



Plan for Development of a Statewide Total Maximum Daily Load for Mercury (Mercury TMDL)

September 2007

Bureau of Laboratories
Division of Water Resource Management
Division of Air Resource Management

PLAN FOR DEVELOPMENT OF A STATEWIDE TOTAL MAXIMUM DAILY LOAD FOR MERCURY (MERCURY TMDL)

Executive Summary

The Bureau of Laboratories convened a workgroup, consisting of staff from the Division of Water Resource Management (DWRM), Division of Air Resource Management (DARM), the Bureau of Labs, and outside consultants, to develop a statewide, scientifically defensible TMDL for mercury. The project consists of gathering and assessing a complex suite of data (involving mercury emission, deposition, and aquatic cycling data) and conducting modeling to quantify the needed mercury reductions to address mercury-related impairment in state surface waters.

Elements of the proposed statewide mercury TMDL study include:

- Comprehensive, highly temporally resolved measurements of wet and dry mercury deposition at four locations, along with a suite of tracers that may be used to link deposition with sources. These sampling areas are referred to as “Supersites”.
- Identification of all significant sources of mercury, whether fixed or mobile, within Florida (emissions inventory).
- Development of an empirical, probabilistically based aquatic cycling model to link mercury deposition with bio-magnification in fish as a function of waterbody geochemistry.
- Conducting atmospheric modeling (both dispersion and receptor models) for the purpose of quantifying Florida mercury sources versus those sources outside Florida that must be controlled to satisfy the TMDL.

Introduction

Under the auspices of the Clean Water Act (CWA), the Florida Department of Environmental Protection (FDEP) has the responsibility to develop Total Maximum Daily Loads (TMDLs) for impaired waters in Florida. To address the mercury impairment of the State’s lakes, rivers, and coastal waters, the FDEP has selected a statewide approach for mercury TMDL development, rather than a waterbody-specific TMDL approach. This decision is based on the following reasons. First, the predominant source of mercury leading to impaired waters in Florida is from atmospheric deposition. Mercury in the atmosphere is transported across multiple watershed boundaries, where it is deposited and biologically magnified through the food web, resulting in unacceptable fish tissue burdens. While a watershed-based TMDL approach is typical for most pollutants, the phenomenon of atmospheric transport of mercury makes a regional or statewide approach the only practical method for TMDL development.

Second, the statewide approach will be far more cost-effective. Although the USEPA's 1999 Consent Decree listed 102 Florida waterbodies as requiring mercury TMDLs, a subsequent sampling of Florida lakes using a stratified-random design suggests the magnitude of lakes alone (not including streams or coastal systems) that will require mercury TMDLs will likely exceed 1,300. Rather than attempt to sample every waterbody in Florida (for mercury in fish tissue) to determine potential contamination, the proposed approach will focus on reducing statewide mercury emissions to benefit all Florida waterbodies, especially those susceptible to mercury bio-magnification (*e.g.*, oligotrophic, low alkalinity systems).

Although the concept of conducting this type of regional TMDL analysis is relatively novel, a similar predicate was established as part of the 1990 National Acid Precipitation Assessment Program Integrated Assessment. For that program, USEPA conducted regional simulations for thousands of lakes in the Upper Midwest, the Adirondacks, and Florida to evaluate how lakes would behave in response to Clean Air Act mandated changes in sulfate emissions, which in turn were predicted to reduce acidic deposition.

TMDL Requirements

Each TMDL must contain certain elements, as explained below:

1. *Describe quantified water quality goals, targets, or endpoints.* The TMDL must establish numeric endpoints for the water quality standards, including beneficial uses to be protected, as a result of implementing the TMDL. This often requires an interpretation that clearly describes the linkage(s) between factors impacting water quality standards.
2. *Analyze/account for all sources of pollutants.* All significant pollutant sources must be described, including the magnitude and location of sources.
3. *Identify pollution reduction goals.* The TMDL plan will include pollutant reduction targets for all point and nonpoint sources of pollution.
4. *Describe the linkage between water quality endpoints and pollutants of concern.* The TMDL must explain the relationship between the numeric targets and the pollutants of concern. That is, how will the required reductions in mercury emissions needed to meet the allocations result in lower deposition rates that will in turn lead to fish tissue levels that are safe to eat?
5. *Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions.* The TMDL must describe how any uncertainties regarding the ability of the plan to meet water quality standards will be addressed. The plan must consider these issues in its recommended pollution reduction targets and must provide reasonable assurance that the appropriate load reductions will be implemented.
6. *Include an appropriate level of public involvement in the TMDL process.* This is usually met by publishing public notice of the TMDL, circulating the TMDL for public comment, and holding public meetings in local communities. Public involvement must be documented in the state's TMDL submittal to USEPA Region 4.

