco Bay Regional Water Resources Control Board (RWQCB) to request a compliance schedule for meeting proposed mercury limits (GWF 2005). GWF was forced to demonstrate that it could not meet the proposed limits, which were developed as average monthly effluent limits (AMELs) and maximum daily effluent limits (MDELs) of 0.020 and 0.042 ng L^{-1} respectively. GWF showed using a statistical analysis of its effluent data that the 99.9^{th} percentile values from its effluent characterization exceeded the maximum effluent concentration (MEC) by almost a factor of two. As part of its petition, GWF agreed to pursue efforts to identify and characterize in plant sources (e.g. cooling tower blowdown, cooling tower makeup water, stormwater, and chemical additives for water treatment). GWF requested a five year compliance schedule for meeting mercury limits. It is not known at this point whether relief from immediate compliance was granted by the RWQCB in this case.

In the State of Maine, the Department of Environmental Protection (DEP) has promulgated interim effluent limitations and controls for the discharge of mercury (see Maine 06-096, Chapter 519). All facilities that come under this rule are expected to develop and implement pollution prevention plans. Facilities must take a minimum of three effluent samples at an interval of at least 30 days between samples. The DEP then establishes interim limits. Using all the valid data points, the mean value plus one standard error of the mean is calculated. This value is then "adjusted" using a multiplier to reflect a 95% level of probability. In the event that this level is below 4.5 ng L^{-1}, the discharger is given an interim average limit of 4.5 ng L^{-1}. Maximum limits are established by multiplying the average limit by a factor of 1.5. Interim limits may be adjusted for water conservation, production changes, and seasonal changes.

4.2.12.3 Minimization Plans

Minimization plans for mercury have been required of all kinds of dischargers in the wake of the first mercury TMDLs and as part of the requirements of statewide variances in Michigan and Ohio. The typical minimization plan requires the following elements:

- data on current influent and effluent concentrations;
- preliminary identification of all known mercury sources;
- a description of plans to reduce/eliminate known mercury sources;
- preliminary identification of other sources;
- a proposed schedule for evaluating sources; and
- a proposed schedule for identifying and evaluating potential reduction, elimination, and prevention methods.

Typically, the permittee is asked to commit to these elements in a compliance schedule associated with the NPDES permit. EPA Region 5 has issued comprehensive guidance for the development of minimization programs and plans (U.S. EPA 2004).

4.2.12.3.1 Sources of Mercury in Power Plants

In contemplating mercury in fossil fuel power plants, first and foremost the source that comes to mind is the fuel itself. Coal and other fossil fuels contain varying levels of mercury and the chief repositories for mercury in the combustion process have been reviewed in Section 2.2. Those repositories appear to be (in order of decreasing mass percentage), fly ash, flue gas emission, FGD scrubber material, wastewater treatment plant sludge, and bottom ash. Obviously, those storages are important to the management of mercury in power plants, as well as the aqueous concentrations that result from contact of this material with water. As reported in Section 2.3, mercury in effluent from an FGD stacking pond had a geometric mean concentration of 18.4 ng L^{-1} and leachate from a FGD material landfill had a geometric mean concentration of 9.7 ng L^{-1}. Mercury in leachates of fly ash can range up to 400 ng L^{-1}. Cooling tower blowdown water at one plant had a geometric mean concentration of 7.6 ng L^{-1}. In addition, coal pile runoff may be a direct source of mercury into stormwater handling facilities.

Equally important, however, may be other sources of mercury introduced into the plant for any number of reasons. The intent of this section is to overview these additional sources with the objective of assisting facilities in developing mercury minimization plans, as they are required. Mercury is and has been used in many products. In a recent report for the Minnesota Pollution Control Agency (MPCA), Barr Engineering (2001) identified fourteen product lines that are potential sources of mercury either because of its desirable physical/chemical properties or because it is a contaminant in the manufacture of these products. These product lines include:

- lamps (fluorescent, high pressure sodium, mercury arc, metal halide, neon, UV disinfectant);
- mercury switches;
- mercury relays;
- timers;
- batteries (alkaline, Hg-Zn, Hg-Cd);
- rectifiers;
- flywheels;
- instruments (manometers, barometers, hydrometers, sphymonometers, thermometers, thermostats);
- mercury-operated flame sensor switches; and
- gas regulators.

Raw materials and chemicals (in addition to coal) that may contain mercury include:

- coal binders;
- ammonium hydroxide;
- chlorine;
- sodium hydroxide;

- sodium hypochlorite;
- sulfuric acid;
- water additives for cooling tower and boiler operations; and
- laboratory chemicals (products and as impurities in products).
  - acetic acid
  - acetone
  - aldehyde
  - ammonia
  - arsenic
  - bleach
  - buffers
  - chloride/chlorine
  - citric acid
  - iron, ferric chloride, ferrous chloride
  - glucose
  - manganese
  - Nessler's Reagent (mercuric potassium iodide, used in ammonia analysis)
  - nitric acid
  - organomercury catalysts
  - phenyl mercuric acetate (PMA)
  - standard mercury solutions
  - thiophene
  - vanadium
  - zinc
  - detergents and cleaners
  - pigments, dyes, stains, inks

For most of these product lines, a brief description follows. However, for some, such as dental preparations, which are unlikely to be a mercury source in a power plant, the reader is referred to Barr Engineering (2001).

Fluorescent lamps use small amounts of mercury to increase efficiency and prolong bulb life. The U.S. EPA estimates that fluorescent lamps manufactured from 1985 to 1991 contained about 55 mg per bulb. When the quantity of bulbs in a typical power plant is considered, this represents a significant source of mercury. It is imperative that used light bulbs are collected and disposed of properly.

Mercury vapor, metal halide, and high pressure sodium lamps also contain mercury. These lamps are widely used in industrial and office settings, especially outdoors. The US EPA estimates that the typical HID (high intensity discharge) lamps manufactured from 1985 to 1991 contains about 25 mg of mercury.

Mercury has been used in tilting-type switches for over forty years and as such may be found in many industrial facilities. The mercury in this type component is readily visible.

Mercury switches are found in many industrial devices including furnaces, thermostats, building security devices, refrigerators/freezers, space heaters, sump pumps, electrical heaters and coolers, rectifiers, oscillators and reactor vessels. Mercury-wetted reed relays are used for reliable switching of signals and power levels.

The instrument category includes manometers, barometers as well as thermostats and thermometers. Applications of mercury manometers and barometers include sphygmomanometers, gas meters, air flow measurement devices, diffusion pumps, steam flow meters and flame sensors. Power plants are known to have used mercury-containing differential pressure gauges across main condensers and flow meters for steam, boiler feed water, and condensate.

Prior to 1993, mercury was added to many types of batteries including alkaline manganese, silver oxide, carbon zinc, and zinc air types to control gassing and to reduce the risk of casing leakage and explosion. At this time, only certain “button cell” batteries still contain mercury, between 33 and 50% by weight. They are normally used in transistorized equipment such as radios, hearing aids, and watches.

Fungicides containing mercury were discussed in Section 4.2.8.4.3. At this time, U.S. registrations for mercurial fungicides have been cancelled; however, some product of this type may still be stored on site in storage sheds that may not have been adequately policed.

Like mercurial fungicides, all U.S. registrations have been cancelled. Some product containing mercury might still be present, however, in unused stores of older products.

Bulk liquid mercury may be present in laboratories but otherwise bulk storage in power plants is unlikely.

The mercury cell process has been used for many years to produce chlorine, caustic soda and hydrogen gas. Caustic soda and chlorine produced by this process normally contains trace quantities of mercury (0.02 to 0.2 ppm); however, in relation to the very low target levels for mercury in water, these are potent sources. One power plant found that its caustic contained 818 ng L^{-1} of mercury. Caustic soda is used routinely for pH adjustment of wastewater and other acids and acidic liquids and chlorine is routinely used for disinfection of wastewaters as a final step in the treatment process. Other products produced in the mercury cell process include potassium hydroxide and muriatic acid. Fortunately for users of these products, much of the caustic and chlorine used in the U.S. at this time is manufactured utilizing a membrane process. However, environmental compliance managers at power plants should check the source of these chemicals and switch to mercury free sources if possible and cost-effective.

Other sources of mercury in power plants include chemicals either used in bulk in certain processes (e.g. wastewater treatment plant) or in laboratories. Sodium hydroxide and sulfuric acid are often used in water and wastewater treatment for pH adjustment. Sulfuric acid, especially if it is procured from smelters, can be a significant source of mercury. One power plant found that its sulfuric acid contained from 432 ng L^{-1} to 181,000 ng L^{-1} of mercury. Environmental compliance managers at power plants should check the source of sulfuric acid and switch to a product containing less mercury if possible. One power plant noted that Nessler's reagent (an aqueous solution of potassium iodide, mercuric chloride, and potassium hydroxide, used as a test for the presence of ammonia) in its on-site laboratory contains mercury. Zenker's solution (a rapid nuclear fixative used as a mordant in some staining procedures) also contains mercury as mercuric chloride. A very helpful source of information on pollution prevention from laboratory facilities is WDNR (1997), which contains information of the mercury content of common cleaning agents as well as alternatives to mercury-containing laboratory chemicals.

4.2.12.3.2 Sampling Source Areas and Interpreting Results

If common sources of mercury are known and can be found by direct identification, alternatives can be sought to eliminate these sources. However, in some cases, it may be not be possible to identify the source without investigative work. Tracking the sources of mercury or any other trace level compound can be expensive; especially so with mercury considering the cost of the low-level analyses. Areas that exhibit high concentrations of mercury are of obvious interest; however, flow measurements should be made where possible so that loads can be calculated. Low concentration areas with higher volume flows can be just as important in overall mercury minimization as high concentration areas.

Although the current research has uncovered few data from internal source monitoring in power plants, two datasets were identified. In the first, twenty-six sump, effluent, backwash, overflow and blowdown sources were sampled during both wet and dry periods at a coal-fired power plant. Mercury concentrations ranged from about 4 ng L^{-1} to 880 ng L^{-1} during dry weather. During wet weather, mercury concentrations from the same sources ranged from about 6 ng L^{-1} to 1660 ng L^{-1}.

In another case, samples were taken of plant intake water, deep wells, cooling tower blowdown, two wastewater retention basins, and the final discharge. Mercury in the plant intake was measured at 3.7 ng L^{-1} (total unfiltered) and 1.8 ng L^{-1} (total filtered). The deep well sample contained 0.12 ng L^{-1} total mercury. Unfiltered samples from two cooling towers contained total mercury at 17 and 18 ng L^{-1}, respectively, while filtered samples from these two sources contained 6.3 and 6.8 ng L^{-1}, respectively. Samples collected for mercury in two wastewater treatment retention ponds ranged were 7 and 54 ng L^{-1} (unfiltered), 1.4 and 12 ng L^{-1} (filtered), and the final effluent contained about 9 ng L^{-1}.

These two studies indicate that the results of sampling individual sources of mercury in power plants can be quite variable. Results will obviously depend on the unit processes that contribute water to each area. There can be substantial differences between wet weather and dry weather flows and removal of solids (filtering) can have a substantial impact on results. While it is not possible to make recommendations for sampling and interpreting data from individual sources within power plants based on this meager data, previous recommendations are supported; that is, both concentration and flow should be measured, sampling should incorporate a range of seasons, and ancillary parameters such as TSS should be measured. Filtration of samples, with supporting TSS measurements, should be helpful in concluding whether simple settling or filtration could be beneficial in reducing loads from certain source areas. Is it probably not necessary to collect a number of samples required for statistical characterization of population statistics because the intent of this monitoring is to identify and minimize loads. However, a sufficient number of samples should be collected to characterize the sources. Resampling of areas with elevated concentrations is recommended prior to taking remedial actions or reporting results to a regulatory agency as part of minimization plan implementation.

4.2.12.4 Monitoring Requirements

Monitoring requirements for mercury in effluents resulting from or pending TMDLs vary widely. Typically, monthly or quarterly monitoring is required. Daily monitoring has not been observed to be required although weekly monitoring could be required by the statutes of some states. In the case of minor dischargers, semi-annual monitoring may be required. The State of Minnesota (MPCA 2002) has developed monitoring guidance for mercury in NPDES permits. For major facilities (i.e. those that discharge greater than 1 MGD) with no low-level mercury data and an existing mercury permit limit, twice monthly sampling is required. If the facility has no mercury permit limit, a permit is issued with quarterly monitoring requirements.

It is likely that the agency monitoring requirements will be structured around compliance with a permit limit or around the development of a minimization plan. In such cases monitoring will likely be for total (unfiltered) mercury. In cases where the TMDL is written in terms of methylmercury, analysis of unfiltered methylmercury samples may be required. In some cases, the agency may require the comparison of influent and effluent samples to determine whether the effluent is above the water quality target and, if so, whether facility operations are adding mercury. In these cases, it may be beneficial to the discharger to collect additional data, especially if he wishes to demonstrate that background sources (i.e. ambient levels, rainfall, stormwater) are resulting in noncompliance. Stakeholders are encouraged to look beyond the requirements of the permit or TMDL and evaluate which data would be best to collect for their long-term benefit.

4.2.12.5 Mixing Zones

Mixing zones are areas in a waterbody where effluent undergoes initial dilution. Mixing zones were originally envisioned as areas where acute and chronic water quality criteria for aquatic life protection could be exceeded without substantially impaired the biological function of the waterbody. Thus, the concept of a mixing zone is not particularly relevant to the development of effluent limits for a bioaccumulative substance like mercury. Environmental groups, however, have made the point that the use of mixing zones would allow the discharge of greater concentrations of mercury if the analysis allowed the WLA to be increased by the dilution factors associated with the mixing zone for other discharged constituents. As a result, mixing zones have been banned in some states with regard to their application to discharges of mercury and the WLA typically is applied at the end-of-pipe.

4.2.13 Time to Attain Standards

While some studies have claimed to have seen reductions in fish tissue due to reductions in atmospheric deposition, the response of a given waterbody is dependent on physical and biogeochemical factors unique to regions of the country and perhaps to specific watersheds and waterbodies. Among the recognized factors, the ratio of the contributing watershed area t o the area or volume of the waterbody is probably one of the most important. In watersheds where there is a considerable terrestrial reservoir of mercury, it may be a very long time before reductions in atmospheric emissions have any impact, if at all. In waterbodies where the contributions from the watershed are small (e.g. the Everglades) response may be more rapid. Estimates in TMDLs of time to attain standards (tens to hundreds of years) typically are not supported by scientific understanding, as it is substantially lacking in this area. This understanding will probably not substantially improve through the use of predictive tools, but will only be gained with experience.

The implication for dischargers is that mercury monitoring and minimization will continue to be a focus of the regulatory agencies for a very long time. Hopefully, progress will be made in reducing fish tissue concentrations as a result of the tremendous and costly efforts that all are expected to make toward this goal. However, if such progress is not apparent, efforts by the regulatory agencies may be redoubled in years to come.

4.2.14 Phased TMDLs

Phased TMDLs were devised as a regulatory means to postpone the establishment of a final TMDL where the data and science necessary to support its development was lacking, and were first used in the Great Lakes. In the case of mercury, many TMDLs have now embraced this approach. In cases where court-mandated deadlines had to be met by the establishment of a TMDL, the phased TMDL was used to establish it initially with the caveat that the TMDL would be revisited on a recurring schedule (e.g. every five years or according to a basin planning cycle). In cases were there were no such court orders, many states have opted to move mercury TMDLs to the bottom of their priority list. In either case, many of the tough decisions regarding the establishment of mercury TMDLs have been postponed.

The greatest cause for concern with a phased TMDL is that the actual establishment of a TMDL target level is almost never postponed and is invariably initially established using the most conservative of assumptions[70]. In such cases, the relaxation of a TMDL target initially set to a very low level based on conservative assumptions may not be possible. This “antibacksliding” provision of the Clean Water Act has not yet been tested in the courts with regard to targets (either fish tissue- or water column-based) established under TMDLs. Advances in the human health and environmental science of mercury (i.e. reduction of uncertainty) could feasibly lead to a situation where the target is ultimately demonstrated to be too low. In such a case, will it be possible to relax a target established under a phased TMDL? It has been observed that TMDL

[70] According to the definition of a TMDL, the margin of safety should be higher in the face of larger uncertainty. Thus, the target is lower and required load reductions are greater.

targets do not carry the same regulatory "weight" as a water quality standard, since standards are established by state legislatures though their administration procedures and TMDLs are not. This may ultimately serve to protect dischargers from prematurely established TMDLs, but perhaps not. In some states (e.g. Idaho, South Carolina) lawmakers have decided that TMDLs cannot be implemented until they are approved by the legislature. Stakeholders faced with a situation in which an agency proposes a phased TMDL should lobby that any sort of numerical target or standard is inappropriate until an appropriate level of confidence in all aspects of the TMDL is attainable.

Notwithstanding the issues discussed in the previous paragraph, there is an upside to phased TMDLs; the main advantage being that everyone, regulators and dischargers alike, have an opportunity to contribute to the understanding of the problem in their particular state, region, or watershed. Stakeholders are encouraged to take advantage of the time afforded, in particular to characterize their effluent and protect themselves individually, and possibly to assist in efforts and decisions to delist those waterbodies under consideration.

4.3 Alternatives to TMDLs

Currently, there appear to be only two alternatives to TMDLs, variances and UAAs. There are discussed in the two sections that follow.

4.3.1 Variances

Variances have been previously but briefly addressed in Section 1.6.8.4. The essence of the discussion is that the existence of a variance has the potential to shift the designation of the waterbody from Category 5 (impaired and in need of a TMDL) to Category 4b (impaired but an alternative regulatory program will lead to attainment), although it does not appear that states have opted to do this. Thus, the apparent effect of the variance is to delay the TMDL while the agency makes progress towards virtual elimination of mercury in NPDES discharges and gathers data that may ultimately be used in a TMDL. Given the *de minimis* status of most point source dischargers and the "reasonable potential" of Clean Air Act regulations to bring down the ambient levels of mercury in waterbodies, stakeholders in states with mercury variances or that may develop statewide mercury variances are encouraged to lobby for the reclassification of mercury impaired waterbodies to Category 4b, thereby eliminating the need for a TMDL.

At this time, it appears that only three states, Indiana, Michigan and Ohio, have statewide variance programs for mercury. Due to the low mercury WQS set for the Great Lakes, EPA Region 5 and the states within its geography have been leaders in developing these programs. Interested readers are referred to the documents that describe these programs which can readily be found on the Internet. In general, these programs allow dischargers that opt into the statewide variance an opportunity the gradually reduce mercury in their discharges. The programs usually allow permittees to discharge at "current" levels, normally determined by analysis of data from a number of similar facilities to determine currently attainable levels. Each facility is required to monitor and develop mercury minimization plans that will gradually lower mercury in their effluents. Over several permit cycles, the allowable discharger levels are ratcheted down as the ability to achieve lower levels improves.

The adoption of a statewide variance for mercury with a reclassification of the impaired waterbody from Category 5 to Category 4b would be an attractive option to mercury TMDLs for specific waterbodies.

4.3.2 Use Attainability Analysis

As discussed in Section 16.8.5, the UAA is probably the least likely alternative to a mercury TMDL at this time. For one, the process is involved and costly. Second, state regulatory agencies are unlikely to consider the elimination of a "fishing" use of a waterbody in light of the unfavorable public opinion that would ensue. Finally, a state is unlikely to pursue a UAA when it has not yet been demonstrated that air emission controls will not effectively lower fish tissue concentrations. Although the day may come when the inability to control mercury to a level that will result in the attainment of target fish tissue levels is apparent, mercury TMDLs will probably long have been established in these waterbodies.

