Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion

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6 TMDLs

6.1 What is a TMDL?

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

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

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

6.2 How have states and tribes approached mercury TMDLs?

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

Given these challenges, EPA is working with states, tribes, and stakeholders to determine how best to use TMDLs to provide a basis for reducing mercury releases to water, including through air deposition, to meet applicable water quality standards and Clean Water Act goals. In areas where large numbers of waterbodies are impaired due to mercury derived from air deposition, some states have begun to explore ways to address mercury impairments efficiently, such as through development of TMDLs on various geographic scales. EPA plans to develop further information on approaches to listing mercury impaired waters and developing mercury TMDLs at a later date.

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

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

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

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

6.2.2 What is the Mercury Maps screening analysis?

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

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

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

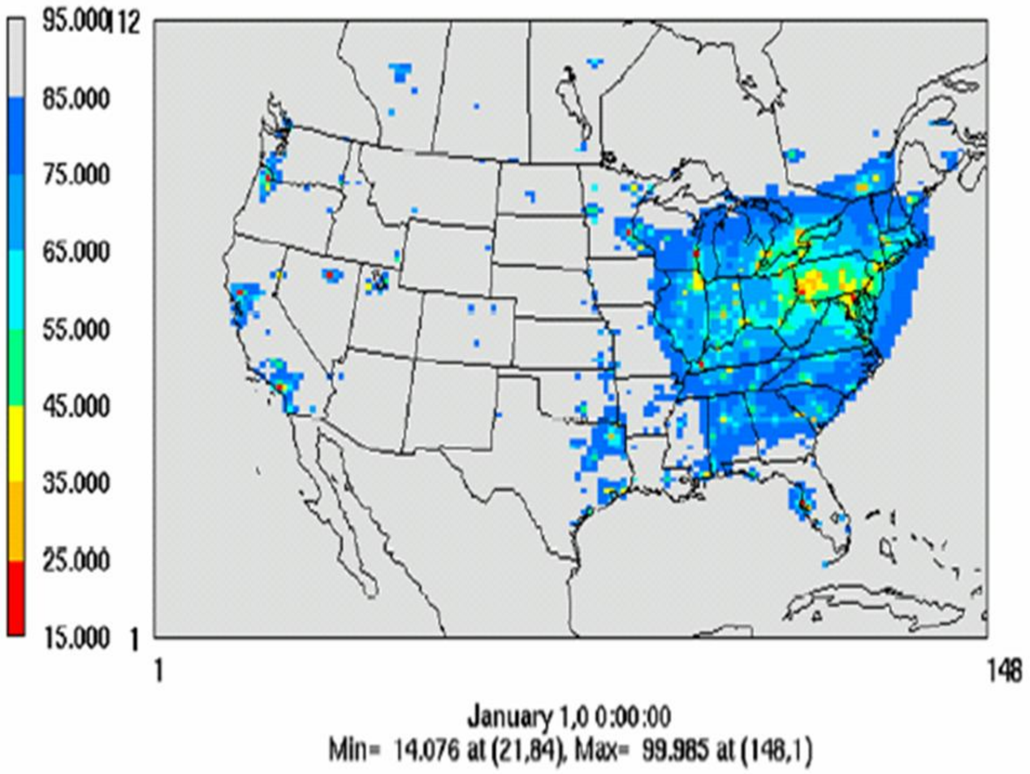


Figure 3. Percent of total mercury deposition attributable to global sources (USEPA 2005c)