This document presents a conceptual research plan (Figure 1) for the collection and analysis of scientific data to address two of the essential elements listed above:

- Analyze/ account for all sources of pollutants, and
- Describe the linkage between water quality endpoints and pollutants of concern.

Development of the statewide mercury TMDL will be closely coordinated within FDEP to ultimately address all required elements.

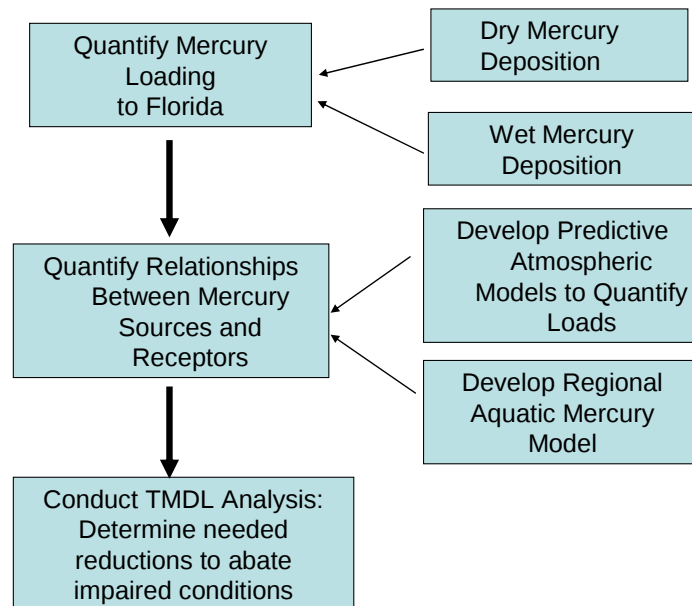


Figure 1. Overview of the technical components of a statewide Mercury TMDL.

Analyze and Account for all Sources of Pollutants

Mercury contamination in aquatic ecosystems in Florida is largely due to atmospheric deposition rather than point source discharges to surface waters or nonpoint source/stormwater inputs from within the respective watersheds. In Florida, the systems most sensitive to mercury contamination are:

- Florida Everglades Protection Area, which receives greater than 98% of its mercury from direct atmospheric inputs;
- Softwater seepage lakes, which receive an estimated 90% to greater than 99% of their mercury from direct atmospheric inputs; and
- Upper reaches of lotic systems containing high dissolved organic carbon (*e.g.*, blackwater streams). The percent of direct atmospheric inputs is unknown, but in all likelihood atmospheric deposition is virtually the sole source.

Atmospheric deposition of mercury includes mercury deposited via both wet and dry processes. The amount of mercury loading from dry deposition is currently not well quantified, but may be equivalent to or exceed wet deposition by up to a factor of five, depending on emission source characteristics, meteorology, and proximity to source. Dry deposition will also have a

characteristically much larger local component than wet deposition, particularly near significant emission sources.

Quantify Wet Deposition of Mercury

The national Mercury Deposition Network, which monitors wet deposition of mercury, currently includes five sites in Florida and two additional, nearby sites that could provide useful data (Figure 2). We propose to increase the number of monitoring sites within Florida to eight sites by adding three sites in major “mercury-sensitive” lake districts in the panhandle, Trail Ridge and Highlands Ridge. Inclusion of these sites will improve spatial coverage of the existing network, and will also improve the database used to calibrate and verify the model used to relate atmospheric emissions of mercury to deposition across Florida.