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A
ONE PAGE SUMMARIES OF TMDLS REVIEWED

EPA Region 2

TMDL Title	Establishment of Phased Total Maximum Daily Loads (TMDLs) for Copper, Mercury, Nickel and Lead in New York-New Jersey Harbor
Date	1/24/1996
State(s)	New York, New Jersey
Watershed ID (HUC)	Not given
Listed Segments	Hudson River Inner Harbor Outer Harbor Arthur Kill / Kill Van Kull East River / Harlem River Jamaica Bay Raritan River / Bay Hackensack River / Passaic River / Newark Bay
Lead Agency	EPA Region 2
Basis for Listing	Exceedances of 25 ng/L standard for marine waters
Listing Trigger Level	25 ng/L
Watershed / Water Column / Fish Tissue Data?	None given
If yes, describe	
Type of Fish used for TMDL calculation	N/A
Water Quality Target or Load	
TMDL	10.9 lb/day
MOS	Not discussed
Point Sources Identified (list if power plant)	Not identified
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	No
Rationale for allocation	Based on water quality model but further information is not provided in the TMDL
Allocations of Reductions to Sources?	Yes

Allocations of Reductions to Sources?	Muni./Ind.	CSOs	Stormwater	Boundary	Atmospheric	Sum
Hudson River	0.185	0.057	0.481	0.138	0.245	1.106
Inner Harbor	0.183	0.034	0.007	0	0.054	0.278
Outer Harbor	0	0.026	0.01	0	1.139	1.175
Arthur Kill / Kill Van Kull	0.328	0.066	0.586	0	0.225	1.205
East River / Harlem River	1.005	0.216	2.16	0	0.679	4.06
Jamaica Bay	0.274	0.106	0.119	0	0.093	0.592
Raritan River / Bay	0.442	0.005	0.628	0.003	0.328	1.406
Hackensack River / Passaic River / Newark Bay	0.215	0.06	0.784	0.002	0.036	1.097
TMDL						10.9

Rationale for allocation	Municipal / industrial loads capped at existing levels, CSOs and Boundary loads 10% reduction, Stormwater 30% reduction, atmospheric 60% reduction.
Narrative Description of Approach	Point sources capped at existing levels, exceddances caused by atmospheric deposition and reductions will come from Clean Air Act regulations. No rationale form reductions to CSOs or stormwater. Additional allocation details are said to be in a document entitled "Total Maximum Daily Loads (TMDLs) for Copper, Mercury, Nickel, and Lead in NY-NJ Harbor". Document could not be located.
Narrative of Implementation Approach	Phase I TMDL.
Comments	

EPA Region 3

TMDL Title	District of Columbia final TMDLs for metals in Rock Creek
Date	2/27/2004
State(s)	District of Columbia
Watershed ID (HUC)	02070010 Middle Potomac-Anacostia-Occoquan watershed
Listed Segments	Upper Rock Creek (DCRCR00R_02) Lower Rock Creek (DCRCR00R_01)
Lead Agency	District of Columbia (Limno-Tech)
Basis for Listing	Fish consumption advisory & exceedance of numeric criteria. However, the TMDL is based on violation of numeric criteria (chronic criteria of 12 ng/L)
Listing Trigger Level	Numeric Water quality standards
Watershed / Water Column / Fish Tissue Data?	Water column data, but no fish tissue data.
If yes, describe	Highest water column concentrations used (only few hits for Hg as the detection limit was 0.2 ppm)
Type of Fish used for TMDL calculation	NA
Water Quality Target or Load	chronic criterion (CCC) 12 ng/L, acute criterion (CMC) 2400 ng/L, and Class D standard (fish-tissue based) 150 ng/L.
TMDL	0.718 lbs/yr for Upper Rock Creek
MOS	Implicit + Explicit (5%)
Point Sources Identified (list if power plant)	Yes - Combined sewer outfalls and stormwater outfalls
Effluent Data for PS?	Yes
If yes, describe	CSO 400 ng/L; stormwater outfalls 190 ng/L
Allocations to sources?	Yes
WLA	0.055 lbs/yr in upper Rock creek, and 0.061 lbs/yr in lower Rock creek
LA	0.409 lbs/yr in Upper Rock creek and 0.682 lbs/yr in Lower Rock Creek
MOS	5% (0.036 lbs/yr in Upper Rock Creek and 0.041 lbs/yr in Lower Rock Creek)
Rationale for allocation	Based on current load, less the amount of reduction calculated from field measurements and model calculations.
Allocations of Reductions to Sources?	Yes
WLA	85-90%
LA	96-97%
Rationale for allocation	Allocation based on current loads and model calcuated need for reduction.
Narrative Description of Approach	88 to 95% of current Hg loading from "upstream" sources, which is all atmospherically deposited on the watershed (17.1 lbs/yr); used a watershed "export" rate (watershed yield) was from lit. value which ranged from 38-84% yr, and the TMDL uses 84% yield (export). From model runs (SWMM) of daily concentrations in the stream, a 97% reduction in "upstream" sources required;
Narrative of Implementation Approach	Control and reduction of mercury air emissions is the primary method for implementation of this TMDL as most of the Hg is from atm. Sources; ongoing CSO regs are expected to reduce Hg loads in point
Comments	Mercury monitoring data has a high detection limit of 0.2 ppb, and were collected between 1989 and 2003. 190 average of 400 highest 7/2000 12 bdl - 1 at 400

TMDL Title	TMDL of Mercury for Deep Creek Lake, Garrett County, MD
Date	12/31/2002 (Approval date of 2/18/2004)
State(s)	Maryland
Watershed ID (HUC)	05020203 Youghiogheny River watershed
Listed Segments	Deep Creek Lake (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.304 ppm. Geomean water column Hg(tot) conc is 1.79 ng/L; avg MeHg (diss.) conc 0.277 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.341 ng/L dissolved Hg (and 1.01 ng/L total Hg)
TMDL	275.8 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	No Point Sources in the watershed
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	None (3% of TMDL set-aside for future point sources
LA	267.5 g/yr (Atmospheric deposition - 44.4% of TMDL; watershed sources - 52.6% of TMDL)
MOS	3% for future allocation; in addition, an implicit margin of safety of 43+ %
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	45.27% reduction
Rationale for allocation	Based on the 45.27% reduction and 3% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 12.30 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition. TMDL based on % reduction to go from current conc. to target conc (45.27% reduction). Target conc based on BAF approach used in GA.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations". This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach one-to-one relationship between atmospheric deposition and water quality std is assumed. In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for Big Piney Run Reservoir (a.k.a. Frostburg Reservoir), Garrett County, MD
Date	12/31/2002 (Approval date of 2/18/2004)
State(s)	Maryland
Watershed ID (HUC)	05020204 Youghiogheny River watershed
Listed Segments	Big Piney Reservoir (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.582 ppm. Geomean water column Hg(tot) conc is 2.56 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.312 ng/L dissolved Hg (and 0.754 total Hg)
TMDL	15.34 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion)
Point Sources Identified (list if power plant)	No Point Sources in the watershed
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	None (3% of TMDL set-aside for future point sources
LA	14.88 g/yr (Atmospheric deposition - 10.7% of TMDL; watershed sources - 86.2% of TMDL)
MOS	3% for future allocation; in addition, an implicit margin of safety of 43+ %
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	71%
Rationale for allocation	Based on the 71.4% reduction and 3% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 12.52 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition. TMDL based on % reduction to go from current conc. (2.56 ng/L) to target conc of 0.754 ng/L (i.e., 71.4% reduction). Target conc based on BAF approach used in
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations".
	This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach
	one-to-one relationship between atmospheric deposition and water quality std is assumed.

TMDL Title	TMDL of Mercury for Lake Lariat, Calvert County, MD
Date	12/20/2002 (Approval date of 1/27/2004)
State(s)	Maryland
Watershed ID (HUC)	02131110 Patuxent River watershed
Listed Segments	Deep Creek Lake (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.915 ppm. Geomean water column Hg(tot) conc is 2.39 ng/L; avg MeHg (diss.) conc 0.016 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.371 ng/L dissolved Hg (and 0.448 ng/L total Hg)
TMDL	1.21 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion)
Point Sources Identified (list if power plant)	No Point Sources in the watershed
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	None (3% of TMDL set-aside for future point sources
LA	1.174 g/yr (Atmospheric deposition - 81% of TMDL; watershed sources - 16% of TMDL)
MOS	3% for future allocation; in addition, an implicit margin of safety of 43+ %
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	81.82% reduction
Rationale for allocation	Based on the 81.82% reduction and 3% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 13.70 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition. TMDL based on % reduction to go from current conc. (with 81.8% reduction). Target conc based on BAF approach used in GA.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations".
	This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach
	one-to-one relationship between atmospheric deposition and water quality std is assumed.
	In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not usedfor TMDL purposes.
	BAF of 57.1 million!!

TMDL Title	TMDL of Mercury for Liberty Reservoir, Baltimore County, MD (DRAFT TMDL)
Date	November 2002 (Final TMDL not found; EPA website states that the TMDL was approved in Dec 2003)
State(s)	Maryland
Watershed ID (HUC)	02130907 Patapsco River Watershed
Listed Segments	Liberty Reservoir (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.262 ppm. Geomean water column Hg(tot) conc is 1.32 ng/L; avg MeHg (diss.) conc 0.030 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.589 ng/L dissolved Hg (and 0.866 ng/L total Hg)
TMDL	149.11 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	10 NPDES permits in the watershed; no measured data; an assumed conc. Of 8 ng/L x annual avg. flow used to estimate point source loads
Effluent Data for PS?	No (assumed conc of 8 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	8% set-aside for point sources + 3% other set aside (11% of TMDL set-aside for future allocation)
LA	132.7 g/yr (Atmospheric deposition - 72.5% of TMDL; watershed sources - 16.5% of TMDL)
MOS	11% for future allocation; in addition, an implicit margin of safety of ~30%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	38.34% reduction
Rationale for allocation	Based on the 38.34% reduction and11% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 13.94 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations". This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach one-to-one relationship between atmospheric deposition and water quality std is assumed. In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for Loch Raven Reservoir, Baltimore County, MD
Date	12/31/2002 (Approved on 8/16/2004
State(s)	Maryland
Watershed ID (HUC)	02130806 Gunpowder River Watershed)
Listed Segments	Loch Raven Reservoir (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.273 ppm. Geomean water column Hg(tot) conc is 4.95 ng/L; avg MeHg (diss.) conc 0.155 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	2.27 ng/L dissolved Hg (and 3.11 ng/L total Hg)
TMDL	843.5 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	9 NPDES permits in the watershed identified; no measured data; an assumed conc. Of 18 ng/L x annual avg. flow used to estimate point source loads
Effluent Data for PS?	No (assumed conc of 18 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	11% set-aside for point sources + 3% other set aside (14% of TMDL set-aside for future allocation)
LA	725.4 g/yr (Atmospheric deposition - 7.11% of TMDL; watershed sources - 37% of TMDL; Load from Prettyboy Reservoir 42%); Future allocation 14%
MOS	14% for future allocation; in addition, an implicit margin of safety of 43%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	34.8% reduction
Rationale for allocation	Based on the 34.8% reduction and14% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 14.12 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations". This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach one-to-one relationship between atmospheric deposition and water quality std is assumed. In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for Prettyboy Reservoir, Baltimore County, MD
Date	12/31/2002 (Approved on 8/16/2004
State(s)	Maryland
Watershed ID (HUC)	02130805 Gunpowder River Watershed)
Listed Segments	Prettyboy Reservoir (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.3084 ppm. Geomean water column Hg(tot) conc is 3.86 ng/L; avg MeHg (diss.) conc 0.041 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	1.56 ng/L dissolved Hg (and 2.15 ng/L total Hg)
TMDL	196.6 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	one NPDES permit in the watershed identified; no measured data; an assumed conc. Of 60 ng/L x annual avg. flow used to estimate point source loads estimate point source loads
Effluent Data for PS?	No (assumed conc of 60 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	8% set-aside for future allocation)
LA	181 g/yr (Atmospheric deposition - 22% of TMDL; watershed sources - 70% of TMDL); Future allocation 8%
MOS	8% for future allocation; in addition, an implicit margin of safety of 43%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	48% reduction
Rationale for allocation	Based on the 48% reduction and 8% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 13.63 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations". This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach one-to-one relationship between atmospheric deposition and water quality std is assumed. In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for Savage River Reservoir, Garrett County, MD
Date	12/20/2002 (Approved on 1/29/2004
State(s)	Maryland
Watershed ID (HUC)	02141006 Potomac River watershed
Listed Segments	Savage River Reservoi (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.4366 ppm. Geomean water column Hg(tot) conc is 1.06 ng/L; avg MeHg (diss.) conc 0.053 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.137 ng/L dissolved Hg (and 0.415 ng/L total Hg)
TMDL	54.57 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	one NPDES permit (wwtp) in the watershed identified; no measured data; an assumed conc. Of 60 ng/L x annual avg. flow used to estimate point source loads
Effluent Data for PS?	No (assumed conc of 60 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	4% set-aside for future allocation)
LA	52.4 g/yr (Atmospheric deposition - 12.6% of TMDL; watershed sources - 83.4% of TMDL); Future allocation 4%
MOS	4% for future allocation; in addition, an implicit margin of safety of 43%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	62% reduction
Rationale for allocation	Based on the 62% reduction and 4% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 12.44 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations". This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach one-to-one relationship between atmospheric deposition and water quality std is assumed. In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for St. Mary's Lake, St. Mary's County, MD
Date	12/20/2002 (Approved on 1/29/2004
State(s)	Maryland
Watershed ID (HUC)	02140103 Lower Potomac River Watershed
Listed Segments	St. Mary's Lake (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.449 ppm. Geomean water column Hg(tot) conc is 2.06 ng/L; avg MeHg (diss.) conc 0.125 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	0.141 ng/L dissolved Hg (and 0.785 ng/L total Hg)
TMDL	6.39 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	one NPDES permit (wwtp) in the watershed identified; no measured data; an assumed conc. Of 60 ng/L x annual avg. flow used to estimate point source loads
Effluent Data for PS?	No (assumed conc of 60 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	3%
LA	6.2 g/yr (Atmospheric deposition - 16.8% of TMDL; watershed sources - 80.2% of TMDL); Future allocation 3%
MOS	3% for future allocation; in addition, an implicit margin of safety of 43%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	63% reduction
Rationale for allocation	Based on the 63% reduction and 3% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 13.69 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations".
	This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach
	one-to-one relationship between atmospheric deposition and water quality std is assumed.
	In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	TMDL of Mercury for Tuckahoe Lake, Caroline County, MD
Date	12/31/2002 (Approved on 1/24/2004
State(s)	Maryland
Watershed ID (HUC)	02130405 Tuckahoe River watershed
Listed Segments	Tuckahoe Lake (also Statewide Advisory for Lakes)
Lead Agency	Maryland Dept. of the Environment
Basis for Listing	Recreational fishing use impairment
Listing Trigger Level	0.235 mg/kg fish tissue; (including a relative source contribution for marine fish lowers the tissue criterion to 0.172 mg/kg (when total Hg in fish tissue are not available, MeHg conc in water used for impairment decisions)
Watershed / Water Column / Fish Tissue Data?	Water column (total & dissolved Hg and MeHg) and fish tissue data
If yes, describe	Trophic level 4 fish collected; geomean Hg conc. 0.289 ppm. Geomean water column Hg(tot) conc is 4.07 ng/L; avg MeHg (diss.) conc 0.063 ng/L
Type of Fish used for TMDL calculation	Largemouth Bass
Water Quality Target or Load	1.33 ng/L dissolved Hg (and 2.42 ng/L total Hg)
TMDL	212.2 g/yr
MOS	Implicit - conservative assumptions (TL 4 fish, lower fish tissue conc target level than EPA criterion etc)
Point Sources Identified (list if power plant)	one NPDES permit (wwtp) in the watershed identified; no measured data; an assumed conc. Of 60 ng/L x annual avg. flow used to estimate point source loads
Effluent Data for PS?	No (assumed conc of 60 ng/L used in calculations)
If yes, describe	
Allocations to sources?	(Includes WLA and future allocation (FA)
WLA	None (3% set aside for future allocation)
LA	205.8 g/yr (Atmospheric deposition - 1.4% of TMDL; watershed sources - 95.6% of TMDL); Future allocation 3%
MOS	3% for future allocation; in addition, an implicit margin of safety of 43%
Rationale for allocation	Current load x reduction factor
Allocations of Reductions to Sources?	
WLA	None
LA	42% reduction
Rationale for allocation	Based on the 42% reduction and 3% set-aside for future allocation.
Narrative Description of Approach	Mass balance approach (flow-in x current conc. = current Hg load; flow-in x target Hg conc = TMDL). Direct atm. Deposition using lake area x 14.91 ug/m2/yr dep. Rate (from NADP); watershed load = current load to reservoir - direct deposition.
Narrative of Implementation Approach	CleanAir Act and other air control measures will ultimately reduce Hg loading to the reservoir, but unquantifiable at present.
Comments	TMDL specifically states that the goal is to protect the general population and " do not have to be protective of more sensitive subpopulations".
	This TMDL similar to the Big Haynes reservoir Hg TMDL in Georgia, with more stringent advisory criteria, and estimation of loads from air dep. And watershed sources using mass balance approach
	one-to-one relationship between atmospheric deposition and water quality std is assumed.
	In Maryland, 43% of air emissions are attributed to power plants; plant-specific air-emission rates provided but not used for TMDL purposes.

TMDL Title	Nutrients and mercury TMDLs for Lake Wallenpaupack, Pike and Wayne Counties, PA
Date	4/1/2005
State(s)	Pennsylvania
Watershed ID (HUC)	02040103 (Lackawaxen River basin)
Listed Segments	Lake Wallenpaupack
Lead Agency	US EPA Region 3
Basis for Listing	Fish Tissue Exceedance
Listing Trigger Level	0.3 mg/kg fish tissue
Watershed / Water Column / Fish Tissue Data?	13 fish tissue samples with a geomean conc of 0.47 mg/kg; watercolumn data for lake collected between 1999 and 2001 utilized higher det. Limit (0.2 ug/L) and not used. BAF and fraction MeHg from EPA's National data (50th percentile value for TL 4 fish)
If yes, describe	
Type of Fish used for TMDL calculation	
Water Quality Target or Load	1.53 ng/L total Hg (or 0.92 ng/L dissolved Hg; the conversion ratio from literature)
TMDL	1.366 g/day (499 g/yr)
MOS	
Point Sources Identified (list if power plant)	No Point sources in the watershed
Effluent Data for PS?	NA
If yes, describe	
Allocations to sources?	
WLA	0
LA	Direct atm. Sources 41% and watershed sources 59%
MOS	Implicit
Rationale for allocation	
Allocations of Reductions to Sources?	40%
WLA	
LA	
Rationale for allocation	
Narrative Description of Approach	Mass balance approach. Current load backcalculated from national BAF value and fraction MeHg. Direct air deposition rate from RELMAP (14.77 ug/m2/yr). Current load minus direct deposition gives watershed contribution. 40% reduction calculated based on existing load (2.56 ng/L x flow) vs. WQT of 1.53 ng/L.
Narrative of Implementation Approach	Reduction under CAA to air emissions.
Comments	This lake created by the Tafton Dike hydroelectric dam, operated by the PA power and light company. Approach similar to the Deep Creek Lake mercury TMDL, MD.

EPA Region 4

TMDL Title	TMDL Development for Total Mercury in the Alapaha Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3120002
Waterbody ID	
Listed Segments	Sand Creek to US Highway129 US Highway 129/GA Highway 11 to Stateline Double Run Creek Alapahoochee River
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Four water column samples for total, methyl mercury (2000/2001), two each sediment and soil samples for total, methyl mercury (2000/2001), four fish tissue samples (2000), ten fish tissue samples
Water Quality Target or Load	5.8 ng/L 3.2 kg/yr 8767 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 7.3 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	56% reduction
WLA	0.16 kg/yr
LA	3.06 kg/yr
MOS	None
Rationale for allocation	Point sources given an allocation of 5% of TMDL. LA is the difference between the TMDL and the LA.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current watershed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	TMDL Development for Total Mercury in Fish Tissue Residue in Altamaha River
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070107
Waterbody ID	
Listed Segments	Confluence of Oconee and Ocmulgee Rivers to ITT Rayonier ITT Rayonier to Penholoway Creek
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two sediment and soil samples for total, methyl mercury, twenty fish tissue samples.
Water Quality Target or Load	4.0 ng/L 52.40 g/yr 144 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Not determined
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	None required, trophic level weighted fish tissue concentration is less then 0.3 mg/kg
WLA	0.007 g/yr
LA	47.2 g/yr
MOS	5.2 g/yr
Rationale for allocation	MOS set at 10% of load. No apparent rationale for WLA. LA calculated from the difference.
Narrative Description of Approach	WQT calculated using a site specific BAF and methylation translator. TMDL calculated using WQT and average annual flow.
Narrative of Implementation Approach	Left up to State NPDES program. No allcoations to individual point sources.
Comments	

TMDL Title	TMDL Development for Total Mercury in Beaver Creek & Patsiliga Creek (Flint River Watershed)
Date	8/30/2000
State(s)	GA
Watershed ID (HUC)	3070107
Waterbody ID	
Listed Segments	Beaver Creek Headwaters to patsiliga Creek Beaver Creek to Flint River
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two sediment samples for total, methyl mercury, fifteen fish tissue samples.
Water Quality Target or Load	3.2 ng/L 0.15 kg/yr 411 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Single sample for total Hg?
Allocations to sources?	Current Load of 0.3 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	49%
WLA	Assigned its current discharge level.
LA	49%
MOS	None
Rationale for allocation	Point sources de minimis, reductions must come from atmopheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Left up to State NPDES program.
Comments	

TMDL Title	TMDL Development for Total Mercury Fish Tissue in Brier Creek (Located in the Savannah River Basin)
Date	8/30/2004
State(s)	GA
Watershed ID (HUC)	3060108
Waterbody ID	
Listed Segments	GA Highway 305 to Confluence Savannah River
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two each sediment and soil samples for total, methyl mercury, 20 fish tissue samples.
Water Quality Target or Load	4.3 ng/L
	2.98 kg/yr 8164 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Total and methyl mercury measured in the effluents of 2 facilities (two wastewater treatment plants).
Allocations to sources?	Current Load of 5.4 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	45% reduction
WLA	2.96 kg/yr
LA	0.02 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned <1% of allowable load, other reductions must come from atmopheric emissions. Point sources for which effluent data were available were assigned loads equal to their current discharges.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. All point sources subject to the aggregate WLA. However, three facilities are capped at their current discharge levels. Since these dischargers were classified as "minor", future monitoring or mercury characterization is left up to the State of Georgia.
Comments	

TMDL Title	TMDL Development for Total Mercury Fish Tissue in the Canoochee (Canoochee Watershed)
Date	8/30/2004
State(s)	GA
Watershed ID (HUC)	3060108
Waterbody ID	
Listed Segments	GA Highway 192 to Fifteen Mile Creek Fifteen Mile Creek to Cedar Creek Cedar Creek to Lotts Creek Lotts Creek to Confluence with Ogeechee River
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two each sediment and soil samples for total, methyl mercury, 19 fish tissue samples.
Water Quality Target or Load	9.3 ng/L 5.24 kg/yr 14356 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Total and methyl mercury measured in the effluents of 3 facilities (two wastewater treatment plants and Ft Stewart).
Allocations to sources?	Current Load of 8.45 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	38% reduction
WLA	5.04 kg/yr
LA	0.2 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned <5% of allowable load, other reductions must come from atmopheric emissions. Point sources for which effluent data were available were assigned loads equal to their current discharges.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. All point sources subject to the aggregate WLA. However, three facilities are capped at their current discharge levels. Since these dischargers were classified as "minor", future monitoring or mercury characterization is left up to the State of Georgia.
Comments	