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

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

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

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

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

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

6.2.3 What are considerations in developing mercury TMDLs?

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

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

6.2.3.1 What are potential mercury sources to waterbodies?

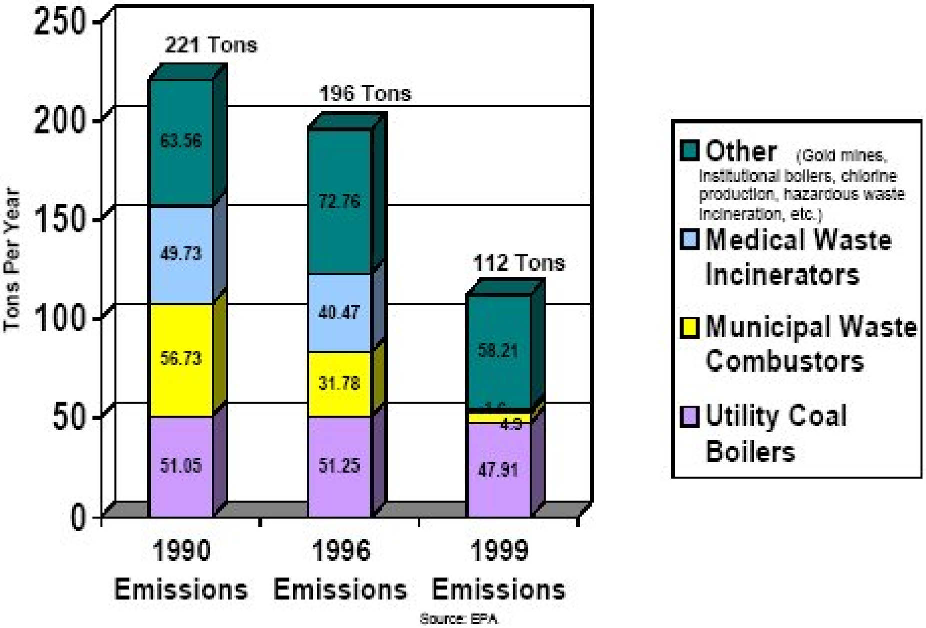
Some of the potential sources of mercury to waterbodies include direct discharges of mercury from water point sources, including industrial dischargers and wastewater treatment plants; atmospheric deposition, including direct deposition to the waterbody surface and deposition to the watershed, which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

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

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

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

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



Source: EPA

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

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

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

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

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

1. The elemental mercury (Hg0) reaction with H_2O_2 assumes the formation of 100 percent RGM rather than 100 percent particulate mercury (HgP).
2. The Hg0 reaction with ozone assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP.
3. The Hg0 reaction with OH assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP.

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

4. The rate constant for the Hg0 + OH reaction was lowered from 8.7 to 7.7 x $10^{-14}cm^{3}molecules^{-1}s^{-1}$.

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

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

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

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

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

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

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

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

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

Natural or "background" levels of mercury in soils—Soils and sediments can include mercury of geologic origin or mercury produced by the weathering of geological materials, together with mercury of anthropogenic origin (i.e., mercury emitted over time from human sources and then deposited on soils). Mercury in soils can also re-emit and subsequently redeposit to soils. Local studies have been used in some TMDLs to estimate the geologic contributions of mercury to waterbodies. For example, a TMDL developed for the Ouachita watershed in Arkansas relied on a study of mercury concentrations in the rocks of the Ouachita Mountains (FTN 2002). The mercury concentration estimated to be of geologic origin was then subtracted from the total concentration of mercury measured in soils to estimate the nongeologic concentration of mercury in soils.

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

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

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

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

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

6.2.3.2.1 Steady state models

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

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

6.2.3.2.2 Continuous simulation and dynamic models

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

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

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

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

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

6.2.3.2.3 Spatially detailed models

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

As with the steady state mass balance model, including additional processes can allow the modeler to determine the impact of different environmental regulatory or management controls on mercury fish tissue concentrations. For example, where mercury transport to a waterbody is predominantly through soil erosion, erosion control might be identified as a valid nonpoint source control on mercury to waterbodies (Balogh et al. 1998). Additionally, controls on acid deposition and, thus, changes in lake pH and its effect on fish tissue mercury concentrations, might also be modeled (Gilmour and Henry 1991, Hrabik and Watras 2002). Finally, spatially detailed models can be used to reflect the local effects of wetlands, which produce significantly more methylmercury per unit area than other types of land use.

6.2.3.2.4 Model selection

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

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

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

6.2.3.2.5 Model limitations

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

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

6.2.3.3 What are the allocation approaches in mercury TMDLs?

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

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

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

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

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

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

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

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

Point sources loadings are not small—For these TMDLs, the reductions in point source loadings, alone or in combination with nonpoint sources, can sufficiently achieve water quality standards. In this situation, the TMDL should consider reductions in both the point sources and nonpoint sources to achieve the water quality standard. Appendix A provides an example of a TMDL where point source loadings of mercury from mining areas are large.

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

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

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

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

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

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

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