TMDL Title	TMDL Development for Total Mercury in Chattahoochee River
Date	8/31/2002
State(s)	GA
Watershed ID (HUC)	3070101
Waterbody ID	
Listed Segments	Soquee River to Lake Lanier
Lead Agency	EPA Region 4
Basis for Listing	Fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two sediment samples for total, methyl mercury, two soil samples for total, methyl mercury, twenty fish tissue samples.
Water Quality Target or Load	1 ng/L 2.30 kg/year 6301 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Y
WLA	None Explicit
LA	None Explicit
MOS	None Explicit
Rationale for allocation	N/A
Allocations of Reductions to Sources?	None explicit
WLA	0.003 kg/yr
LA	2.07 kg/yr
MOS	0.2 kg/yr
Rationale for allocation	Sum of permitted flows for permitted facilities times the WQT. 10% MOS. The remainder goes to the nonpoint sources.
Narrative Description of Approach	TMDL calculated using the WQT and the average annual flow for the river. A TMDL was established even though the fish tissue data collected showed the trophic level weighted average concentration to be less than 0.3 mg/kg.
Narrative of Implementation Approach	None
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in the Etowah River
Date	2/27/2004
State(s)	GA
Watershed ID (HUC)	3150104
Waterbody ID	
Listed Segments	Clear Creek to Forsyth County Line (Dawson County, GA)
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury (plus one duplicate), 20 fish tissue samples.
Water Quality Target or Load	2.2 ng/L 0.50 kg/yr 1369.86 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	None explicit
LA	None explicit
MOS	None explicit
Rationale for allocation	
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate of the river.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL Development for Total Mercury in Kinchafoonee Creek (Flint River Watershed)
Date	8/30/2000
State(s)	GA
Watershed ID (HUC)	3070107
Waterbody ID	
Listed Segments	Kinchafoonee Creek
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two sediment and soil samples for total, methyl mercury, twenty fish tissue samples.
Water Quality Target or Load	2.3 ng/L 1.68 kg/yr 4603 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Single samples for total Hg?
Allocations to sources?	Current Load of 2.44 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	31%
WLA	Assigned its current discharge level.
LA	31%
MOS	None
Rationale for allocation	Point sources de minimis, reductions must come from atmopheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Left up to State NPDES program.
Comments	

TMDL Title	TMDL Development for Total Mercury in the Ochlockonee Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3120002
Waterbody ID	
Listed Segments	Oquina Creek to Stateline State Route 37 Downstream Moultrie to Upstream CR222 Bridge Creek to Big Creek
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Four water column samples for total, methyl mercury (2000/2001), four sediment samples for total, methyl mercury (2000/2001), seventeen fish tissue samples (5-2000/12-2001).
Water Quality Target or Load	1.9 ng/L 1.50 kg/yr 4110 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Not provided in TMDL document
Allocations to sources?	Current Load of 5 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	70% reduction overall
WLA	0.08 kg/yr
LA	1.43 kg/yr
MOS	Implicit
Rationale for allocation	Point sources given an allocation of 5% of TMDL. LA is the difference between the TMDL and the LA.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenuation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current watershed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Jackson Lake and Ocmulgee River
Date	2/28/2002
State(s)	GA
Watershed ID (HUC)	3070104
Waterbody ID	
Listed Segments	Pulaski/Wilcox County Line to House Creek House Creek to Altamaha River
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two each sediment and surface soil samples for total, methyl mercury, 21 fish tissue samples.
Water Quality Target or Load	7.4 ng/L 47.40 kg/yr 129863.01 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0.2 g/yr
LA	42.48 g/yr
MOS	4.72 g/yr
Rationale for allocation	WLA assigned the cumulative flow of NPDES permitted facilities times the WQT. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate of the river.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Oconee River
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070101
Waterbody ID	
Listed Segments	Confluence of North & Middle Oconee Rivers to Barnett Shoals Dam Barnett Shaols to lake Oconee Apalachee River: Marburg Creek to Lake Oconee
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total, methyl mercury, one each sediment and surface soil samples for total, methyl mercury, 12 fish tissue samples.
Water Quality Target or Load	4.9 ng/L 9.00 g/yr 24.66 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N 30 point sources said to be in the watershed, none identified individually
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0.01 g/yr
LA	8 g/yr
MOS	0.9 g/yr
Rationale for allocation	WLA assigned a small quantity. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL Development for Total Mercury Fish Tissue in Ogeechee River (Ogeechee Watershed)
Date	8/30/2004
State(s)	GA
Watershed ID (HUC)	3110203
Waterbody ID	
Listed Segments	Highway 102 to US Highway 301 US Highway 301 to Black Creek Black Creek to Richmond Hill
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Four water column samples for total, methyl mercury (2000/2001), four each sediment and soil samples for total, methyl mercury, 40 fish tissue samples.
Water Quality Target or Load	1.7 ng/L 8.99 kg/yr 24630 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Total and methyl mercury measured in the effluents of 3 facilities, two wastewater treatment plants and one industrial facility.
Allocations to sources?	Current Load of 16.4 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	45% reduction
WLA	8.79 kg/yr
LA	0.2 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned <5% of allowable load, other reductions must come from atmopheric emissions. Point sources for which effluent data were available were assigned loads equal to their current discharges.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. All point sources subject to the aggregate WLA. However, three facilities are capped at their current discharge levels. Since these dischargers were classified as "minor", future monitoring or mercury characterization is left up to the State of Georgia.
Comments	

TMDL Title	TMDL Development for Total Mercury in Fish Tissue Residue in Ohoopee Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070107
Waterbody ID	
Listed Segments	GA Hwy 147 to confluence with Altamaha River Hwy 292 to Hwy 147 Little Ohoopee River to US Hwy 292 Neels Creek to Litle Ohoopee Sand Hill Lake Gum Creek Swamp
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column samples for total, methyl mercury, one sediment and soil sample for total, methyl mercury, ten fish tissue samples.
Water Quality Target or Load	3.4 ng/L 3.80 kg/yr 10411 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Single total Hg sample for each facility?
Allocations to sources?	Current load from all sources of 5 kg/yr
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	Current load established through watershed modeling.
Allocations of Reductions to Sources?	27% from current load
WLA	0.19 kg/yr
LA	3.58 kg/yr
MOS	Implicit
Rationale for allocation	WLA calculated from permitted flow rates for all NPDES facilities times the WQT. LA is the difference between WLA and TMDL.
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current watershed load.
Narrative of Implementation Approach	Point sources judged to be de minimis. Reductions must come from air emissions. Point sources are given two options - to take an end-of-pipe limit equal to the WQT or to identify and adopt mercury minimization plans.
Comments	

TMDL Title	TMDL Development for Total Mercury in the Satilla Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070201
Waterbody ID	
Listed Segments	US Highway 84 to GA Highway 38 GA Highway 15 to Bullhead Bluff Dupree Creek Purvis Creek Terry Creek Turtle River System Gibson Creek
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Six water column samples for total, methyl mercury (2000/2001), three each sediment and soil samples for total, methyl mercury (2000/2001), five fish tissue samples (2000), 12 fish tissue samples
Water Quality Target or Load	2.0 ng/L 3.2 kg/yr 8767 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y Georgia Power McManus (NPDES # GA0003794)
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 9.7 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	67% reduction
WLA	0.16
LA	3.02
MOS	Implicit
Rationale for allocation	Point sources given 5% of current estimated total load, major reductions from atmospheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	**TMDL Development for Total Mercury & Fish Consumption Guidelines in the Middle & Lower Savannah River Watershed**
Date	12/8/2000
State(s)	GA
Watershed ID (HUC)	3070201
Waterbody ID	
Listed Segments	Clarks Hill Lake to Stevens Creek Dam Stevens Creek Dam to US Highway 78/2 & 78 Us Highway 78/278 to Butler Creek Butler Creek to McBean Creek McBean Creek to Screven County Line Brier Creek to Ebenezer Creek Ebenezer Creek to Tide Gate
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Eighteen water column samples for total, methyl mercury, 14 sediment and samples for total, methyl mercury, five fish tissue samples (2000), 79 fish tissue samples.
Water Quality Target or Load	2.83 ng/L 32.8 kg/yr 89808 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y Georgia Power Vogtle (NPDES # 0026786) Savannah Electric Effingham (Plant McIntosh NPDES # 0003883) Savannah Electric Riverside Savannah Electric Wentworth (Plant Kraft NPDES # 0003816)
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 58.77 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	44% reduction
WLA	0.33 kg/yr
LA	32.45 kg/yr
MOS	Implicit
Rationale for allocation	Point sources given 5% of current estimated total load, major reductions from atmospheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	This TMDL was ultimately withdrawn by EPA because the impaired segments were delisted. Delisting was prompted by a re-evaluation of fish tissue data by the State of Georgia.

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Spring Creek
Date	2/27/2004
State(s)	GA
Watershed ID (HUC)	3150104
Waterbody ID	
Listed Segments	Etowah River Tributary (Floyd County, GA)
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total, methyl mercury, 10 fish tissue samples.
Water Quality Target or Load	2.2 ng/L 0.10 kg/yr 273.97 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	None explicit
LA	None explicit
MOS	None explicit
Rationale for allocation	
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate of the creek.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL Development for Total Mercury in the St. Mary's Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070204
Waterbody ID	
Listed Segments	Headwaters to Cedar Creek Cedar Creek to South Prong St. Mary's River South Prong St. Mary's River to St. Mary's Cut
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury (2000/2001), two sediment samples for total, methyl mercury (2000/2001), five fish tissue samples (2000), eleven fish tissue samples (2001).
Water Quality Target or Load	2.3 ng/L 2.1 kg/yr 5753 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 5.4 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	60%
WLA	0.11 kg/yr
LA	2.02 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned 5% of allowable load, other reductions must come from atmopheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	TMDL Development for Total Mercury in the Suwannee Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3110201
Waterbody ID	
Listed Segments	Suwannee Canal - Okefenokee Swamp Suwannee River mainstem Suwannee Canal to Stateline
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Four water column samples for total, methyl mercury (2000/2001), two each sediment and soil samples for total, methyl mercury (2000/2001), five fish tissue samples (2000), 12 fish tissue samples
Water Quality Target or Load	3.4 ng/L 3.2 kg/yr 8767 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 6.1 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	47% reduction
WLA	0.16 kg/yr
LA	3.04 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned 5% of allowable load, other reductions must come from atmopheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Talking Rock Creek
Date	2/27/2004
State(s)	GA
Watershed ID (HUC)	3150102
Waterbody ID	
Listed Segments	Ga Highway 136 to Pickens/Gilmer County Line (Pickens County, GA)
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury (plus one duplicate), 20 fish tissue samples.
Water Quality Target or Load	2.2 ng/L 0.40 kg/yr 1095.89 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	None explicit
LA	None explicit
MOS	None explicit
Rationale for allocation	
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate of the creek.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL Development for Lead, Copper and Mercury in the Taylors Creek In the Ogeechee River Basin
Date	11/10/1999
State(s)	GA
Watershed ID (HUC)	3060203
Waterbody ID	
Listed Segments	4 mile section of Taylors Creek from the confluence with the Canoochee Rier to WWTP outfall
Lead Agency	EPA Region 4
Basis for Listing	Exceedance of WQS of 12 ng/L for Hg
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Water column samples indicated exceedances of the 12 ng/L standard. However, more recent water column data suggested the creek was not impaired.
Water Quality Target or Load	12 ng/L 40.00 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Y
WLA	40 mg/day
LA	0
MOS	Implicit
Rationale for allocation	100% of the allocation given to the Hinesville/Ft. Stewart WWTP.
Allocations of Reductions to Sources?	None explicit
WLA	None explicit
LA	None explicit
MOS	None
Rationale for allocation	Since recent sampling data indicated no impairment, all of the allocation was assigned to the WWTP.
Narrative Description of Approach	TMDL calculated using the WQS and the 7Q10 low flow for the creek.
Narrative of Implementation Approach	None
Comments	

TMDL Title	TMDL Development for Total Mercury in the Withlacoochee Watershed
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3110203
Waterbody ID	
Listed Segments	Headwaters to New River New River to Bay Branch Little River to Stateline Banks Lake Bay Branch to Little River Turkey Branch
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Six water column samples for total, methyl mercury (2000/2001), three sediment samples for total, methyl mercury (2000), five fish tissue samples (2000), 12 fish tissue samples (2001).
Water Quality Target or Load	8.3 ng/L 7 kg/yr 18904 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	Current Load of 9.7 kg/yr determined from all sources
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	29% reduction
WLA	0.35 kg/yr
LA	6.58 kg/yr
MOS	Implicit
Rationale for allocation	Point sources assigned 5% of allowable load, other reductions must come from atmopheric emissions
Narrative Description of Approach	TMDL calculated using BAF and methylation translator measured in the waterbody. WCS used to estimate watershed loads. Attenutation of load calculated for tributaries. WASP5 used to calculate instream concentrations. Load reduction required calculated from 1- ratio of water quality target to highest simulated segment concentration times current waterhed load.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Identified major facilities may take an end-of-pipe limit equal to the WQT or identify sources and develop a minimization plan, if influent/effluent monitoring shows a net addition of mercury. All other point sources are cumulatively subject to the WLA.
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Big Haynes Reservoir
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070103
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total, methyl mercury, one each sediment and surface soil sample for total, methyl mercury, eleven fish tissue samples.
Water Quality Target or Load	4.1 ng/L 0.27 g/yr 0.74 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0 g/yr
LA	0.24 g/yr
MOS	0.03 g/yr
Rationale for allocation	WLA assigned 0. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Jackson Lake and Ocmulgee River
Date	2/28/2002
State(s)	GA
Watershed ID (HUC)	3070104
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, two each sediment and surface soil samples for total, methyl mercury, 21 fish tissue samples.
Water Quality Target or Load	7.4 ng/L 10.50 kg/yr 28767.12 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0.2 g/yr
LA	9.45 g/yr
MOS	1.05 g/yr
Rationale for allocation	WLA assigned the cumulative flow of NPDES permitted facilities times the WQT. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Lake Bennett
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070102
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total, methyl mercury, one each sediment and surface soil sample for total, methyl mercury, twelve fish tissue samples.
Water Quality Target or Load	7.1 ng/L 0.16 g/yr 0.44 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0 g/yr
LA	0.14 g/yr
MOS	0.02 g/yr
Rationale for allocation	WLA assigned 0. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Lake Oconee
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070101
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Ten water column samples for total, methyl mercury, nine each sediment and surface soil samples for total, methyl mercury, 78 fish tissue samples.
Water Quality Target or Load	17.6 ng/L 2.70 g/yr 7.40 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0 g/yr
LA	2.4 g/yr
MOS	0.27 g/yr
Rationale for allocation	WLA assigned 0. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Stone Mountain Lake
Date	8/30/2001
State(s)	GA
Watershed ID (HUC)	3070103
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total, methyl mercury, one each sediment and surface soil sample for total, methyl mercury, twelve fish tissue samples.
Water Quality Target or Load	4.4 ng/L 0.09 g/yr 0.25 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	0 g/yr
LA	0.08 g/yr
MOS	0.01 g/yr
Rationale for allocation	WLA assigned 0. MOS given 10% of total load. LA calculated by difference.
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	TMDL for Total Mercury in Fish Tissue Residue in Lake Yonah
Date	8/30/2004
State(s)	GA
Watershed ID (HUC)	3060102
Waterbody ID	
Listed Segments	
Lead Agency	EPA Region 4
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Two water column samples for total, methyl mercury, 22 fish tissue samples.
Water Quality Target or Load	1.3 ng/L 1.20 kg/yr 3287.67 mg/day
MOS	N/A
Point Sources Identified (list if power plant)	N
Effluent Data for PS?	N
If yes, describe	
Allocations to sources?	N/A
WLA	N/A
LA	N/A
MOS	N/A
Rationale for allocation	N/A
Allocations of Reductions to Sources?	No reductions required, trophic level weighted fish tissue concentration below 0.3 mg/kg.
WLA	None explicit
LA	None explicit
MOS	None explicit
Rationale for allocation	N/A
Narrative Description of Approach	WQT calculated using BAF and methylation translator measured in the waterbody. TMDL calculated using the WQT and average annual flow rate through the lake.
Narrative of Implementation Approach	None identified
Comments	

TMDL Title	Bogue Chitto River Phase 1 Total Maximum Daily Load for Mercury, Pearl River Basin, Lincoln, Pike, and Walthall Counties, Mississippi
Date	12/15/2000
State(s)	MS
Watershed ID (HUC)	3180005
Waterbody ID	
Listed Segments	MSBGCHTRM1 MSBGCHTRM2 MSBGCHTRM3 MSBGCHTRM4
Lead Agency	MS DEQ
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Fish tissue data, 71 tissue samples from locations in the four listed segments.
Water Quality Target or Load	12 ng/L, total recoverable, fresh water 8.23 gm/day
MOS	
Point Sources Identified (list if power plant)	Y Pike Generation, TMDL document identifies this facility with NPDES permit # MS0056782 with a mercury limit. However, a search of the EPA PCS database does not show this permit. Instead it shows Pike Generation as having permit # MSG130042 (which is probably a general stormwater permit) and does not show a mercury limit.
Effleuent Data for PS?	N
If yes, describe	
Allocations to sources?	
WLA	
LA	
MOS	
Rationale for allocation	Sum of facility permitted flows times WQT. MOS set at 50%. LA = TMDL - MOS - WLA
Allocations of Reductions to Sources?	
WLA	0.198 gm/day 2% of TMDL
LA	3.917 gm/day 48% of TMDL
MOS	4.115 gm/day 50% of TMDL
Rationale for allocation	
Narrative Description of Approach	Phase one, point sources only. TMDL calculated as product of WQT and 7Q10 low flow.
Narrative of Implementation Approach	Moratorium on any increase in mercury discharges. Increased monitoring for facilities with flows greater than 0.05 MGD. Also recommends pollution prevention alternatives and activities.
Comments	

TMDL Title	Escatawpa River Phase One TMDL for Mercury
Date	6/26/2000
State(s)	MS
Watershed ID (HUC)	03170008
Waterbody ID	MS107M1, MS107M2, MS107M3
Listed Segments	Segment 1, Fresh Water Segment 2, Fresh Water Segment 3, Salt Water
Lead Agency	MS DEQ
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	One water column sample for total mercury, 2.94 ng/L. Fish tissue data, 104 tissue samples.
Water Quality Target or Load	12 ng/L, total recoverable, fresh water 25 ng/L, total recoverable, salt water 3.56 gm/day, Segment 1 4.73 gm/day, Segment 2
MOS	
Point Sources Identified (list if power plant)	Y
Effleuent Data for PS?	Y
If yes, describe	Escatawpa WWTP, influent/effluent samples
Allocations to sources?	
WLA	0.00 gm/day
LA	1.18 gm/day
MOS	3.55 gm/day 75%
Rationale for allocation	No point sources in segments 1 or 2. Moratorium sets the WLA to zero. LA set by multiplying ambient water column concentration times the 7Q10.
Allocations of Reductions to Sources?	
WLA	
LA	
MOS	
Rationale for allocation	
Narrative Description of Approach	TMDL calculated as product of WQT and 7Q10 low flow.
Narrative of Implementation Approach	Phase 1 only concerned with point sources. Moratorium on any mercury discharges. Increased monitoring.
Comments	

TMDL Title	Pearl River and Yockanookany Ribers Phase 1 Total Maximum Daily Load for Mercury, Pearl River Basin
Date	1/1/2004
State(s)	MS
Watershed ID (HUC)	03180001, 03180002
Waterbody ID	
Listed Segments	MSUMPRLR2M, Pearl River MS147M1 MS146YE
Lead Agency	MS DEQ
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Fish tissue data, 64 tissue samples, Pearl River segments, 68 samples Yockanookany segments
Water Quality Target or Load	12 ng/L, total recoverable, fresh water 2.41 gm/day
MOS	
Point Sources Identified (list if power plant)	Y
Effleuent Data for PS?	N
If yes, describe	
Allocations to sources?	
WLA	
LA	
MOS	
Rationale for allocation	Sum of facility permitted flows times WQT. MOS set at 50%. LA = TMDL - MOS - WLA
Allocations of Reductions to Sources?	
WLA	0.652 gm/day 27% of TMDL
LA	0.553 gm/day 23% of TMDL
MOS	1.205 gm/day 50% of TMDL
Rationale for allocation	
Narrative Description of Approach	Phase one, point sources only. TMDL calculated as product of WQT and 7Q10 low flow.
Narrative of Implementation Approach	Moratorium on any increase in mercury discharges. Increased monitoring for facilities with flows greater than 0.05 MGD. Also recommends pollution prevention alternatives and activities.
Comments	

TMDL Title	Yocona River and Enid Reservoir Phase One TMDL for Mercury (Yazoo Basin, Yalobusha, Panola, and Tallahatchie Counties, MS
Date	12/31/2002
State(s)	MS
Watershed ID (HUC)	08030203
Waterbody ID	MS288ELM, MSYOCRM
Listed Segments	MS288ELM, Enid Reservoir MSYOCRM, Yocona River
Lead Agency	MS DEQ
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Fish tissue data, 83 tissue samples from Enid Reservoir, 40 from Yocona River.
Water Quality Target or Load	12 ng/L, total recoverable, fresh water 1.47 gm/day
MOS	
Point Sources Identified (list if power plant)	Y
Effleuent Data for PS?	N
If yes, describe	
Allocations to sources?	
WLA	
LA	
MOS	
Rationale for allocation	Sum of facility permitted flows times WQT. MOS set at 50%. LA = TMDL - MOS - WLA
Allocations of Reductions to Sources?	
WLA	0.305 gm/day
LA	0.43 gm/day
MOS	0.735 gm/day 50% of TMDL
Rationale for allocation	
Narrative Description of Approach	Phase one, point sources only. TMDL calculated as product of WQT and 7Q10 low flow.
Narrative of Implementation Approach	Moratorium on any increase in mercury discharges. Increased monitoring for facilities with flows greater than 0.05 MGD. Also recommends pollution prevention alternatives and activities.
Comments	

TMDL Title	Total Maximum Daily Load for mercury in the Cashie River, North Carolina
Date	7/1/2004
State(s)	NC
Watershed ID (HUC)	03010107
Waterbody ID	
Listed Segments	24-2-(1)a 24-2-(1)b 24-2-(9) 24-2-(11) 24-2-(15)
Lead Agency	NC DENR
Basis for Listing	Fish Consumption, fish consumption guidelines
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Four sampling dates for water column Hg, analyses for Total Hg, Total MeHg, Dissolved total Hg, Dissolved MeHg, 47 fish tissue analyses from 2 sampling dates, two sediment samples from two different dates analyzed for total Hg and MeHg.
Water Quality Target or Load	0.464 ng/L Total MeHg or 1.5 to 3.9 Total Hg. WQT is based on 75% percentile value of BAFs measured in the waterbody and tissue target of 0.4 mg/kg in a 40 cm largemouth bass reference fish. 535 g/yr 1465.753 mg/day
MOS	
Point Sources Identified (list if power plant)	Y
Effluent Data for PS?	Y
If yes, describe	Two measurements of WWTP effluent from 2003, nine additional measurements from 2005
Allocations to sources?	Y
WLA	12 g/yr
LA	1994 g/yr
MOS	
Rationale for allocation	Measurements and flow estimates for the two WWTPs. Modeling for the current NPS load.
Allocations of Reductions to Sources?	73% reduction
WLA	8 32% reduction
LA	535 73% reduction
MOS	96 5% explicit
Rationale for allocation	No apparent rationale to 32 % reduction from point sources. All of the required reductions must come from nonpoint sources, and ultimately from reductions in air emissions.
Narrative Description of Approach	WQT calculated using 75th percentile of BAFs calculated for waterbody and a fish tissue target of 0.4 mg/kg. WCS used to estimate watershed loads. WASP5 used to calculate instream concentrations. Loads of MeHg were reduced and a response curve for steady state MeHg concentrations in the water column was developed. The required % reduction is taken from the response curve for the segment needing the greatest reduction to achieve the target.
Narrative of Implementation Approach	Air emission reductions will be achieved under the Clean Air Act. Modeling suggests that significant redcutions could come from erosion control.
Comments	Allocation of load reductions to specific land uses is troubling.

TMDL Title	TMDL Study Phase I: Mercury Loads to Impaired Waters in the Lumber River Basin, North Carolina
Date	11/1/1999
State(s)	NC
Watershed ID (HUC)	030750
Waterbody ID	Lumber River
Listed Segments	Drowning Creek Lumber River Big Swamp Porter Swamp Ashpole Swamp Pages Lake Pit Lake (Pit Links Lake) Watson Lake Waccamaw River Waccamaw River Big Creek White Marsh
Lead Agency	NC DENR
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Summaries of fish tissue data used for listing
Water Quality Target or Load	12 ng/L, total recoverable, fresh water 0 to 2000 g/yr (5.5 g/day)
MOS	
Point Sources Identified (list if power plant)	Y CP&L Weatherspoon (NPDES # 0005363), no effluent data in TMDL document, no mercury monitoring requirement per EPA PCS database.
Effluent Data for PS?	Y
If yes, describe	Summaries of effluent data, primarily for WWTPs, all of which used Method 245 with a detection limit of 200 ng/L.
Allocations to sources?	
Waccamaw River	About 9,000 g/yr (25 g/day)
Rationale for allocation	Estimates of direct and indirect wet and dry deposition and point sources. Only 1 point source had data analyzed using Method 245. Load estimate is based on 1/2 detection limits (0.1 ppb) for non detections. Other point sources were not considered.
Allocations of Reductions to Sources?	
WLA	40% of TMDL
LA	60% of TMDL
MOS	0% of TMDL
Rationale for allocation	No apparent rationale for 40/60 split
Narrative Description of Approach	Phase one was done as a simplistic "place holder" only. TMDL calculated as product of WQT and average flow rate. DENR expects that EPA Region 4 to provide an analysis for the Waccamaw River or portions thereof that can be applied to the Lumber River as well.
Narrative of Implementation Approach	State of North Carolina continues to make ambient measurements of mercury in receiving waters and has embarked on an aggressive program requiring point sources to self-monitor using Method 1631.
Comments	

EPA Region 5

TMDL Title	TMDL for mercury for Hammell Creek, Houghton County, Michigan
Date	
State(s)	
Watershed ID (HUC)	4020103 (Waterbody ID # 221001O)
Listed Segments	Five miles of Hammell Creek in the vicinity of the city of Osceola.
Lead Agency	Michigan Dept. of Environmental Quality
Basis for Listing	Water quality exceedance for Hg (for the protection of wildlife)
Listing Trigger Level	1.3 ng/L (protection of wildlife), the most stringent water quality criteria for Hg
Watershed / Water Column / Fish Tissue Data?	Water column data; no fish data
If yes, describe	Upstream of abandoned mine 0.83 ng/L (geomean tot. Hg); discharge from the mine 127 ng/L (geomean)
Type of Fish used for TMDL calculation	
Water Quality Target or Load	
TMDL	0.000018 lbs/day
MOS	Implicit (Conservative assumptions in critical flow 90Q10)
Point Sources Identified (list if power plant)	None (The only nonpoint source of mercury is discharge from the abandoned mine)
Effluent Data for PS?	NA
If yes, describe	
Allocations to sources?	Yes
WLA	None
LA	0.000018 lbs/day (2.5 cfs x 1.3 ng/L)
MOS	None
Rationale for allocation	Water quality target (1.3 ng/L) multiplied by avg mine discharge rate of 2.5 cfs.
Allocations of Reductions to Sources?	Yes
WLA	None (no point sources)
LA	99% reduction in Osceola mine discharge loading (to go from current conc of 127 ng to 1.3 ng/L)
Rationale for allocation	Based on required reduction from current conc (127 ng/L) to WQT from the single source (abandoned mine)
Narrative Description of Approach	The single source of mercury in Hammell Creek is from the abandoned mine (Osceola mine). Water quality target based on the most stringent numeric criteria for wildlife. TMDL based on 90Q10 flow times water quality target.
Narrative of Implementation Approach	Implementation Plan not developed yet
Comments	

TMDL Title	Minnesota's TMDL Study of Mercury - Draft
Date	5/24/2005
State(s)	Minnesota
Watershed ID (HUC)	Statwide - Divided into two regions: NE and SW
Listed Segments	Statewide (820 Lakes & 419 River impairments)
Lead Agency	Minnesota Pollution Control Agency (MPCA)
Basis for Listing	Fish tissue based (0.2 ppm); 12 lakes and 20 river reaches impaired for Hg in fish tissue and water; 808 lakes and 399 river reaches impaired for fish tissue only
Listing Trigger Level	0.2 ppm, calculated by using a fish cons rate of 30 g/day and no RSC for marine fish
Watershed / Water Column / Fish Tissue Data?	Water column & fish data. Fish tissue data collected between 1988-1992 used.
If yes, describe	Avg Hg conc in Walleye is 0.572 ppm in NE region and 0.405 in SW region.
Type of Fish used for TMDL calculation	Standard length (40cm) Walleye
Water Quality Target or Load	90th percentile fish tissue conc for a standard length walleye compared to the fish tissue criterion of 0.2 ppm
TMDL	404 kg/yr for NE region and 798 kg/yr for SW region (based on 1990 estimated load x reduction factor based on fish tissue)
MOS	
Point Sources Identified (list if power plant)	
Effluent Data for PS?	
If yes, describe	
Allocations to sources?	Yes
WLA	4 kg/yr in NE region and 7 kg/yr for SW region (1% of TMDL or equal to the estimated point source load, whichever is lower)
LA	400 kg/yr in NE region and 565 kg/yr in SW region (TMDL minus WLA)
MOS	Implicit - Selection of Walleye instead of northern pike; selection of NE region emission reduction value for throughout the State, and reduction in sulfate deposition resulting in lower methylation. Explicity MOS of 226 kg/yr for SW region.
Rationale for allocation	Proportional to estimated load in 1990 x reduction factor based on fish tissue conc.
Allocations of Reductions to Sources?	Yes (Reduction factor based on regional 90th percentile conc in fish tissue minus the target level of 0.2 ppm
WLA	Reduction based on max. allowed 1% of total current load.
LA	All load reductions must come from anthropogenic sources, which are 70% of the total atm. Hg deposition (this is further divided into 30% global and 40% regional sources). 68% reduction achieved from 1990 to 2000. Another 27% reduction from 1990 levels still required. NE region requires a reduction of 93% from anthropogenic emission sources, and SW region 73% - the more conservative 93% (NE region) reduction goal adopted for throughout the State.
Rationale for allocation	WLA set at 1% of TMDL or equal to the estimated point source load, whichever is lower. The remaining is allocated to LA.
Narrative Description of Approach	Point source load = avg effluent conc of 5 ng/L x facility design flow; Non-point source load is atm. Dep. Flux in 1990 (12.5 g/km2/yr) and surface area. Reduction goals based on 90th percentile conc in wallye vs. target conc of 0. 2 ppm. All reduction expected from anthropogenic sources (93% in NE region and 73% in SW region). 93% anthropogenic reduction is TMDL goal.
Narrative of Implementation Approach	Not developed yet. Adaptive management approach to be used (monitoring plan, interim targets, and a timeline). Additional restrictions will be imposed on point sources if de-minimus (I.e., <1%)
Comments	It is asserted that mercury in MN soils is from atmospheric sources, and there are no significant natural sources. BAF-based water concentration, although not used, was calculated at 0.52 ng/L. Median Hg conc in urban runoff and Agricul. Runoff comparable (19.7 ng/L vs. 21.7 ng/L)

EPA Region 6

	TMDLs for Segments Listed for Mercury in Fish Tissue for the Ouachita River Basin, and Bayou Bartholomew, Arkansas and Louisiana to Columbia
Date	5/30/2002
State(s)	AR, LA
Watershed ID (HUC)	08040201, 08040202, 08040203, 08040205, 08040207, 080101
Waterbody ID	
Listed Segments	Ouachita River 08040201 -002 08040201 -004 08040202 -002 08040202 -003 08040202 -004 Saline River 08040203 -001 08040204 -001 08040204 -002 08040204 -004 08040204 -006 Moro Creek 08040201 -001 Champagnolle Creek 08040201 -003 Little Champangnolle Creek 08040202 -003 Bayou Bartolomew 08040205 -002 08040205 -012 Cutoff Creek 08040205 -007
Lead Agency	EPA Region 6
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Graphical summaries of sediment data, Ouachita River. Maximum fish tissue concentrations, 54 tissue samples from various basin locations.
Water Quality Target or Load	384,946 g/yr 1,054,647 mg/day
MOS	
Point Sources Identified (list if power plant)	Y AECC-McClellan Generating Station, El Dorado Co., AR Union Generating Station, Saline Co., AR
Effleuent Data for PS?	Y
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.
Allocations to sources?	
Total Current Load	769,893 g/yr
WLA	942 g/yr Estimated using effleuent data from 5 POTWs and permit limits for 1 industrial facility
LA	768,951 g/yr Sum
MACT Sources	233,881 g/yr National Toxics Inventory
Direct Atmos (wet+dry) load	58961 g/yr Estimated from open water percentage and wet and dry deposition rates.
Local	4053 g/yr Estimated from local source emissions and airshed area.
Regional	54909 g/yr Difference of total deposition and local sources.
Erosion	
Soils	118332 g/yr (Upper bound estimate, soils concentration times erosion rates)
Geologic	591658 g/yr (Upper bound estimate, rock concentration times erosion rates)
MOS	N/A
Rationale for allocation	See description of how estimate was made for each individual source above
Allocations of Reductions to Sources?	Y
% Reduction	50% Calculated percentage of TMDL to total current load
WLA	942 g/day (Assumed to be less than 1% of total loading).
LA Local Atmos Sources	3129 g/day 22% reduction from current load
Regional Atmos Sources	27454 g/day 50% reduction from current load
Erosion	
MOS	20% based on the factor of safety in fish tissue action levels.
Rationale for allocation	A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. Additional reductions in atmospheric sources for other MACT categories are required to achieve the TMDL.
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.
Comments	

		TMDLs for Lakes Listed for Mercury in Fish Tissue for the Ouachita River Basin, Arkansas		
Date		11/20/2003		
State(s)		AR		
Watershed ID (HUC)		08040204		
Waterbody ID		Lake Monticello		
Listed Segments		08040204		
Lead Agency		EPA Region 6		
Basis for Listing		Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?		Y		
If yes, describe		Tabular summaries of fish tissue data.		
Water Quality Target or Load		None Explicit		
MOS				
Point Sources Identified (list if power plant)		Y AECC-McClellan Generating Station, El Dorado Co., AR Union Generating Station, Saline Co., AR		
Effleuent Data for PS?		Y		
If yes, describe		None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?				
Total Current Load		766,111	g/yr	
WLA		1031	g/yr	Estimated using effluent data from 5 POTWs and permit limits for 1 industrial facility
LA		765,080	g/yr	Sum
	MACT Sources	233,881	g/yr	National Toxics Inventory
	Direct Atmos (wet+dry) load	55090	g/yr	Estimated from open water percentage and wet and dry deposition rates.
	Local	3929	g/yr	Estimated from local source emissions and airshed area.
	Regional	51161	g/yr	Difference of total deposition and local sources.
	Erosion			
	Soils	118332	g/yr	(Upper bound estimate, soils concentration times erosion rates)
	Geologic	591658	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS		N/A		
Rationale for allocation		See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?		Y		
% Reduction		23% to 55%		Calculated percentage of TMDL to total current load
WLA		896		(Assumed to be less than 1% of total loading).
LA	Local Atmos Sources	3065	g/day	22% reduction from current load
	Regional Atmos Sources	25581	g/day	50% reduction from current load
	Erosion	223688		
MOS		20% based on the factor of safety in fish tissue action levels.		
Rationale for allocation		A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach		Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach		Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments				

	TMDLs for Segments Listed for Mercury in Fish Tissue for Selected Arkansas Watersheds		
Date	9/17/2002		
State(s)	AR		
Watershed ID (HUC)	11110206		
Waterbody ID	Fourche la Fave		
Listed Segments	11110206-02-8.7 Dry Fork Lake Cove Creek Lake Lake Nimrod		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load	69,854	g/yr	
MOS			
Point Sources Identified (list if power plant)	Y, See Appendix C		
Effluent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?	Y		
Total Current Load	102,686	g/yr	
WLA	4.4	g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA	102,682	g/yr	Sum
MACT Sources	293,103	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	568	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	72	g/yr	Estimated from local source emissions and airshed area.
Regional	496	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	17019	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	85095	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	32%		Calculated percentage of TMDL to total current load
WLA	3.5	g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA Local Atmos Sources	67	g/day	7% reduction from current load
Regional Atmos Sources	248	g/day	50% reduction from current load
Erosion	76532	g/day	
MOS	17462	g/day	20%
Rationale for allocation	A 7% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

	TMDLs for Segments Listed for Mercury in Fish Tissue for Selected Arkansas Watersheds		
Date	9/17/2002		
State(s)	AR		
Watershed ID (HUC)	11140203		
Waterbody ID	Bayou Dorcheat		
Listed Segments	11140203-20-11.9 11140203-22-8.4 11140203-24-7 11140203-26-23.3 Columbia Lake		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load	31,132	g/yr	
MOS			
Point Sources Identified (list if power plant)	Y, See Appendix C		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?	Y		
Total Current Load	56,661	g/yr	
WLA	63	g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA	56,598	g/yr	Sum
MACT Sources	255,316	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	3299	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	403	g/yr	Estimated from local source emissions and airshed area.
Regional	2896	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	8883	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	44416	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	45%		Calculated percentage of TMDL to total current load
WLA	51	g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA Local Atmos Sources	315	g/day	22% reduction from current load
Regional Atmos Sources	1448	g/day	50% reduction from current load
Erosion	29315	g/day	
MOS	7783	g/day	20%
Rationale for allocation	A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

	TMDLs for Segments Listed for Mercury in Fish Tissue for Selected Arkansas Watersheds		
Date	9/17/2002		
State(s)	AR		
Watershed ID (HUC)	11010014		
Waterbody ID	South Fork Little Red River		
Listed Segments	11010014 Johnson Hole		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load	18,037	g/yr	
MOS			
Point Sources Identified (list if power plant)	Y, See Appendix C		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?	Y		
Total Current Load	22,546	g/yr	
WLA	56	g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA	22,490	g/yr	Sum
MACT Sources	75,995	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	22.4	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	1.4	g/yr	Estimated from local source emissions and airshed area.
Regional	21	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	3745	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	18723	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	20%		Calculated percentage of TMDL to total current load
WLA	45	g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA Local Atmos Sources	1	g/day	2% reduction from current load
Regional Atmos Sources	10	g/day	50% reduction from current load
Erosion	17978	g/day	
MOS	4805	g/day	20%
Rationale for allocation	A 2% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

		TMDLs for Segments Listed for Mercury in Fish Tissue for Selected Arkansas Watersheds	
Date		9/17/2002	
State(s)		AR	
Watershed ID (HUC)		11110201	
Waterbody ID		Shepherd Springs Lake	
Listed Segments		11110201	
Lead Agency		EPA Region 6	
Basis for Listing		Fish Consumption, Fish consumption advisory	
Watershed / Water Column / Fish Tissue Data?		Y	
If yes, describe		Tabular summaries of fish tissue data.	
Water Quality Target or Load		4,707 g/yr	
MOS			
Point Sources Identified (list if power plant)		Y, See Appendix C	
Effleuent Data for PS?		Y	
If yes, describe		None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.	
Allocations to sources?		Y	
Total Current Load		4,801 g/yr	
WLA		0 g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA		4,801 g/yr	Sum
	MACT Sources	146,378 g/yr	National Toxics Inventory
	Direct Atmos (wet+dry) load	23.8 g/yr	Estimated from open water percentage and wet and dry deposition rates.
	Local	2.8 g/yr	Estimated from local source emissions and airshed area.
	Regional	21 g/yr	Difference of total deposition and local sources.
	Erosion		
	Soils	796 g/yr	(Upper bound estimate, soils concentration times erosion rates)
	Geologic	3981 g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS		N/A	
Rationale for allocation		See description of how estimate was made for each individual source above	
Allocations of Reductions to Sources?		Y	
% Reduction		2%	Calculated percentage of TMDL to total current load
WLA		0 g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA	Local Atmos Sources	3 g/day	1% reduction from current load
	Regional Atmos Sources	10 g/day	50% reduction from current load
	Erosion	4418 g/day	
MOS		1108 g/day	20%
Rationale for allocation		A 1% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.	
Narrative Description of Approach		Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.	
Narrative of Implementation Approach		Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.	
Comments			

	TMDLs for Segments Listed for Mercury in Fish Tissue for Slected Arkansas Watersheds		
Date	9/17/2002		
State(s)	AR		
Watershed ID (HUC)	11110207		
Waterbody ID	Spring Lake		
Listed Segments	Spring Lake		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load	150	g/yr	
MOS			
Point Sources Identified (list if power plant)	Y, See Appendix C		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?	Y		
Total Current Load	196	g/yr	
WLA	0	g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA	196	g/yr	Sum
MACT Sources	99,163	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	12.2	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	1.2	g/yr	Estimated from local source emissions and airshed area.
Regional	11	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	31	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	153	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	24%		Calculated percentage of TMDL to total current load
WLA	0	g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA — Local Atmos Sources	1	g/day	14% reduction from current load
Regional Atmos Sources	6	g/day	50% reduction from current load
Erosion	144	g/day	
MOS	38	g/day	20%
Rationale for allocation	A 14% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

	TMDLs for Segments Listed for Mercury in Fish Tissue for Selected Arkansas Watersheds		
Date	9/17/2002		
State(s)	AR		
Watershed ID (HUC)	08040203, 11110207		
Waterbody ID			
Listed Segments	Lake Winona Lake Sylvia		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load	1,713	g/yr	
MOS			
Point Sources Identified (list if power plant)	Y, See Appendix C		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?	Y		
Total Current Load	1,903	g/yr	
WLA	0	g/yr	Estimated using effluent data from 5 POTWs (x permitted flows) and permit limits for 1 industrial facility
LA	1,903	g/yr	Sum
MACT Sources	94,426	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	104	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	8	g/yr	Estimated from local source emissions and airshed area.
Regional	96	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	300	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	1499	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	10%		Calculated percentage of TMDL to total current load
WLA	0	g/day	Calculated as 15 ng/L x sum of permitted flow rates
LA Local Atmos Sources	7	g/day	11% reduction from current load
Regional Atmos Sources	48	g/day	50% reduction from current load
Erosion	1658	g/day	
MOS	428	g/day	20%
Rationale for allocation	An 11% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

	TMDLs for Lakes Listed for Mercury in Fish Tissue for the Ouachita River Basin, Arkansas		
Date	11/20/2003		
State(s)	AR		
Watershed ID (HUC)	08040204		
Waterbody ID	Grays Lake		
Listed Segments	08040204-27		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load			
MOS	None Explicit		
Point Sources Identified (list if power plant)	Y AECC-McClellan Generating Station, El Dorado Co., AR Union Generating Station, Saline Co., AR		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?			
Total Current Load	766,111	g/yr	
WLA	1031	g/yr	Estimated using effluent data from 5 POTWs and permit limits for 1 industrial facility
LA	765,080	g/yr	Sum
MACT Sources	233,881	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	55090	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	3929	g/yr	Estimated from local source emissions and airshed area.
Regional	51161	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	118332	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	591658	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	23% to 55%		Calculated percentage of TMDL to total current load
WLA	896		(Assumed to be less than 1% of total loading).
LA — Local Atmos Sources	3065	g/day	22% reduction from current load
Regional Atmos Sources	25581	g/day	50% reduction from current load
Erosion	223688		
MOS	20% based on the factor of safety in fish tissue action levels.		
Rationale for allocation	A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

	TMDLs for Lakes Listed for Mercury in Fish Tissue for the Ouachita River Basin, Arkansas		
Date	11/20/2003		
State(s)	AR		
Watershed ID (HUC)	08040201		
Waterbody ID	Big Johnson		
Listed Segments	08040201-80		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Tabular summaries of fish tissue data.		
Water Quality Target or Load			
MOS	None Explicit		
Point Sources Identified (list if power plant)	Y AECC-McClellan Generating Station, El Dorado Co., AR Union Generating Station, Saline Co., AR		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of sampling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?			
Total Current Load	766,111	g/yr	
WLA	1031	g/yr	Estimated using effluent data from 5 POTWs and permit limits for 1 industrial facility
LA	765,080	g/yr	Sum
MACT Sources	233,881	g/yr	National Toxics Inventory
Direct Atmos (wet+dry) load	55090	g/yr	Estimated from open water percentage and wet and dry deposition rates.
Local	3929	g/yr	Estimated from local source emissions and airshed area.
Regional	51161	g/yr	Difference of total deposition and local sources.
Erosion			
Soils	118332	g/yr	(Upper bound estimate, soils concentration times erosion rates)
Geologic	591658	g/yr	(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	23% to 55%		Calculated percentage of TMDL to total current load
WLA	896		(Assumed to be less than 1% of total loading).
LA — Local Atmos Sources	3065	g/day	22% reduction from current load
Regional Atmos Sources	25581	g/day	50% reduction from current load
Erosion	223688		
MOS	20% based on the factor of safety in fish tissue action levels.		
Rationale for allocation	A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. It is anticipated that reductions necessary to achieve safe levels in fish can be met with local and regional MACT reductions.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.8 mg/kg for Arkansas). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and change in permit limits is recommended.		
Comments			

		TMDLs for Segments Listed for Mercury in Fish Tissue for Coastal Bays and Gulf Waters of Louisiana	
Date		4/40/2005	
State(s)		LA	
Watershed ID (HUC)		010901, 021102, 042209, 070601, 110701, 120806	
Waterbody ID			
Listed Segments		Atchafalaya Bay and Delta (010901) Barataria Basin Coastal Bays (021102) Lake Pontchartrain Basin Coastal Bays (042209) Mississippi River Basin Coastal Bays (070601) Sabine River Basin Coastal Bays (110701) Terrebonne River Basin Coastal Bays (120806)	
Lead Agency		EPA Region 6	
Basis for Listing		Fish Consumption, Fish consumption advisory	
Watershed / Water Column / Fish Tissue Data?		Y	
If yes, describe		Graphical summaries of tissue concentrations in King Mackeral. Tabular summaries of concentration data for 20 ocean species (275 data points). Thirty (30) samples for dissolved total mercury in coastal bays and gulf waters. Nine data points for sediment (total and methyl mercury).	
Water Quality Target or Load		0.5 mg/kg in King Mackeral	
		1,013,721 g/yr	2,777,318 mg/day
MOS		N/A	
Point Sources Identified (list if power plant)		Y, over 600 dischargers Check Appendix C	
Effleuent Data for PS?		N	
If yes, describe			
Allocations to sources?		Y	
Total Current Load		2,467,450 g/yr	
WLA		2067 g/yr	See "Narrative Description of Approach" below.
	Atchafalaya	174 g/yr	
	Barataria	324 g/yr	
	Pontchartrain	527 g/yr	
	Mississippi River	0 g/yr	
	Sabine	57 g/yr	
	Terrebonne	985 g/yr	
LA		2,465,383 g/yr	
	Atchafalaya	55,629 g/yr	
	Barataria	94590 g/yr	
	Pontchartrain	52188 g/yr	
	Mississippi River	2127578 g/yr	
	Sabine	20077 g/yr	
	Terrebonne	115321 g/yr	
MOS		N/A	
Rationale for allocation		See "Narrative Description of Approach" below.	
Allocations of Reductions to Sources?		Y	
% Reduction		59%	Calculated percentage of TMDL to total current load
		1013721 g/yr	
WLA		2067 g/yr	(Assumed to be less than 1% of total loading).
	Atchafalaya	174 g/yr	
	Barataria	324 g/yr	
	Pontchartrain	527 g/yr	
	Mississippi River	0 g/yr	
	Sabine	57 g/yr	
	Terrebonne	985 g/yr	
LA		1011654 g/yr	22% reduction from current load
	Atchafalaya	22879 g/yr	50% reduction from current load
	Barataria	38915 g/yr	
	Pontchartrain	21613 g/yr	
	Mississippi River	872307 g/yr	
	Sabine	8255 g/yr	
	Terrebonne	47685 g/yr	
MOS		Implicit	
Rationale for allocation		Since point sources are not expected to be major sources, all of the reduction is slated to come from nonpoint sources, with reductions in air deposition to achieve this. However, no analysis is done to assure that reduction of air emissions alone can achieve the required reductions.	
Narrative Description of Approach		Air deposition estimates are made using EPA's REMSAD (Regional Model System for Aerosols and Deposition). Wastewater loads are estimated using permitted flow rates and an assumed effluent concentration of 12 ng/L. Contribution of the Mississippi River is estimated using mercury concentrations in water and sediment and TSS concentrations measured between 2001 and 2004 and assuming the bottom sediments are in equilibrium with suspended sediments. Watershed load is calculated using BASINS, with REMSAD deposition rates as inputs. 100% of generated mercury loads are assumed to reach the aquatic systems. Percent reduction calculated by determining ratio of King Mackeral average concentration to the safe level (0.5 mg/kg).	
Narrative of Implementation Approach		Municipal WWTPs over 0.1 MGD are assigned an individual WLA. A group allocation is provided for other point sources but facilties <0.1 MGD are exempt from allocation. Point source reductions not required, thus a 59% reduction in the nonpoint source load is required. Industrial point sources greater than 0.1 MGD are required to monitor using Method 1631. If Hg is detected, they are required to develop a mercury minimization plan. Monitoring required for POTWs; if Hg detected, minimization plans are required.	
Comments		Much of the reduction required would be from the Mississippi River, which would involve reductions in air sources far outside the basins for which this TMDL was done.	

	Mercury TMDLs for Little River and Catahoula Lake Watershed
Date	2/28/2003
State(s)	LA
Watershed ID (HUC)	081601, 081602, 081603, 081605
Waterbody ID	
Listed Segments	Little River, Confluence of Castor Creek and Dugdemona River to junction with Bear Creek, 081601 Little River from Bear Creek to Catahoula Lake, 081602 Catahoula Lake, 081603 Little River from Catahoula Lake to dam at Archie, 081605
Lead Agency	EPA Region 6
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Five (5) water column samples for total mercury, 73 fish tissue samples, four sediment samples for total mercury.
Water Quality Target or Load	0.5 mg/kg in fish tissue 51 kg/yr 138,685 mg/day
MOS	Implicit
Point Sources Identified (list if power plant)	Y
Effleuent Data for PS?	N
If yes, describe	
Allocations to sources?	Y
Total Current Load	74.95 g/yr
WLA	0.35 kg/yr Estimated using 12 ng/L and design flow rates for permitted facilities.
LA	74.60 kg/yr Sum
Runoff	63.82 kg/yr Assumed to be the same concentration as rainfall (based on MDN data). Runoff estimated using BASINS PLOAD Model.
Erosion	10.78 kg/yr No soils data for this watershed. Estimates were made based on data from the Savannah River collected by EPA and adjusted by assuming that the soil concentrations were linear with respect to deposition rates. Erosion estimates were made using BASINS PLOAD model.
MOS	N/A
Rationale for allocation	Reduction of 32% was applied to nonpoint sources; point sources are allowed to continue to discharge at current levels, subject to the WLA.
Allocations of Reductions to Sources?	Y
% Reduction	32% Calculated percentage of TMDL to total current load
WLA	0.35 kg/yr Calculated from
LA	50 kg/yr 32% reduction from current load
MOS	Implicit
Rationale for allocation	TMDL assumes that necessary reductions can come from air emission reductions. Not clear if those reductions need to extend beyond the existing MACT categories.
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in all species to the target safe level (0.5 mg/kg). Linearity of the response in fish tissue to atmospheric deposition is implied.
Narrative of Implementation Approach	Point sources are assumed to be deminimis. However, EPA stills believes that minimization of mercury is a priority. Points sources would be reuired to certify that they have no potential to discharge mercury, otherwise they would be required to monitor using Method 1631. If the water quality standard of 12 ng/L were to be exceeded, mercury minimization plans would be required.
Comments	

	TMDL for Mercury in Fish Tissue for Coastal Waters of the Calcasieu River Basin		
Date	5/28/2002		
State(s)	LA		
Watershed ID (HUC)	031201		
Waterbody ID			
Listed Segments	Calcasieu River, Coastal Waters, 031201		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	41 fish tissue data points		
Water Quality Target or Load	0.24 mg/kg in King Mackeral (TMDL was also calculated for a target of 0.4 mg/kg in King Mackeral)		
	896 g/yr	2,455 mg/day	
MOS			
Point Sources Identified (list if power plant)	Y		
	Calcasieu Power LLC		
	Entergy Gulf States, Inc.		
Effluent Data for PS?	Y		
If yes, describe	None for Generating Plants. Effluent data for two point sources with mercury in their permits was mostly ND at fairly high detection levels (200-500 ng/L).		
Allocations to sources?			
Total Current Load	3,447 g/yr		
WLA Calcasieu River	2023 g/yr	Estimated using effluent data (upper bound, most likely, lower bound). Most of the data was ND at 200-500 ng/L.	
LA	1,424 g/yr	Sum	
Local Atmos Sources	1,247 g/yr	National Toxics Inventory	
Regional Atmos Sources	177 g/yr	National Toxics Inventory	
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	74%	Calculated percentage of TMDL to total current load	
WLA Calcasieu River	0 g/day	Point source discharges would have to be zero to meet TMDL	
LA Local Atmos Sources	997 g/day	20% reduction from current load expected	
Regional Atmos Sources	88 g/day	50% reduction from current load	
MOS	20% based on the factor of safety in fish tissue action levels.		
Rationale for allocation	A 20% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. In addition to point sources in the Calcasieu needing to contribute a zero load, additional reductions in atmospheric sources for other MACT categories are required to achieve the TMDL.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in King Mackeral to the target safe level (0.24 mg/kg). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	There is no language concerning implementation relative to point sources in this TMDL.		
Comments	Contrary to other TMDLs in Region 6, this one calculates point sources in the Calcasieu to be a major contributor of mercury.		

	TMDLs for Segments Listed for Mercury in Fish Tissue for the Ouachita River Basin, and Bayou Bartholomew, Arkansas and Louisiana to Columbia		
Date	5/30/2002		
State(s)	LA		
Watershed ID (HUC)	080101, 080401, 080402		
Waterbody ID			
Listed Segments	Ouachita River - Arkansas State Line to Columbia 080401 Bayou Bartholomew 080401 080402		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Graphical summaries of sediment data, Ouachita River. Maximum fish tissue concentrations, 54 tissue samples from various basin locations.		
Water Quality Target or Load			
MOS	256,631 g/yr	703,099 mg/day	
Point Sources Identified (list if power plant)	Y AECC-McClellan Generating Station, El Dorado Co., AR Union Generating Station, Saline Co., AR		
Effleuent Data for PS?	Y		
If yes, describe	None for Generating Plants. Summary of samling conducted by ADEQ indicates an average for POTWs of 15 ng/L.		
Allocations to sources?			
Total Current Load	769,893 g/yr		
WLA	942 g/yr		Estimated using effleuent data from 5 POTWs and permit limits for 1 industrial facility
LA	768,951 g/yr		Sum
MACT Sources	233,881 g/yr		National Toxics Inventory
Direct Atmos (wet+dry) load	58961 g/yr		Estimated from open water percentage and wet and dry deposition rates.
Local	4053 g/yr		Estimated from local source emissions and airshed area.
Regional	54909 g/yr		Difference of total deposition and local sources.
Erosion			
Soils	118332 g/yr		(Upper bound estimate, soils concentration times erosion rates)
Geologic	591658 g/yr		(Upper bound estimate, rock concentration times erosion rates)
MOS	N/A		
Rationale for allocation	See description of how estimate was made for each individual source above		
Allocations of Reductions to Sources?	Y		
% Reduction	67%		Calculated percentage of TMDL to total current load
WLA	942 g/day		(Assumed to be less than 1% of total loading).
LA — Local Atmos Sources	3129 g/day		22% reduction from current load
Regional Atmos Sources	27454 g/day		50% reduction from current load
Erosion	653190 g/day		
MOS	20% based on the factor of safety in fish tissue action levels.		
Rationale for allocation	A 22% reduction is expected from local atmospheric sources. A 50% reduction is expected from regional atmospheric sources. Additional reductions in atmospheric sources for other MACT categories are required to achieve the TMDL.		
Narrative Description of Approach	Estimate of existing load is first made. Reductions are estimated as ratio of the average fish tissue concentration in large mouth bass to the target safe level (0.4 mg/kg for Louisiana). Linearity of the response in fish tissue to atmospheric deposition is implied.		
Narrative of Implementation Approach	Point sources are assumed to be deminimis. Therefore, the water quality standard of 12 ng/L is assmued to be protective and no change in permit limits is recommended.		
Comments			

	Mercury TMDLs for Subsegments Within Mernaentau and Vermilion-Teche River Basins	
Date	1/19/2001	
State(s)	LA	
Watershed ID (HUC)	060203, 061201	
Waterbody ID	Vermilion-Teche River Basin	
Listed Segments	Bayou Plaquemine Brule (050201) Seventh Ward Canal subsegemnt of 050702) Bayou Des Cannes (050101) Portion of the Gulf of Mexico (050901)	
Lead Agency	EPA Region 6	
Basis for Listing	Fish Consumption, Fish consumption advisory	
Watershed / Water Column / Fish Tissue Data?	Y	
If yes, describe	Summaries of fish tissue data.	
Water Quality Target or Load	0.4 mg/kg in fish tissue 56 kg/yr	153,973 mg/day
MOS		
Point Sources Identified (list if power plant)	N	
Effleuent Data for PS?	N	
If yes, describe	Summary of sampling conducted indicates an average for dishcargers of 15 ng/L.	
Allocations to sources?		
Total Current Load	167 kg/yr	
WLA	0.7 kg/yr	Estimated using permitted flow rates and an assumed effluent concentation of 15 ng/L.
LA	166 kg/yr	Sum
Wet	125 kg/yr	National Toxics Inventory
Dry	41.5 kg/yr	Estimated from open water percentage and wet and dry deposition rates.
MOS	N/A	
Rationale for allocation	Ratio of worst case average fish tissue concentration in bowfin to the safe level.	
Allocations of Reductions to Sources?	Y	
% Reduction	66%	Calculated percentage of TMDL to total current load
WLA	0.7 kg/yr	Calculated
LA	56 kg/yr	
Wet	42 kg/yr	67% reduction from current load
Dry	14 kg/yr	67% reduction from current load
MOS	20% based on the factor of safety in fish tissue action levels (0.4 versus 0.5 mg/kg)	
Rationale for allocation	A 50% reduction is expected from regional atmospheric sources. Additional reductions in atmospheric sources for other MACT categories are required to achieve the TMDL.	
Narrative Description of Approach	Estimate of existing load is first made from wet and dry deposition data and watershed area. Reductions are estimated as ratio of the "worst case" average fish tissue concentration (in this case 1.191 mg/kg measured in bowfin in Bayou Palquemine Brule) to the target safe level (0.4 mg/kg). Linearity of the response in fish tissue to atmospheric deposition is assumed.	
Narrative of Implementation Approach	Point sources are assumed to be a minor part of the mercury load. Point sources are expected to be handled using the normal "reasonable potential" approach in the NPDES permitting process.	
Comments		

	Mercury TMDLs for Subsegments Within Mernaentau and Vermilion-Teche River Basins		
Date	1/19/2001		
State(s)	LA		
Watershed ID (HUC)	060203, 061201		
Waterbody ID	Vermilion-Teche River Basin		
Listed Segments	Chicot Lake 060203 Vermilion-Teche River Basin Gulf Water to 3-mile Limit 061201		
Lead Agency	EPA Region 6		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Summaries of fish tissue data.		
Water Quality Target or Load	0.4 mg/kg in fish tissue		
	61	kg/yr	166,027 mg/day
MOS			
Point Sources Identified (list if power plant)	N		
Effleuent Data for PS?	N		
If yes, describe	Summary of sampling conducted indicates an average for dishcargers of 15 ng/L.		
Allocations to sources?			
Total Current Load	176	kg/yr	
WLA	2.7	kg/yr	Estimated using permitted flow rates and an assumed effluent concentation of 15 ng/L.
LA	174	kg/yr	Sum
Wet	130	kg/yr	National Toxics Inventory
Dry	43.4	kg/yr	Estimated from open water percentage and wet and dry deposition rates.
MOS	N/A		
Rationale for allocation	Ratio of worst case average fish tissue concentration in bowfin to the safe level.		
Allocations of Reductions to Sources?	Y		
% Reduction	66%		Calculated percentage of TMDL to total current load
WLA	2.7	kg/yr	Calculated
LA	58	kg/yr	
Wet	43	kg/yr	67% reduction from current load
Dry	15	kg/yr	67% reduction from current load
MOS	20% based on the factor of safety in fish tissue action levels (0.4 versus 0.5 mg/kg)		
Rationale for allocation	A 50% reduction is expected from regional atmospheric sources. Additional reductions in atmospheric sources for other MACT categories are required to achieve the TMDL.		
Narrative Description of Approach	Estimate of existing load is first made from wet and dry deposition data and watershed area. Reductions are estimated as ratio of the "worst case" average fish tissue concentration (in this case 1.191 mg/kg measured in bowfin in Bayou Palquemine Brule) to the target safe level (0.4 mg/kg). Linearity of the response in fish tissue to atmospheric deposition is assumed.		
Narrative of Implementation Approach	Point sources are assumed to be a mnor part of the mercury load. Point sources are expected to be handled using the normal "reasonable potential" approach in the NPDES permitting process.		
Comments			

EPA Region 7

TMDL Title	Neosho Basin Total Maximum Daily Load, South Cottonwood River
Date	
State(s)	
Watershed ID (HUC)	11070202
Listed Segments	17 and 18 beginning at confluence with the Cottonwood River and continuing upstream to headwaters in w. Marion County Tributary segments include Antelope Creek (19), Stony Brook (25), and Unnamed Stream (456).
Lead Agency	Kansas Department of Health and Environment
Basis for Listing	Expected Aquatic Life Support
Listing Trigger Level	12 ng/L (Aquatic Life Use Chronic WQS)
Watershed / Water Column / Fish Tissue Data?	Watercolumn data; no fish data
If yes, describe	Water column data at one location (Station 635) based on a detection limit of 0.5 ug/L.
Type of Fish used for TMDL calculation	
Water Quality Target or Load	
TMDL	0.000596 lb/day
MOS	0.000059 lb/day
Point Sources Identified (list if power plant)	Yes (Hillsboro MWTP)
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	Yes
WLA	0.0000038 lb/day
LA	0.031 lb/day
MOS	
Rationale for allocation	Flow x WQS used to calculate allocation for point sources; the WLA and MOS subtracted from TMDL to calculate LA
Allocations of Reductions to Sources?	Yes
WLA	No Reduction
LA	0.000530 (98.3% reduction)
MOS	0.000059 lb/day (10% of TMDL) in addition to implicit MOS (conservative assumptions)
Rationale for allocation	LA is calculated as the TMDL minus the MOS and WLA
Narrative Description of Approach	Generalized watershed Loading Function Model (GWLF) used to calculate Hg loads and sediment yield, and REMSAD (Regional Modeling system for Aerosols and Deposition) was used to simulate wet and/or dry deposition to the watershed.
Narrative of Implementation Approach	Stated as low priority for implementation. Desired implementation activities include monitoring any anthropogenic contributions of Hg loading to river.
Comments	GWLF model based on avg sediment Hg concentrations (0.2 ppm) derived from USGS studies in Kansas and not site-specific info. Wasteload allocation and wq data based on "detection limit" of 0. 5 ug/L (including 2001 data) Estimated Hg conc in runoff = Hg in rainfall (I.e., no retention in watershed).

EPA Region 8

TMDL Title	TMDLS FOR MERCURY IN MCPHEE & NARRAGUINNEP RESERVOIRS, COLORADO
Date	12/1/2003
State(s)	Colorado
Watershed ID (HUC)	14030002 McPhee Reservoir is impoundment of Dolores River 14080202 Narraguinnep reservoir privately owned (625 acres); majority of water to Narraguinnep is via interbasin transfer from McPhee reservoir
Waterbody ID	
Listed Segments	Mainstem of the Dolores R from a point immediately above the confluence with Bear Creek to the bridge at Bradfield Ranch including McPhee Reservoir Narraguinnep, Pruett, and Totten reservoir
TMDL Segments	McPhee Reservoir Narraguinnep Reservoir
Lead Agency	Colorado Department of Public Health & Environment
Basis for Listing	Fish consumption advisory
Listing Trigger Level	0.5 ppm (also numeric std of 10 ng/L based on based on Fish Residue value of 1 ppm; but this has not been exceeded)
Watershed / Water Column / Fish Tissue Data?	Y
Type of Fish used for TMDL calculation	15-inch smallmouth bass for McPhee and 18-inch walleye for Narraguinnepp
If yes, describe	
Water Quality Target or Load	
TMDL	2,592 g/yr McPhee 39.1 g/yr Narraguinnep
MOS	
Point Sources Identified (list if power plant)	Yes (one municpal WWTP and one pvt plant) (Two power plants identified under atmospheric sources)
Effluent Data for PS?	No
If yes, describe	
Allocations to sources?	Yes

McPhee Reservoir		Narraguinnep Reservoir	
WLA	0	WLA	0 g/yr
LA	3049 g/yr	LA	78.1 g/yr
Atmospheric Deposition	251 g/yr	Atmospheric Deposition	36.8 g/yr
Rico/Silver Creek Mining Area	1030 g/yr	Inter-Basin Transfer from McPhee	15.9 g/yr
Dunton Mining Area	708 g/yr		
La Plata Mining Area	141 g/yr		
Watershed Background	919 g/yr	Watershed Background	25.4 g/yr
Unallocated Reserve	778 g/yr (30%)		11.8 g/yr (15%)

Rationale for allocation	Model predicts a 15% reduction in loading to achieve 0.5 ppm levels in McPhee; and 50% reduction for Narraguinnep
Allocations of Reductions to Sources?	

McPhee Reservoir		Narraguinnep Reservoir	
WLA	0 g/yr	WLA	0 g/yr
LA	1814 g/yr	LA	27.3
Atmospheric Deposition	63 g/yr	Atmospheric Deposition	9.2 g/yr
Rico/Silver Creek Mining Area	507 g/yr	Inter-Basin Transfer from McPhee	9.5 g/yr
Dunton Mining Area	348 g/yr		
La Plata Mining Area	69 g/yr		
Watershed Background	827 g/yr	Watershed Background	8.6 g/yr
Unallocated Reserve (includes MOS)	778 g/yr (30%)	Unallocated Reserve (includes MOS)	11.8 g/yr (15%)

Rationale for allocation	Based on impacts to both reservoirs (e.g., atm. Reduction would impact Narraguinnep more than McPhee). Therefore, a 25% MOS was added to the 50% reduction needed for Narraguinnep and applied to both Reservoirs.
Narrative Description of Approach	Watershed loading of Hg and sediment calculated using Generalized Watershed Loading Funciton (GWLF) model. Lake modeling by D-MCM. Atm. Deposition from wet deposition rates. D-MCM run with 15% load reductions for McPhee and 50% reduction for Narraguinnep produced desired Hg levels in fish tissue.
Narrative of Implementation Approach	Allocations are described as "potential" rather than "final" allocations (which will be made in Phase II TMDL)
Comments	Reference dose is 0.3 ppm for general population and 0.075 ppm for preg. Women and children Ingestion rate of 227 g/meal for a 70-kg adult Two large coal-powered plants (Arizona Public Service - Four Corners Station, and Pub.Svc company of New Mexico - San Juan Plant located within 50 miles of the McPhee & Narraguinnep reservoirs. "Atmospheric deposition accounts for a relatively small proportion (<10%) of the total Hg load to McPhee.

EPA Region 9

TMDL Title	Total Maximum Daily Load and Implementation Plan for Mercury Arivaca Lake, Arizona
Date	10/15/1999
State(s)	AZ
Watershed ID (HUC)	15050304
Waterbody ID	
Listed Segments	Arivaca Lake
Lead Agency	AZ DEQ, US EPA Region 9
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	19 fish tissue samples, 7 water samples for total and dissolved Hg, 4 surface, 3 from various depths, 12 sediment samples (in lake) 26 sediment samples (watershed and tributaries)
Water Quality Target or Load	1 mg/kg in fish tissue 155 g/day
MOS	
Point Sources Identified (list if power plant)	N
Effleuent Data for PS?	N/A
If yes, describe	
Allocations to sources?	
Watershed	178.89 g/day
Ruby Dump	0.68 g/day
Direct Atmosheric to lake	4.21 g/day
Total	183.78 g/day
Rationale for allocation	GWLF Model for watershed load, MDN measurements for direct atmospheric deposition to lake
Allocations of Reductions to Sources?	Y
Watershed	111.2 g/day 38 % Reduction
Ruby Dump	0.68 g/day 0 % Reduction
Direct Atmosheric to lake	4.21 g/day 0 % Reduction
Unallocated Reserve	38.7 g/day 25 % of loading capacity
Total	154.79 g/day
Rationale for allocation	Watershed load is reduced in the model until the alolwable concentrations in fish are met.
Narrative Description of Approach	GWLF model is coupled to MCM. MCM caculates the tissue concentration in 5 year old large mouth bass as the basis for assessing if the 1 mg/kg criterion in fish tissue is met.
Narrative of Implementation Approach	Improved range / grazing management in the watershed.
Comments	

TMDL Title	Total Maximum Daily Load and Implementation Plan for Mercury Pena Blanca Lake, Arizona
Date	10/15/1999
State(s)	AZ
Watershed ID (HUC)	15050301
Waterbody ID	
Listed Segments	Pena Blanca Lake
Lead Agency	AZ DEQ, US EPA Region 9
Basis for Listing	Fish Consumption, Fish consumption advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	148 fish tissue samples, 3 water samples for total and methyl Hg from various depths, 4 sediment samples (in lake) 16 sediment samples (watershed and tributaries)
Water Quality Target or Load	1 mg/kg in fish tissue 145 g/day
MOS	
Point Sources Identified (list if power plant)	N
Effleuent Data for PS?	N/A
If yes, describe	
Allocations to sources?	
Watershed	58.6 g/day
St. Patrick Mine Ball Mill Site	133 g/day
Direct Atmosheric to lake	2.3 g/day
Total	193.9 g/day
Rationale for allocation	GWLF Model for watershed load, MDN measurements for direct atmospheric deposition to lake
Allocations of Reductions to Sources?	Y
Watershed	58.6 g/day 0 % Reduction
St. Patrick Mine Ball Mill Site	18.6 g/day 86 % Reduction
Direct Atmosheric to lake	2.3 g/day 0 % Reduction
Unallocated Reserve	65.2 g/day 25 % of loading capacity
Total	144.7 g/day
Rationale for allocation	Watershed load is reduced in the model until the alolwable concentrations in fish are met.
Narrative Description of Approach	GWLF model is coupled to MCM. MCM caculates the tissue concentration in 5 year old large mouth bass as the basis for assessing if the 1 mg/kg criterion in fish tissue is met.
Narrative of Implementation Approach	Cleanup of St. Patrick Ball Mill Mine Site by the USFS
Comments	

TMDL Title	Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin Basins for the Control of Mercury in Cache Creek, Bear Creek, Sulphur Creek and Harley Gulch Staff Report and Functionally Equivalent Document Public Review Draft June 2005	
Date	6/30/2005	
State(s)	CA	
Watershed ID (HUC)		
Waterbody ID		
Listed Segments	Cache Creek (Clear Lake to NF Conf.) NF Cache Creek Harley Gulch Davis Creek Bear Creek Cache Creek @ Yolo Bypass Bear Creek @ Bear Valley Road Sulphur Creek Bear Creek @ Hwy 20	
Lead Agency	California Regional Water Quality Control Board, Central Valley Region	
Basis for Listing	Fish Consumption, Mercury in water and sediment	
Watershed / Water Column / Fish Tissue Data?	Y	
If yes, describe	Summaries of mean concentrations of MeHg in fish tissue by trophic level. Summaries of total mercury in water samples (233 samples), suspended sediment (five-year average concentrations at 9 locations).	
Water Quality Target or Load	0.12 mg/kg trophic level 3 fish; 0.23 mg/kg trophic level 4 fish for protection of human health and wildlife, including bald eagles in Cache Creek; in Harley Gulch, 0.05 mg/kg in trophic level 2 fish.	
TL 3 Objective Cache Creek)	0.15 ng/L of MeHg	
TL 4 Objective Cache Creek)	0.14 ng/L of MeHg	
Bear Creek	0.06 ng/L of MeHg	
Harley Gulch	0.09 ng/L of MeHg	
MOS	N/A	
Point Sources Identified (list if power plant)	Y, 11 mining sites	
Effleuent Data for PS?	No	
If yes, describe		
Allocations to sources?	Y	Allocations are methyl, not total mercury reductions
Cache Creek (Clear lake to NF Conf.)	36.8 g/yr	
NF Cache Creek	12.4 g/yr	
Harley Gulch	1 g/yr	
Davis Creek	1.3 g/yr	
Bear Creek	21.1 g/yr	
In-channel production & ungaged tribs	49.5 g/yr	
Cache Creek @ Yolo Bypass	122 g/yr	
Bear Creek @ Bear Valley Road	1.7 g/yr	
Sulphur Creek	8 g/yr	
In-channel production & ungaged tribs	11.4 g/yr	
Bear Creek @ Hwy 20	21.1 g/yr	
Atmospheric Deposition	0.02 kg/yr	
Rationale for allocation	Contained in Appendices; not reviewed	
Allocations of Reductions to Sources?		
Cache Creek (Clear lake to NF Conf.)	11 g/yr	70 % Reduction
NF Cache Creek	12.4 g/yr	0 % Reduction
Harley Gulch	0.04 g/yr	96 % Reduction
Davis Creek	0.7 g/yr	46 % Reduction
Bear Creek	3 g/yr	86 % Reduction
In-channel production & ungaged tribs	32 g/yr	35 % Reduction
Cache Creek @ Yolo Bypass	66 g/yr	46 % Reduction
Cache Creek MOS	7 g/yr	10% of acceptable load
Bear Creek @ Bear Valley Road	0.9	47 % Reduction
Sulphur Creek	0.8	90 % Reduction
In-channel production & ungaged tribs	1	91 % Reduction
Bear Creek @ Hwy 20	3	86 % Reduction
Bear Creek MOS	0.3	10% of acceptable load
	0.02 kg/yr	0 % Reduction
Rationale for allocation	Contained in Appendices; not reviewed	
Narrative Description of Approach	Fish tissue targets selected based on protection of human health and wildlife.	
Narrative of Implementation Approach	Combination of projects to reduce erosion and trasnport of mercury and generation of methylmercury including: remediation of inactive mines (including adjacent stream banks), control of erosion in mercury enriched areas from activities such as grazing and road maintenance, possible remediation of Harley Gulch sediment delta, control of Hg/MeHg source in lower watershed, identification/removal of floodplain sediments. A 95% reduction in Hg is required from abandoned mine sites. Any new reservoir or wetland projects will be reviewed for its potential to produce MeHg.	
Comments	Water quality targets corresponding to TL3 and TL 4 levels in fish were detemined by regression equations. Not clear if reductions are based on comparisons of current to required concentrations in the water column or in sediment. Review TMDL document in addition to basin plan amendment.	

TMDL Title	Total Maximum Daily Load Technical Support Analysis for Mercury Impairment of Clear Creek and Hernandez Reservoir
Date	3/10/2004
State(s)	CA
Watershed ID (HUC)	
Waterbody ID	Clear Creek and Hernandez Reservoir
Listed Segments	Clear Creek Hernandez Reervoir
Lead Agency	California Regional Water Quality Control Board, Central Coast Region
Basis for Listing	Fish Consumption (Hrenandez Reservoir) and Exceedance of WQS (0.050 ug/L - Clear Creek)
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Summaries of fish tissue data. 49 samples for total Hg, 45 samples of Hg in sediments.
Water Quality Target or Load	0.3 mg/kg in tissue of trophic level 4 fish, 0.050 ug/L in the water column
MOS	N/A
Point Sources Identified (list if power plant)	Y, inactive mine site
Effleuent Data for PS?	No
If yes, describe	
Allocations to sources?	N
Rationale for allocation	
Allocations of Reductions to Sources?	N, current load was not established
Clear Creek	236 g/yr
Hernadez Reservoir	1015 g/yr
Tributary Creeks	779 g/yr
MOS	Implicit
Rationale for allocation	Allocation for Clear Creek and Hernandez Reservoir were calculated by multipying the mean annual flow times the WQT of 0.050 ug/L. NPS allocation is the difference between the allocation for Hernandez Reservoir and Clear Creek.
Narrative Description of Approach	Fish tissue targets selected based on protection of human health and wildlife.
Narrative of Implementation Approach	No additional implementation measures are anticipated because the BLM has been undertaking mine reclamation and this activity appears to be bringing about a decline in sediment concentrations and water column data support the conclusion that conditions are improving. Water quality will be monitored until the WQS is achieved in Clear Creek. Reduction of sediment mercury loads to "background" value of 0.2 mg/kg is assumed to bring the associated necessary reductions in fish tissue and water column mercury.
Comments	

TMDL Title	Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin Basins for the Control of Mercury in Clear Lake (Lake County) Staff Report and Functionally Equivalent Document Final Report December 2002
Date	12/30/2002
State(s)	CA
Watershed ID (HUC)	
Waterbody ID	Clear Lake
Listed Segments	513.52 (Clear Lake), 511/513 (Clear Lake to Yolo Bypass)
Lead Agency	California Regional Water Quality Control Board, Central Valley Region
Basis for Listing	Fish Consumption
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Summaries of means, standard deviations of Hg in individual fish species. Summaries of mercury in Clear Lake sediments.
Water Quality Target or Load	0.09 mg/kg trophic level 3 fish; 0.19 mg/kg trophic level 4 fish for protection of human health and wildlife, including bald eagles
Sediment targets	
Upper Arm	0.8 mg/kg
Lower Arm	1 mg/kg
Oaks Arm	3 to 16 mg/kg
MOS	N/A
Point Sources Identified (list if power plant)	Y
Effleuent Data for PS?	No
If yes, describe	
Allocations to sources?	Y
Active Sediment Bed Layer	Not estimated
Sulfur Bank Mercury Mine	1 to 568 kg/yr
Tributary Creeks	1 to 60 kg/yr
Atmospheric Deposition	2 kg/yr
Rationale for allocation	Existing data / measurements
Allocations of Reductions to Sources?	70% reduction in fish tissue
Active Sediment Bed Layer	70 % Reduction
Sulfur Bank Mercury Mine	95 % Reduction
Tributary Creeks	80 % Reduction
Atmospheric Deposition	0 % Reduction
Rationale for allocation	Fish tissue must be reduced by 60% with a 10% margin of safety. Since fish tissue is assumed to be linked directly to sediment concentrations, sediment concentrations must be reduced by 70%. Atmospheric sources are assumed to be minimal and no reductions are mandated. Sediment reductions are to be achieved by reduction of tributary inputs and remediation of the Sulphur Bank Mercury Mine and passive burial of in-lake sediments.
Narrative Description of Approach	Fish tissue targets selected based on protection of human health and wildlife.
Narrative of Implementation Approach	Requires submittal of a remediation plan for the Sulfur Bank Mercury Mine. USFS, BLM and other land management agencies to identify hot pots in tributaries and develop monitoring and implementation plans to achieve reductions. An 80 year time frame is expected to achieve compliance.
Comments	

TMDL Title	Mercury in San Francisco Bay Total Maximum Daily Load (TMDL) Proposed Basin Plan Amendment and Staff Report		
Date	9/2/2004		
State(s)	CA		
Watershed ID (HUC)			
Waterbody ID	San Francisco Bay		
Listed Segments	Sacramento / San Joaquin Delta		
	Suisun Bay		
	Carquinez Strait		
	San Pablo Bay		
	Richardson Bay		
	Central San Franscisco Bay		
	Lower San Francisco Bay		
	South San Francisco Bay		
	Castro Cove		
	Oakland Inner Harbor		
	San Leandro Bay		
Lead Agency	California Regional Water Quality Control Board, San Francisco Bay Region		
Basis for Listing	Fish Consumption Advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Summaries of total mercury concentations in water column, mercury concentration profiles in sediments, concentration and mass estimates at various sites on Bay margins,		
Water Quality Target or Load	0.2 mg/kg in fish tissue (adjusted based on a fish consumption rate of 32 g/day); 0.5 mg/kg in bird eggs; median conentration in sediment of 0.2 mg/kg		
Point Sources Identified (list if power plant)	Y	WLA	
	GWF Power Systems, Site I	0.002 kg/yr	No permit in PCS
	GWF Power Systems, Site V	0.003 kg/yr	No permit in PCS
	PG&E, Hunters Point Power Plant	0.022 kg/yr	Permit expired, no data in PCS
	Southern Energy California, Pittsburg Power Plant	0.008 kg/yr	Has Hg Data
	Southern Energy Delta LLC, Portrero Power Plant	0.003 kg/yr	Permit expired, no Hg Data
Effleuent Data for PS?	No		
If yes, describe			
Allocations to sources?	Y		
Bed Erosion	460 kg/yr		
Central Valley Watershed	440 kg/yr		
Urban Stormwater Runoff	160 kg/yr		
Guadalupe River Watershed	92 kg/yr		
Atmospheric Deposition	27 kg/yr		
Non-urban Stormwater Runoff	25 kg/yr		
Wastewater (municipal and industiral)	20 kg/yr		
Sediment Dredging and Disposal	Net loss		
Total	1224		
Rationale for allocation	Existing data / measurements		
Allocations of Reductions to Sources?	70% reduction in fish tissue		
Bed Erosion	220 kg/yr	52 % Reduction	
Central Valley Watershed	330 kg/yr	25	
Urban Stormwater Runoff	82 kg/yr	49	
Guadalupe River Watershed	2 kg/yr	98	
Atmospheric Deposition	27 kg/yr	0	
Non-urban Stormwater Runoff	25 kg/yr	0	
Wastewater (municipal and industiral)	20 kg/yr	0	
Sediment Dredging and Disposal	< ambient concentration		
Total	706 kg/yr	42 % Reduction (TMDL document says a 50% reduction is required)	
MOS	Implicit		
Rationale for allocation	Fish tissue must be reduced by 50% (marker species is striped bass). Since the sediment concentration target is 0.2 mg/kg, reductions from the Central Valley watershed, Guadalupe River watershed, and urban stormwater are based on reductions from current sediment concentrations. Atmospheric sources, non-urban stormwater and wastewater loads are assumed to be minimal and no reductions are mandated.		
Narrative Description of Approach	Fish tissue targets selected based on protection of human health and wildlife. Reductions in sediment concentrations are assumed to lead to 1:1 percentage reduction in biota tissue concentrations.		
Narrative of Implementation Approach	Reduce contollable mercury sources. Reduce the amount of mercury transformed to methylmercury, improve technical understanding of mercury fate and transport in the Bay, encourage implementation plans that target multiple pollutants. With regard to air emission sources, the implementation plans calls for supporting and tracking national efforts such as the Clear Skies Act and the Quicksilver Caucus.		
Comments	Bay sediments estimated to reach 0.2 mg/kg in 120 years		

TMDL Title	Sacramento - San Joaquin Delta Estuary TMDL for Methyl and Total Mercury, Staff Report
Date	8/1/2005
State(s)	CA
Watershed ID (HUC)	
Waterbody ID	Sacramento - San Joaquin Delta
Subregions of the Legal Delta	San Joaquin River Central Delta Marsh Creek West Delta Sacramento River Cosumnes / Mokolumne River Yolo Bypass South Yolo Bypass North
Lead Agency	California Regional Water Quality Control Board, Central Valley Region
Basis for Listing	Fish Consumption Advisory
Watershed / Water Column / Fish Tissue Data?	Y
If yes, describe	Summaries of mean concentrations of MeHg in 350 mm standardized largemouth bass, summareis of fish data used in the linkage analysis. Summaries of total MeHg in water samples. Summaries of total mercury/TSS/Flow data used to calculate inputs to / outputs from Delta
Water Quality Target or Load	0.28 mg/kg in a 350 mm (14 inch) largemouth bass for protection of human health and wildlife; 0.06 ng/L total MeHg (equivalent to the fish tissue criterion); Sediment target of 0.2 mg/kg (prescribed by SF
Total MeHg Water Column	0.06 ng/L of MeHg
MOS	18% based on staff recommended 0.073 ng/L MeHg and the criterion of 0.06 ng/L above.
Point Sources Identified (list if power plant)	Y California State Central Plant GWF Power Systems Mirant Delta LLC (Antioch Plant)
Effleuent Data for PS?	Y
If yes, describe	Effluent data for municipal and industrial NPDES dischargers, including power plants Central Heating/Cooling Plant, # CA0078581, Hg data in TMDL Report, No Hg data in PCS GWF Power Systems, Site IV, Petroleum coke fired, # CA0082309, Hg Data in TMDL Report, No Hg Da Mirant Delta LLC (Antioch Plant), natural gas-fired, # CA0004863, Hg Data in TMDL Report and in PCS
Allocations to sources?	Y, loads are for MeHg
San Joaquin River	478 g/yr
Marsh Creek	6.6 g/yr
Central Delta	524 g/yr
West Delta	320 g/yr
Sacramento River	2414 g/yr
Mokolumne River	123 g/yr
Yolo Bypass	1068 g/yr
Rationale for allocation	MeHg loads were determined by the product of flow volume and measured total water column methyl mercury concentrations. Total mercury loads were determined on relationships between flow, TSS and suspended sediment concentration. Power plants within the Delta were considered to contribute minor
Allocations of Reductions to Sources?	Allocations are for MeHg
San Joaquin River	179 g/yr — 63 % Reduction
Marsh Creek	1.8 — 73 % Reduction
Central Delta	524 g/yr — 0 % Reduction
West Delta	320 g/yr — 0 % Reduction
Sacramento River	1341 g/yr — 44 % Reduction
Mokolumne River	44 g/yr — 64 % Reduction
Yolo Bypass	235 g/yr — 78 % Reduction
Rationale for allocation	Methylmercury reductions are based on bringing methylmercury concentrations in the various subbasins to 0.06 ng/L. Percent reductions are in proportion to the magnitude of the difference between the current measured concentrations and the target. Total mecury reductions are based on meeting the 330 kg/yr input limitation to SF Bay.
Narrative Description of Approach	See above
Narrative of Implementation Approach	Responsible parties must characterize mercury in their effluent. If concentrations are greater than the target, they could be required to adopt controls. Loads from NPDES and MS4s are estimated at 2% of total but may be capped at 2005 levels. Point sources may be able to participate in a mercury offset program in the future.
Comments	The water quality target corresponding to 0.28 mg/kg in largemouth bass were detemined by regression equations.

EPA Region 10

TMDL Title	DRAFT Willamette Basin TMDL - Chapter 3: Mercury TMDL		
Date	9/30/2004		
State(s)	OR		
Watershed ID (HUC)	170900		
Waterbody ID			
Listed Segments	Mainstem Coast Fork (17090002) Dorena & Cottage Grove Reservoirs		
Lead Agency	Oregon DEQ		
Basis for Listing	Fish Consumption, Fish consumption advisory		
Watershed / Water Column / Fish Tissue Data?	Y		
If yes, describe	Summaries of fish data in Food Web Biomagnification Model support document, individual data in spreadsheets (not available with TMDL), summaries of water and sediment samples from 18 locations in river basin, individual data in spreadsheets (not available with TMDL)		
Water Quality Target or Load	0.92 ng/L		
	104.7 kg/yr	Mainstem Willmette	
	0.27 kg/yr	Dorena Watershed	
	0.31 kg/yr	Cottage Grove Watershed	
MOS	N/A		
Point Sources Identified (list if power plant)	Y		
Effleuent Data for PS?	Not provided in TMDL		
If yes, describe			
Allocations to sources?	Y		
Runoff of atmospherically dep Hg	61.9 kg/yr		
Erosion of Hg containing soils	71.5 kg/yr		
Legacy mine discharges	3.2 kg/yr		
Sediment resuspension	0 kg/yr		
POTWs	4.1 kg/yr		
Industrial discharges	1.5 kg/yr		
Total	142.2 kg/yr		
Reserve Capacity	NA		
Rationale for allocation	Modeled runoff and erosion loads and discharges from mine areas, loads from POTWs based on measurements in effluent and permitted flow rates. Mercury output from Willamette based on a relationship of flow/TSS/Hg concentrations, net sediment deposition load estimated by difference between basin inputs and river outputs.		
Allocations of Reductions to Sources?			
Runoff of atmospherically dep Hg	45.2 kg/yr	27 % Reduction	
Erosion of Hg containing soils	52.2 kg/yr	27 % Reduction	
Legacy mine discharges	2.3 kg/yr	28 % Reduction	
Sediment resuspension	0 kg/yr	0 % Reduction	
POTWs	3 kg/yr	27 % Reduction	
Industrial discharges	1.1 kg/yr	27 % Reduction	
Total	103.8 kg/yr	27 % Reduction	
Reserve Capacity	0.9 kg/yr	0.6 % of total load	
MOS	Implicit, due to use of a single TL-4 species tissue concentration to calculate WQT, also a 15% explicit MOS due to the use of EPA;s 0.3 mg/kg criterion, rather than Oregon's 0.35 mg/kg listing criterion.		
Rationale for allocation	All sources were given the same percent reduction (within mainstem, Dorena, Cottage Grove segments)		
Narrative Description of Approach	Allocation was detemined by establishing an average water column concentration and comparing to the water column concentration required to bring Northern pikeminnow tissue concentration to 0.3 mg/kg, based on the results of the Food Web Biomagnification Model (average water column concentration was 1.25 ng/L, WQT target from FWB Model was 0.92 ng/L).		
Narrative of Implementation Approach	Moratorium on any increase in mercury discharges. Increased monitoring for facilities with flows greater than 0.05 MGD. Also recommends pollution prevention alternatives and activities.		
Comments	Reductions for the Dorena and Cottage Grove Reservoirs are 29% and 67%, respectively, based on a similar analysis.		

B
REVIEW OF MODELS SUITABLE FOR USE IN MERCURY TMDLS

This appendix contains an overview of computer models available for use in mercury TMDLs[71]. Eleven models are reviewed. Of the eleven, five have documented use in mercury TMDLs. Another five have been developed and evaluated using test cases akin to the type of analysis required by mercury TMDLs and therefore could easily be used for this purpose, without adaptation. The eleventh is currently under development but is included because of its pending availability.

The eleven models are:

- WARMF
- TRIM.FaTE
- SERAFM
- GWLF
- WCS Mercury Tool
- GBMM
- SWEM/CARP
- WASP
- MCM
- BASS
- FWBM

[71] Reasonable attempts were made to verify the accuracy of the model descriptions provided. This included in some cases contacting the model authors. In cases where there was no response, decriptions may contain inadvertent inaccuracies or omissions.

Of these eleven, the first three (WARMF, TRIM.FaTE, and SERAFM) are fully integrated in that they include watershed loading, receiving water, and bioaccumulation modules or computations. The next three (GWLF, WCS, and GBMM) are watershed loading models and require linkage to receiving water and bioaccumulation models to perform a TMDL analysis. The next two (SWEM/CARP and WASP) model the receiving water only and require watershed loads (if applicable) from a watershed loading model. MCM models the receiving water and has a bioaccumulation module as well. The final two models (BASS, FWBM) model only bioaccumulation and as such require inputs of mercury water column and sediment concentrations from a receiving water model. The models are summarized in Table B-1 and are described in greater detail below. Table B-2 provides additional information, such as citations and where models can be found and procured.

Table B-1
Comparison of Models Suitable for Use in Mercury TMDLs

	Model										
Model Capabilities	**WARMF**	**TRIM. FaTE**	**SERAFM**	**GWLF**	**WCS**	**GBMM**	**SWEM/ CARP**	**WASP**	**MCM**	**BASS**	**FWBM**
Atmospheric Deposition	■	1	■		2	■	■	■	■		
Watershed											
Forest	■	■	3	■	■	■					
Throughfall	■	■									
Litterfall	■	■				■					
Plant Uptake	■	■									
Agriculture	■	■		■	■	■					
Urban (Impervious)	■	?	■	■	■	■					
Wetlands	■		■			■					
Terrestrial Environmental Fate & Transport Processes Accounted For											
Runoff	■	■	■	■	■	■					
Erosion	■	■	■	■	■	■					
By particle size	■										
Groundwater	■	■		■		■					
Bedrock Weathering						■					
Sorption/Desorption	■	■			■						
Methylation	■	■				■					
Demethylation	■	■									
Reduction	■	■			4	■					
Oxidation		■									
Evasion	■	■			4	■					
Bioaccumulation (terrestrial biota)		■									
State Variables											
Hg-T			■	■	■	■					
Hg(0)	■	■									
Hg (II)	■	■									
MeHg	■	■									
DO	■										
DOC	■										
TSS	■		■		■	■					
Point Sources	■	?				■	■	■	■		
Hydraulics	■		5,6	5	5		■		■		
Receiving Water											
Rivers	■	■	■				■	■	■		
Lakes	■	■	■					■	■		
Vertically mixed											
Multilayered	■	■	■				■	■	■		
Stratification	■										
Estuaries							■				
Ocean							■				
Sediment	■	■						■			
Diagenesis							■				
Aquatic Environmental Fate & Transport Processes Accounted For											
Sorption/Desorption	■	■	■				■	■	■		
Methylation	■	■	■				7	■	■		
Demethylation	■	■	■				■	■	■		
Oxidation		■	■				■	■	■		
Reduction	■	■	■				■	■	■		
Speciation			■				■				
Hydroxides			■				■				
Sulfides			■				■				
Chlorides			■				■				
DOC			■				■				
Volatilization	■		■				■	■	■		
Sedimentation	■		■				■	■	■		
Diffusion (Sediment/Water)	■	■	■				■	■	■		
State Variables											
Hg(0)	■	■	■				■	■	■		
Hg (II)	■	■	■				■	■	■		
MeHg	■	■	■				■	■	■		
DOC	■										
TSS	■		■				■	■	■		
S	■						■				
N	■										
P	■										
DO	■						■				
Phytoplankton	■						■				
Zooplankton							■				
Bioaccumulation											
Periphyton									■	8	■
Phytoplankton	■	■	■						■	8	■
Zooplankton	■		■						■	8	■
Benthic Invertibrates	■								■		■
Fish	■	■	■							■	■
Food Chain Model	■	■								■	■
BAF			■								
Other		■									
Wildlife		■	■								

Footnotes:
1 Simulates atmospheric deposition
2 Uses atmospheric deposition in an external routine to estimate a steady-state soil concentration
3 Simulates an "upland" pervious land use
4 Reduction and evasion are accounted for by an external calculation that determines surface soil concentration from atmospheric deposition
5 Calculates runoff as a function of precipitation, land use
6 Assumes steady-state hydraulics for waterbody
7 Predicts methylation rates based on mercury speciation and sediment microbial activity
8 Proposed addition in Version 2.2

Table B-2
Additional Information on Models Reviewed in this Appendix

MODEL	Primary Contact / Affiliation / Sponsor	Documented use in mercury TMDL?		Publicly Available?
WARMF	Carl Chen / Systech Engineering / EPRI	N	Case study only	N
TRIM.FaTE	Deirdre Murphy / US EPA, Research Triangle Park, NC	N	Case study only	Y
SERAFM	Chris Knightes / US EPA, Athens, GA	N	Case study only	Y
GWLF	Doug Haith / Cornell University	Y		Y
WCS	Tim Wool / US EPA Region 4, Atlanta, GA	Y		Y
GBMM	Bob Ambrose / US EPA, Athens, GA	N	No known TMDL application	Not at this time
SWEM/CARP	Robert Santore / Hydroqual / Hudson River Foundation	N	Case study only; a precursor to this model was used in the NY/NJ Harbor mercury TMDL,1994.	N
WASP	Tim Wool / US EPA Region 4, Atlanta, GA	Y		Y
MCM	Reed Harris / TetraTech	Y		N
BASS	Craig Barber / US EPA, Athens, GA	N	No known TMDL app.	Y
FWBM	Bruce Hope / Oregon DEQ, Salem, OR	Y		Y

B.1 WARMF

WARMF is one of the three fully integrated models available for performing the analyses required by the mercury TMDL process and was specifically built with this as an objective. It was developed by Systech Engineering for EPRI (EPRI 2003). WARMF uses a network of land catchments, river segments, and lake segments with stratified water layers to represent a river basin. Upland catchments with flat slopes are used to model upland wetlands. Shallow river segments with flat slopes are used to model lowland wetlands. WARMF uses a Geographic Information System (GIS) as the basis for its spatial structure.

WARMF has a framework that allows it to route precipitation through soil layers of land catchments according to Darcy's Law (groundwater) and Manning's equation (surface runoff). On the land surface, pollutants are deposited on a vegetative canopy or directly to the soil. Pollutants accumulated on the canopy dissolve into precipitation and enter the soil as throughfall. Water and pollutants are then routed through soil horizons or in surface runoff and enter river segments as the nonpoint source load. WARMF also uses surface runoff to calculate erosion from the land surface. Specified pollutants are then routed through various river or lake segments using mass balance equations. These equations include source and sink terms for accumulation, adsorption/desorption, dissolution, and advection.

With regard to mercury, WARMF accepts inputs of wet and dry deposition to a vegetative canopy or to bare soil and water surfaces. It accounts for various land use types including forest, agriculture, and wetland. On the land surface, mercury interactions with soil particulates, methylation and reduction are modeled. Three mercury species are simulated including elemental, divalent, and methylmercury (Hg(0), Hg(II) and MeHg). WARMF is the only watershed model that simulates DO and initiates mercury methylation in soils when an anaerobic condition develops in the soil. However, the reduction of Hg(II) to Hg(0) does not appear to be a function of soil DO levels.

WARMF can accommodate the introduction of mercury to a waterbody from point sources and internally makes hydraulic computations. The three mercury species identified above are tracked as state variables in the river and lake segments. In addition, WARMF simulates and tracks DOC, TSS, DO, and temperature as state variables. As such, the model can internally calculate the thermal regime in lakes including turnover and the resulting mixing of pollutants from various lake levels. In waterbodies, the processes of methylation and demethylation, reduction, volatilization, sedimentation and diffusive exchange between sediments and overlying water are simulated. Methylation is simulated as a function of sulfate availability and DO level.

WARMF now includes a bioenergetics model for bioaccumulation (EPRI 2006). Passive exchange occurs between water column mercury and algae. Fish tissue concentrations are modeled by calculating the average exposure of fish to methylmercury and the age of the fish. Neither BAFs or a foodchain model are used making it somewhat unique among the models in its representation of the bioaccumulation process. It appears that although WARMF simulates mercury in lowland wetlands, it does not simulate bioaccumulation in these areas (fish are present in lake segments). If so, this may represent a limitation of the model in that fish in these areas appear to bioaccumulate more mercury in response to higher levels of methylmercury in the water column.

B.2 TRIM.Fate

TRIM.FaTE Version 3.3 is a multimedia model developed by Oak Ridge National Laboratory for the U.S. EPA Office of Air Quality Planning and Standards (U.S. EPA 2002). The following discussion of the model is taken primarily from Imhoff et al. (2004). It represents fate and transport of chemicals (specifically mercury) in both terrestrial and aquatic compartments. The TRIM.Fate software package provides a flexible interface built around this compartmental model framework. Within the model's interface nearly all equations and compartments can be edited and linked together. Thus, many different models may be built on the same framework, customized for a given aquatic ecosystem. TRIM.FaTE also comes with a prepackaged "library" that provides a complete set of compartments and the algorithmic relationships between them.

TRIM.FaTE was not designed to address mercury TMDLs *per se* but rather to model exposures to aquatic and terrestrial wildlife given chemical levels in the various compartments it models. It was selected for review here because the scope of the processes it models for mercury could easily be adapted for use in a TMDL analysis. The model can be configured so that atmospheric deposition occurs to both land and water compartments. Rather than accept external values of wet and dry deposition, it calculates these quantities for the user. When soil compartments are included in the model, it simulates loadings from watershed runoff and groundwater into a modeled waterbody. A limitation of Version 3.3 is that mercury loss due to erosion from land compartments is not specifically modeled.

TRIM.FaTE models deposition to vegetative canopies, bare soil and direct to the waterbody. The processes of throughfall, litterfall and plant uptake are supported in both forested and agricultural parameterizations of land compartments. It is not known if impervious surfaces or wetlands are specifically modeled. Representation of these types of land use may be possible with certain parameterizations. In land compartments, the processes of methylation/demethylation, sorption/desorption, oxidation/reduction, evasion and bioaccumulation in terrestrial biota are specifically modeled. Three mercury species, Hg(0), Hg(II) and MeHg are modeled in land compartments.

TRIM.FaTE does not simulate the hydrodynamics of the waterbodies it represents as aquatic compartments. Flows from one compartment to the next are user (externally) defined. It is not known whether TRIM.FaTE can accept point source loads to the waterbody but the flexibility of the modeling framework suggests this possibility. Water compartments are multilayered and the processes of sorption/desorption, methylation/demethylation, oxidation/reduction, volatilization, sedimentation and diffusive transport between sediments and overlying water are modeled. The three species modeled in land compartments are also simulated and tracked as state variables in water compartments.

The bioenergetic-based aquatic food chain bioaccumulation submodel is based on Thomann (1989). Algae and macrophytes bioaccumulate mercury from the water column and sediments. The model tracks mercury in herbivorous invertebrates, fish, marine birds and mammals.

TRIM.FaTE has not been used to this researcher’s knowledge in an actual TMDL application. However, it has been evaluated in a test case which is the subject of an EPA report (Lee et al. 2005).

B.3 SERAFM

SERAFM (Spreadsheet-based Ecological Risk Assessment for the Fate of Mercury) is a relatively new model recently developed and tested by EPA (Knightes and Ambrose, Unpublished). It is described as a screening model. The following description is taken from the draft report.

[SERAFM] was designed to model a watershed and associated water body which receives atmospheric deposition of mercury and has had historical loadings of mercury to the sediments, such as one associated with a facility that had historically disposed of mercury to the watershed and/or water body. The SERAFM model runs its calculations assuming steady-state and using process-based mathematical governing equations to describe the fate and transport of mercury within the ecosystem. The SERAFM model specifically calculates the mercury concentrations (HgII, MeHg, Hg0) in the water column (dissolved and total), in the food web (plankton, zooplankton, benthic invertebrates, and trophic level 3 and 4 fish), and the hazard indices of exposed wildlife as well as humans.

The model [ ]consists of a steady state, process based model incorporating a series of modules, with each module fitting into the scheme of mercury modeling to create a whole picture of mercury exposure and risk. The model is written using Microsoft© Excel 2003. The model is implemented using a spreadsheet program for several reasons. MS Excel is a program that is generally understood and used by the general population, so that it can reach and be implemented by a wider audience. [ ] By being in a spreadsheet format, all manipulations, parameters, and equations are readily available and transparent to the user. This allows adjustments as the user sees fit. However, the model is organized with a simple, upfront user interface so that upper level use can be performed without having to dig into the depths of the program itself. Microsoft© Excel 2003 can act as it sown database, and the formula auditing toolbar allows tracing of precedent and dependent cells. Additionally, as a spreadsheet, it is a *programming environment that allows each module to be separated into its own worksheet. This is effectively similar to having distinct subroutines for each set of operations. [ ] Additionally, notes and equations are provided in the spreadsheets themselves so that SERAFM can act as its own user's manual.*

The model consists of a series of modules each solved independently using one parameter database and linked modules for input. Thereby, the model works in a step-by-step fashion proceeding towards the solution of the interested parameters (e.g., fish mercury concentrations and wildlife hazard indices) in a feed-forward fashion. The first part of the model calculates the total loading of each mercury species to the water body. This incorporates direct loading to the water body via wet and dry deposition as well as indirect loading from watershed sources. Next, the solids balance module calculates the concentrations of solids in the water body. The concentrations for abiotic, biotic, and organic solids are solved using a series of simultaneous equations. The equations are derived as coupled differential equations that are then solved assuming steady state conditions. Using the solution for the solids balance, the mercury cycling equations are solved. The mercury equations are similarly coupled differential equations that are solved simultaneously assuming stead state conditions. Using the calculated mercury concentrations, bioaccumulation factors are used to predict concentrations in the different types of aquatic biota. Then, assuming daily ingestion rates of contaminated aquatic biota, hazard indices are estimated for the wildlife and human receptors.

The following lists the overall conceptual model used to describe mercury fate and transport in [SERAFM]:

- *Atmospheric mercury deposition to the watershed and water body;*
- *Deposition processing by the watersheds followed by transport to the water body via runoff, erosion, and tributaries;*
- *Mercury transformation processes in the water body:*
  - *photolytic processes of oxidation, reduction, and degradation;*
  - *biochemical and abiotic oxidation; and*
  - *methylation and demethylation,*
- *Sorption and complexation processes to describe partitioning of mercury species with silts, sands, biotic solids, and dissolved and particulate organic matter;*
- *Settling, resuspension, and burial of particulates in sediments;*
- *Bioavailability of mercury complexes with hydroxides, chlorine, sulfide, and*
- *dissolved organic carbon;*
- *Dissolved MeHg accumulation in aquatic vegetation, phytoplankton, and benthic invertebrates;*
- *Bioaccumulation of MeHg through:*
  - *zooplankton predation of phytoplankton,*
  - *fish predation of zooplankton and benthic invertebrates*

– *fish predation on fish transfers MeHg up the food chain to prey and predator fish.*

As shown in Table G-1, a feature of SERAFM that is shared by only one other model available for mercury TMDLs is the speciation/complexation of mercury by hydroxides, chlorides, and sulfides. SERAFM also calculates complexation with DOC, as several other models do.

SERAFM has been applied to several test cases which are reported in U.S. EPA (2005). A unique feature of these case studies is a side-by-side comparison of SERAFM and WASP, which will be discussed at the conclusion of this appendix.

B.4 GWLF

GWLF (Generalized Watershed Loading Functions) is a watershed loading model, originally developed for providing loads to receiving waterbodies from agricultural watersheds. It has been in existence for some time and has received widespread use. The description of the model below is liberally borrowed from Haith et al. (1996).

Recently, GWLF has been used in a number of TMDL applications for mercury, although it was not originally designed for this purpose. As a result, it does not model in any detail the complex processes that affect transformations of mercury on the landscape. Rather, mercury is treated like any other pollutant, with estimates of total mercury in runoff, eroded sediment and groundwater being the calculated loads. Methylmercury loads could be simulated by treated it as a separate parameter. Thus, there is no interaction between mercury and methylmercury in the simulation.

The Generalized Watershed Loading Functions (GWLF) model estimates dissolved and total pollutant loads in streamflow from complex watersheds. Both surface runoff and groundwater sources are included, as well as loads from point sources and on-site wastewater disposal (septic) systems. In addition, the model provides monthly streamflow, soil erosion and sediment yield values.

Dissolved loads from each source area are obtained by multiplying runoff by dissolved concentrations. Runoff is computed by using the Soil Conservation Service Curve Number Equation. Solid-phase rural (forest, agriculture) pollutant loads are given by the product of monthly sediment yield and average sediment nutrient concentrations. Erosion is computed using the Universal Soil Loss Equation and the sediment yield is the product of erosion and sediment delivery ratio. The yield in any month is proportional to the total transport capacity of daily runoff during the month. Urban pollutant loads, assumed to be entirely solid-phase, are modeled by exponential accumulation and washoff functions.

Streamflow consists of runoff and discharge from groundwater. The latter is obtained from a lumped parameter watershed water balance. Daily water balances are calculated for unsaturated and shallow saturated zones. Infiltration to the unsaturated and shallow saturated zones equals the excess, if any, of rainfall and snowmelt less runoff and evapotranspiration. Percolation occurs when unsaturated zone water exceeds field capacity. The shallow saturated zone is modeled as a linear groundwater reservoir.

The GWLF model requires daily precipitation and temperature data, runoff sources and transport and chemical parameters. Transport parameters include areas, runoff curve numbers for antecedent moisture condition II and the erosion product **K*LS*C*P** for each runoff source. Required watershed transport parameters are groundwater recession and seepage coefficients, the available water capacity of the unsaturated zone, the sediment delivery ratio and monthly values for evapotranspiration cover factors, average daylight hours, growing season indicators and rainfall erosivity coefficients. Initial values must also be specified for unsaturated and shallow saturated zones, snow cover and 5-day antecedent rain fall plus snowmelt.

Input pollutant data for rural source areas are concentrations in runoff and sediment. Daily accumulation rates are required for each urban land use. Loads from point sources are assumed to be in dissolved form and must be specified for each month. The remaining required data are dissolved pollutant concentrations in groundwater.

The GWLF program provides its simulation results in tables as well as in graphs. The following principal outputs are provided:

- monthly streamflow;
- monthly watershed erosion and sediment yield;
- monthly total pollutant loads in streamflow;
- annual erosion from each land use; and
- annual pollutant loads from each land use.

The program also provides:

- monthly precipitation and evapotranspiration;
- monthly ground water discharge to streamflow;
- monthly watershed runoff;
- monthly dissolved pollutant loads in streamflow; and
- annual dissolved pollutant loads from each land use.

GWLF and associated programs are written in QuickBASIC 4.5 for personal computers using the MS-DOS operating system and VGA graphics.

B.5 WCS Mercury Tool

WCS (Watershed Characterization System) is an Arcview-based system designed to provide users tools and watershed data (i.e. soil, land use, elevation, climate and streamflow) for characterizing and thereby understanding their watersheds. While it has many capabilities, the function of greatest importance to this discussion is its ability to calculate pollutant loads to adjacent waterbodies. WCS was first developed in 2000 for EPA Region 4. Also in 2000 in response to a court-ordered mandate to develop a number of mercury TMDLs in the State of Georgia, the Mercury Tool, an extension to the basic WCS, was developed. The core mathematical formulas in the Tool are based on a mercury mass balance model, IEM v2.05, which was described in the Mercury Study Report to Congress (U.S. EPA 1997).

The mercury watershed soils mass balance model calculates surface soil concentrations, including dissolved, sorbed and gas phases. The model uses wet and dry deposition to the soil surface and allows for dissipation through volatilization, runoff, leaching, and erosion. The algorithm calculates the equilibrium distribution of dissolved and adsorbed phase mercury using linear partitioning. Loss rate constants are calculated for leaching, runoff, erosion, and reduction to gas phase mercury. These rate constants are then used in a first-order differential equation that solves for the buildup of mercury in the soil over time. The mass balance is done over an incorporation depth, which the user may vary. The resulting soil concentration is used in the WCS model as the pollutant concentration where runoff and erosional mercury loads are calculated. The hydrology in WCS is based on the SCS Curve Number approach and erosion is based on the Universal Soil Loss Equation. Mercury deposited to impervious surfaces is all assumed to be removed to the waterbody.

The WCS Mercury Tool has been used in a number of TMDL applications in EPA Region 4.

B.6 GBMM

GBMM (Grid-based Mercury Model) is a second generation version of the WCS Mercury Tool. The description provided below is based on the National Exposure Research Laboratory Research Abstract entitled “Watershed Mercury Simulation Software for TMDL Assessments”, which can be found on EPA’s Office of Research and Development website.

GBMM is a spatially distributed model simulates flow, sediment transport, and mercury dynamics on a daily timestep across a diverse landscape. The model is composed of six major components, as follows:

- an ArcGIS interface for processing spatial input data;
- a basic hydrologic module;
- a sediment transport module;
- a mercury transport and transformation module;
- a spreadsheet-based model post-processor; and
- links to other models such as WASP.

The model fully uses the grid processing capacity of the latest ArcGIS technology. The water balance, sediment generation and transport, and mercury dynamics are calculated for every grid within a watershed. Water and pollutants are routed daily throughout the watershed based on a unique and flexible algorithm that characterizes a watershed in many runoff travel-time zones.

The mercury transport and transformation module simulates the following key processes:

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

By using the grid-based technology, flow and mercury dynamics can be examined at any of several points in the watershed. The model is capable of supporting large-scale modeling with high-resolution raster datasets. The model is programmed in Visual Basic and requires two ArcGIS (version 9.0) components – ArcView 9 and the Spatial Analyst extension. The software is still under development by EPA and its contractors and is not yet publicly available. Additional documentation is provided in Tetra Tech (2004) and Tetra Tech (2006).

B.7 SWEM/CARP

The CARP model is a recent upgrade to the SWEM model used in 1994 to establish TMDLs for a number of metals in the New York/New Jersey Harbor. SWEM was developed by the New York City Department of Environmental Protection (NYCDEP) from 1994 to 1998 and models hydrodynamics, eutrophication and sediment dynamics. It features state-of-the-art science and has been well-calibrated and peer reviewed.

The goals of the CARP model development included the prediction of future water quality conditions given various management and remediation options. To accomplish this, a mechanistic approach for projecting mercury and methylmercury concentration in the water column, sediments, and fish tissue was required. Some of the impediments to model development included a wide variety of environments and flow regimes, and little data with limited opportunity to collect site-specific process level measurements such as methylation rates. Because of these limitations, the modeling strategy was to make use of case studies of other similar systems in the literature and to develop robust process algorithms that would require little variation in calibration across the modeling domain.

The mercury model in SWEM/CARP simulates and tracks three mercury species including Hg(0), Hg(II) and MeHg. Hg(0) in the water column may volatilize, exchange with gas phase mercury in sediments, or be oxidized to Hg(II). Hg(II) may be reduced to Hg(0) by photolysis, partition between the water column and particulates (which settle and may be resuspended), and exchange via diffusion with Hg(II) in sediment pore water. Hg(II) may also be methylated and demethylated in both water and sediments. Like Hg(II), MeHg sorbs to and desorbs from particulates and exchanges diffusively with sediment pore water. SWEM/CARP is one of the few receiving water models that speciates mercury through interaction with inorganic anions including chlorides, hydroxides and sulfur species. SWEM/CARP also simulates interactions with dissolved organic matter (DOM) and particulate organic matter (POM) using a multi-site binding model.

One of the unique features of this model is a diagenetic sediment model which predicts methylation rates. It is the only model reviewed with such a feature[72]. The model relies on relationships between sulfate activity and methylation rate in which maximum methylation occurs between log[SO_4^{2-}] of -3 and -4. Below this level sulfate limits MeHg production and above this level sulfide limits MeHg production. Maximum methylation appears to occur at sulfate levels typical of the transition between fresh and estuarine waters. SWEM/CARP appears to be capable of simulating methylation rates commensurate with those observed by others over a range of sulfate reduction rates. Methylation rates are limited in the model by the fraction of bioavailable mercury, which in turn is a function of DOM, salinity, pH, and total sulfide. Simulated methylation rates appear to track rates observed over a period of several months in the Hudson River and Long Island Sound and the model appears to track total and methylmercury concentrations with reasonable accuracy.

B.8 WASP

The following description of the WASP program is borrowed liberally from the Version 6.0 documentation (Wool et al. Undated).

The Water Quality Analysis Simulation Program (WASP Version 6.0) is a dynamic compartment-modeling system for aquatic systems, including both the water columns and the underlying benthos. The time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange are represented in the basic program. Water quality processes are represented in special kinetic subroutines that are either chosen from a library or written by the user. WASP is structured to permit easy substitution of kinetic subroutines into the overall package to form problem-specific models. WASP comes with two such models – TOXI for toxicants (organic chemicals, metals, and sediment) and EUTRO for conventional water quality (including dissolved oxygen, biological oxygen demand, nutrients and eutrophication). WASP has been used in many such applications.

The flexibility afforded by WASP is unique. It permits users to structure one, two, or three dimensional models, allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions, and permits tailored structuring of the kinetic processes, all within a larger modeling framework without having to write or rewrite large sections of computer code.

The WASP6 program consists of two stand-alone computer programs, DYNHYD5 and WASP6, which can be run in conjunction of separately. The hydrodynamics program, DYNHYD5, simulates the movement of water while the water quality program, WASP6, simulates the fate and transport of pollutants within the aquatic system. Other hydrodynamic programs may be used with WASP. RIVMOD, also available through the EPA's Center for Exposure Assessment Modeling (CEAM) in Athens, GA, simulates unsteady flow in rivers and SED3D (also available

[72] See the discussion of the MCM model below as well.

through CEAM) simulates unsteady three-dimensional flow in lakes and estuaries. The basic principal of both the hydrodynamic and water quality programs is the conservation of mass. Water volume and specified state variables are tracked and accounted for over time and space using a series of mass balance equations. In the hydrodynamics programs, energy is also conserved.

By choosing the correct hydrodynamics program and properly configuring the model, WASP can be used to simulate mercury fate and transport in rivers, lakes, and estuaries. WASP does not have a watershed component, however, and must be linked to a loading model (like GWLF or WCS) to provide watershed loads. In addition, WASP is not self-contained with regard to bioaccumulation and must be linked to a bioaccumulation model such as BASS or FWBM to simulated mercury concentrations in fish tissue. Point sources of pollutants are simulated. WASP simulates sorption/desorption, methylation/demethylation, oxidation/reduction reactions as well as volatilization of Hg(0), sedimentation and diffusion between sediments and overlying water. Unlike SERAFM and SWEM/CARP, WASP does not speciate mercury. Like WARMF, it does simulate the complexation of mercury by DOC. It tracks the three most prominent mercury species in freshwater environments, Hg(0), Hg(II), and MeHg along with TSS as state variables.

WASP runs in and is accessible from a WINDOWS environment and features a WINDOWS-based preprocessor, making it easy to install and run.

B.9 MCM

The description of the MCM model provided below is primarily taken from Imhoff et al. (2004). Additional information was gleaned from FDEP (2001).

MCM is an aquatic fate and bioaccumulation model that simulates mercury movement in the water column, three macrophyte species, and four sediment layers, as well as an aquatic food web including eight biotic groups with up to 20 fish age classes. Dietary and direct uptake of both Hg(II) and MeHg are simulated. Watershed loads are provided to MCM via external linkages as well as direct atmospheric loadings to the waterbody. MCM is self-contained with regard to hydrodynamics and requires no external program to provide flows or exchanges between water column layers. A water balance including inflows, outflows as well as vertical groundwater flow is simulated. The model allows for time-dependent stratification and the formation of distinct surface and bottom water layer compartments, if desired. MCM is currently configured to simulate only lakes or wetlands, which is a limitation of its application in many TMDLs. MCM has the capability to simulate point sources as inflows through external linkages to datafiles.

MCM accounts for the major mercury transformation processes including adsorption/desorption, methylation/demethylaton, oxidation/reduction, volatilization, sedimentation and diffusive transfer between sediments and the overlying water column. For detrital, suspended and sediment solids, two types of Hg(II) exchange are provided; (1) instantaneous, and (2) slow exchange governed by adsorption/desorption kinetics. Like WASP and WARMF, MCM complexes mercury with DOC. While WARMF simulates DOC as a state variable, however, DOC is an input parameter to MCM, along with pH and DO. MCM also complexes mercury with sulfides, but full sulfur cycling is not simulated and complexation with other anions (e.g. hydroxides, chlorides) is not performed. The model tracks Hg(0), Hg(II), and MeHg in various compartments, along with TSS, as state variables. A diagenetic model along the lines of that described by Gilmour et al. (2003) is apparently slated to become incorporated into MCM in the future.

The simplified food web in MCM allows for simulation of bioaccumulation. MCM does not simulate the mass of the biotic compartments dynamically. It tracks mercury in detritus, periphyton, phytoplankton, zooplankton, benthic invertebrates, shrimp, *Gambusia*, and trophic level 3 and 4 fish. Bioaccumulation in the food chain is simulated using BAFs, which are supplied by the user.

The model can be run both in steady-state and dynamic modes. Although it was originally programmed for the MacIntosh, E-MCM Version 1.0 runs on WINDOWS-based computers. MCM has been used to study mercury dynamics in the Florida Everglades and a companion version D-MCM (Version 2.0) (EPRI, 2002), has been used in a number of mercury TMDLs, often linked to GWLF to provide watershed loadings.

B.10 BASS

The following discussion of the BASS model is taken primarily from Imhoff et al. (2004).

BASS (Bioaccumlation and Aquatic System Simulator) is a bioaccumulation model and relies on a receiving water mode like WASP to provide ambient concentrations of pollutants to be simulated in water and sediment (Barber 2001). BASS predicts the population and bioaccumulation dynamics of age-structured fish assemblages exposed to hydrophobic pollutants and metals that complex with sulfhydryl groups (e.g. cadmium, copper, lead, mercury, nickel, silver, and zinc). The model's bioaccumulation algorithms are based on diffusion kinetics and are coupled to a processed-based model for the growth of individual fish. The model's exchange algorithms consider both biological attributes of fishes and physico-chemical properties of the chemicals of concern that determine diffusive exchange across gill membranes and intestinal mucosa. BASS simulates the growth of individual fish using a standard mass balance, bioenergetic model. Population dynamics are generated by predatory mortalities defined by the community's food web and standing stocks, size-dependent physiological mortality rates, the maximum longevity of the species, and toxicological responses to chemical exposures.

BASS's model structure is general and flexible. Uses can simulate both small, short-lived species (e.g. daces, minnows) and large, long-lived species (e.g. bass, perch, sunfishes and trout) by specifying either monthly or yearly age classes for any given species. The community's food web is defined by identifying one or more foraging classes for each fish species based on body-weight, body length, or age. The dietary composition of each of these foraging classes is then specified as a combination of benthos, incidental terrestrial insects, periphyton/attached algae, phytoplankton, zooplankton, and/or other fish species, including its own. There are no restrictions on the number of fish species that can be simulated, or the number of cohorts, age classes, or foraging classes for a given species.

BASS has been used to investigate methylmercury bioaccumulation in the Florida Everglades. It has also been used to simulate mercury bioaccumulation in the Eagle Butte case study in the CAMR RIA (U.S. EPA 2005).

B.11 FWBM

This discussion of the FWBM (Food Web Bioaccumulation Model) is taken from Hope (2003).

FWBM was developed by Bruce Hope of the Oregon Department of Environmental Quality (ODEQ). The model simulates mercury (as Hg(II) and MeHg) accumulation in fish through a basin-specific food web in response to chemical exposure, based on mass balances for aquatic biota. It equates rates of change in chemical concentration within a fish (and other aquatic organisms) to the sum of the chemical fluxes into and out of the organism. These fluxes include direct uptake of the chemical from water, uptake through feeding, loss of chemical due to elimination (desorption and excretion), and dilution due to growth. It addresses the potential for bioconcentration (concentration from water), bioaccumulation (concentration from diet as well as water) and biomagnification (systematic concentration as chemicals are passed to higher trophic levels) of Hg(II) and MeHg. To predict tissue levels in fish destined for human consumption, the model is repeatedly applied to organisms at each trophic level to simulated mercury transfer from primary to secondary producers, through a variety of intermediate invertebrate and fish species to top predators.

The model food web for the Willamette River consists of 17 compartments selected to represent important components of the river's aquatic ecosystem: 3 source media, 1 secondary carbon source (detritus), 3 primary producers, 6 primary consumers, 2 secondary consumers, and 1 tertiary consumer. Model variables (for each species) include the following:

- bioconcentration factor;
- chemical dietary assimilation efficiency;
- chemical elimination rate;
- normalized food intake rate;
- body weight;
- dietary fraction,
- predator-prey size relationship factor; and
- water temperature.

Since total and methylmercury concentrations in water and sediment and observed data in fish tissue manifest a high degree of variability, the FWBM was set up to run as a stochastic model. Users supply distributions of input parameters and the model outputs distributions of biotic tissue concentrations. The model can be run using single-valued parameters as well. The model is constructed in an MS EXCEL® spreadsheet environment. Probabilistic analyses are performed using EXCEL compatible software capable of performing 1-D and 2-D Monte Carlo analyses (Crystal Ball ®, Decisioneering, Denver CO) using Latin hypercube sampling.

B.12 Model Comparison

There are several ways models may be compared. One simple way is to compare their capabilities as has been done in Table G-1. While a comparison of this type is not very satisfying, it does give the analyst or manager a way to form initial opinions. However, it reveals little of what needs to be known to intelligently select a model for the purposes of performing a TMDL.

Another way is to compare model output to observed data for accuracy. This is not really possible at this time beyond the simplest of comparisons. Most of the models reviewed in this section have been developed around limited data sets. Some of TMDL applications may have one of two data point to compare with model simulations. This paucity of data has provided little in the way of opportunities to calibrate/verify these models in the conventional manner, in which the model is calibrated on a portion of the dataset and verified on another portion, as has frequently been done with hydrologic models in relatively data-rich environments. All of the models reviewed in this section are relatively new in terms of their development and there have been few opportunities to run them in different environments from where they were originally developed and calibrated. Where these models have been calibrated in the environments they were built to simulate, all of them do a creditable job of reproducing concentrations of mercury in various environmental media. However, there is not enough experience with these models to be assured that they are truly predictive; that is that they could be taken from their developmental environment and accurately simulate mercury concentrations in another environmental setting. Most experts agree that this is not yet possible. It is not to be construed that this is the fault of the scientists and engineers that have developed them, far from it. The principal impediment to developing truly predictive models for mercury is the evolution of the understanding of the complex biogeochemical interactions that affect methylation and bioaccumulation. Better models will have to await better science.

Yet another way to compare models is to compare them to one another. There has been little opportunity to do this either. Although the following discussion is limited to two such models, it is revealing in that it shows typical results from the application of SERAFM and WASP in several different case studies. In the CAMR RIA, 5 case studies were performed and in three of them, Eagle Butte, SD, Patuckaway Lake, NH, and Lake Waccamaw, NC, WASP and SERAFM were both applied in the analysis. This comparison in also interesting in that WASP represents a “state-of-the-art” simulation program for assessing environmental fate of mercury while SERAFM is a screening-level model. The lakes also cover a wide range of environmental conditions comprising a small, shallow Midwestern lake, a medium sized, deeper Northeastern lake and a large Southern “bay” lake.

Tables B-3 and B-4 show some illustrative results.

In all three cases, SERAFM and WASP appear to predict values in the range of the observed total and methylmercury concentrations in the water column and sediments[73]. WASP tends to consistently predict higher water column and sediment total and methylmercury than SERAFM. However, neither model appears to consistently over- or underpredict relative to the observed

[73] Note that most of the WASP concentrations were read from graphs and are only approximate to the actual numerical results.

means. More dramatic differences arise in the prediction of response times of the three lakes (Table B-4). Recall that the “fast”, “medium” and “slow” response times arise from varying the sediment diffusion parameters (see Section 3.4.5.1). Also note that there is no better or worse answer, since the predicted response times are speculative. Neither model appears to consistently over- or underpredict the other. For the shallow Eagle Butte and Waccamaw lakes WASP tends to predict longer response times. In the case of Pawtuckaway, a deeper lake, however, WASP predicted response times tend to be substantially shorter than those predicted by SERAFM.

The BASS model was used to simulate fish tissue concentrations (given WASP inputs) only at the Eagle Butte location. While the text of the CAMR RIA reports indicates that “predicted concentrations for northern pike, yellow perch, black bass and black crappie agree with observed field concentrations for these species” it is noted that observed concentrations in northern pike appear to range from about 0.5 mg kg^{-1} to 2 mg kg^{-1}, the model predictions appear to have northern pike concentrations at a level between 4 and 5 mg kg^{-1}. SERAFM prediction for age 4 northern pike was 0.97 mg kg^{-1}; however, the BAF for northern pike was calculated and input to SERAFM, while BASS does not use BAFs in predicting bioaccumulation. This would make an accurate prediction by SERAFM more likely in a situation were the models are not intensively calibrated.

Table B-3
Measured and Simulated (SERAFM/WASP) Compartment Mercury Concentrations for Three North American Lakes

Compartment	Measured Range	Mean	SERAFM Prediction	WASP Prediction
Eagle Butte, SD				
Water Column MeHg, unfiltered ng L^{-1}	0.4 to 2.9	1.0	0.82	1.3
Water column HgT, unfiltered ng L^{-1}	0.5 to 100	6.9	10.2	9.5
Sediment MeHg ng g^{-1}, dry weight	0.062 to 1.74	0.40	0.29	0.52
Sediment HgT ng g^{-1}, dry weight	28.1 to 95	44.1	63.9	175
Pawtuckaway Lake, NH				
Epilimnion MeHg, unfiltered ng L^{-1}	0.14 to 0.24	0.19	0.35	0.7
Epilimnion HgT, unfiltered ng L^{-1}	0.71 to 3.8	2.26	3.57	8
Hypolimnion MeHg, unfiltered ng L^{-1}	2.38 to 3.44	2.91	0.38	1
Hypolimnion HgT, unfiltered ng L^{-1}	6.94 to 34.5	20.7	5.63	15

Table B-3 (continued)
Measured and Simulated (SERAFM/WASP) Compartment Mercury Concentrations for Three North American Lakes

Compartment	Measured Range	Mean	SERAFM Prediction	WASP Prediction
Sediment MeHg ng g^{-1}, dry weight		7	6	6.2
Sediment HgT ng g^{-1}, dry weight		290	237	300
Waccamaw Lake, NC				
Water Column MeHg, unfiltered, ng L^{-1}	0.132 to 4.99	0.483	0.17	0.37
Water column HgT, unfiltered ng L^{-1}	1.06 to 18.4	4.79	1.95	2.8
Sediment MeHg ng g^{-1}, dry weight	0.033 to 0.20	0.13	0.2	2.4
Sediment HgT ng g^{-1}, dry weight	1.66 to 36.4	22.8	1.5	15

Table B-4
Response Times (Years) for Forecasted Mercury Concentrations to Reach Steady State Following 50% Load Reductions

Compartment	Fast		Medium		Slow	
	SERAFM	**WASP**	**SERAFM**	**WASP**	**SERAFM**	**WASP**
Eagle Butte						
Epilimnion	2	5	2	9	4	14
Surface Sediments	3	6	4	11	6	16
Pawtuckaway						
Epilimnion	59	20	115	36	179	55
Hypolimnion	79	23	154	43	>180	66
Sediments	80	24	125	44	>180	69
Waccamaw						
Epilimnion	1	8	2	11	1	11
Sediment	3	10	6	15	12	17

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FREQUENTLY USED ACRONYMS

AAMEC	Average Annual Mercury Effluent Concentration
AWQC	Ambient Water Quality Criteria
AML	Average Monthly Limit
BAF	Bioaccumulation Factor
BMP	Best Management Practice
CAA	Clean Air Act
CAIR	Clean Air Interstate Rule
CAMR	Clean Air Mercury Rule
CCP	Coal Combustion Product
CPP	Continuing Planning Process
CDF	Cumulative Distribution Function
CFR	Code of Federal Regulations
CSO	Combined Sewer Overflow
CV	Coefficient of Variation
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
CWA	Clean Water Act
DEP	Department of Environmental Protection
DEQ	Department of Environmental Quality
DMA	Designated Management Agency
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EPA	Environmental Protection Agency
ESP	Electrostatic Precipitator
EPRI	Electric Power Research Institute
FDA	Food & Drug Administration
FGD	Flue Gas Desulfurization
FOIA	Freedom of Information Act
GIS	Geographic Information System
GLI	Great Lakes Initiative
GPS	Global Positioning System
Hg(0)	Elemental Mercury
Hg(II)	Divalent Mercury
HUC	Hydrologic Unit Code
IQ	Intelligence Quotient
K-S	Kolmogorov-Smirnoff
LA	Load Allocation
LCA	Level Currently Achievable

LOI	Loss on Ignition
MACT	Maximum Achievable Control Technology
MDN	Mercury Deposition Network
MEC	Maximum Effluent Concentration
MDL	Maximum Daily Limit
MeHg	Methylmercury
MPCA	Minnesota Pollution Control Agency
MOS	Margin of Safety
MW	Megawatt
NPDES	National Pollutant Discharge Elimination System
ORACWA	Oregon Association of Clean Water Agencies
ORNL	Oak Ridge National Laboratory
OTCW	Once Through Cooling Water
PISCES	Power Plant Integrated System-Chemical Emissions Study
PCS	Permit Compliance System
PDF	Probability Density Function
PMP	Pollution Minimization Plan
POM	Particulate Organic Matter
POS	Plan of Study
PRB	Powder River Basin
RfD	Reference Dose
RIA	Regulatory Impact Analysis
RP	Reasonable Potential
RPD	Relative Percent Difference
RSC	Relative Source Contribution
RWCQB	Regional Water Quality Control Board
SBAF	Sediment Bioaccumulation Factor
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SRS	Savannah River Site
THg	Total Mercury
TL	Trophic Level
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TRV	Trophic Residue Value
TSS	Total Suspended Solids
TWA	Trophic Weighted Average
USDA	United States Department of Agriculture
USFWS	United States Fish & Wildlife Service
USGS	United States Geological Survey
USLE	Universal Soil Loss Equation
WERF	Water Environment Research Foundation
WLA	Waste Load Allocation
WQS	Water Quality Standard
WQT	Water Quality Target

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