Wet deposition monitoring at the Mercury Deposition Network sites involves collecting weekly-integrated samples for total mercury and rainfall depth. Although these data are very useful in quantifying long-term deposition patterns and trends, because the network uses both time-integrated samples and has a limited suite of monitored parameters, the Mercury Deposition Network sites have limited value for elucidating the relationship between emission sources and the amount of mercury deposited at a given receptor site. Because of this, we also intend to implement comprehensive atmospheric deposition monitoring at a highly resolved temporal scale (for example, event-based wet deposition of mercury and other trace metals, continuous measurements of ambient concentrations of mercury, SO₂, and NO_x, and 12- to 24-hour integrated samples of ambient aerosol concentrations of mercury and other trace elements) at three to five additional sites (known as “Supersites”). Supersites will be established at selected locations near major emission sources of mercury within Florida to better quantify the impact these sources have on mercury deposition and improve input for models. Collecting a Supersite suite of parameters will enable quantitative assessment of local vs. larger-scale source contributions to mercury deposition. This will be important for calibrating atmospheric emissions/deposition models for determining source-receptor relationships.

Quantify Dry Deposition of Mercury

The dry deposition program has two components. The first aspect involves measuring mercury dry deposition via high-frequency measurements of reactive gaseous mercury (the primary species that deposits in a dry form) as well as particulate and elemental mercury. Sample integration periods typically will be five minutes for elemental mercury and two hours for both reactive gaseous and particulate mercury. These measurements will be conducted during annual intensive studies for several weeks at each of the Supersites to improve both the quantification of mercury dry deposition fluxes and improve the analytical methods.

Because it may be cost-prohibitive to conduct sophisticated continuous dry deposition monitoring at multiple sites for the period of interest (2007 through 2010), the second component will involve conducting parallel studies to relate the dry deposition fluxes measured at the Supersites to a cost-effective “surrogate-surface” technique. The surrogate surface we intend to use is a cationic polyethersulfone membrane that captures, through ion exchange, any reactive gaseous mercury that comes into contact with the surface. We would then deploy the surrogate surface

monitors at all the Florida Mercury Deposition Network sites to measure spatial differences in mercury dry deposition across the state. This is critical because (1) the magnitude of the fluctuation of dry deposition may be more important than wet deposition, (2) it is likely that dry deposition has a larger component derived from local compared to regional and global scale sources, and (3) dry mercury deposition probably varies more widely than wet deposition across Florida.

Quantify Mercury Source & Receptor Relationships

The relationship between mercury emission sources and deposition at various locations (*i.e.*, receptors) needs to be quantified so that an appropriate strategy for source reductions can be devised. Linking sources to receptor sites is critical for quantifying the necessary source load reductions that will be established by this TMDL. This element of the TMDL has three components.

The first task is to conduct a statewide mercury emissions inventory. The loadings from all significant emission sources within Florida must be quantified and their resultant impact on mercury deposition needs to be determined as part of defining the actual TMDL allocation. This work will involve direct emissions monitoring beginning in 2009 mandated by the Clean Air Mercury Rule (CAMR) and by the FDEP (*e.g.*, continuous emissions monitoring of cement kiln emissions), and estimated emissions derived from various other sources (using plant operating data and appropriate emissions factors).

The second component involves relating local source contributions to mercury dry and wet deposition fluxes at Florida Supersites. Establishing linkages between mercury deposition and existing mercury sources is essential for TMDL development. Establishing these linkages ideally involves:

- Continuous measurements at the Supersites of reactive gaseous mercury and suitable tracers of emission sources such as sulfur dioxide and nitrogen oxides,
- High-frequency (*e.g.*, 12-hour) integrated ambient samples for particulate mercury and various trace elements used to identify emission and natural or background sources, and
- Event-based wet deposition samples for both mercury and trace element tracers.

Coupling data from the Supersites with data from the emissions inventory is critical for calibrating and validating atmospheric emissions & deposition models.

The third component involves conducting modeling of atmospheric mercury deposition to determine contributions of emissions within Florida versus emissions and background sources from beyond Florida. This modeling will provide estimates of wet and dry deposition at a highly resolved scale of spatial resolution across Florida. The model outputs are the basis for determining the reductions in mercury emissions from specific sources needed to meet the TMDL target.

Describe the Linkage Between Water Quality Endpoints and Pollutants of Concern

Develop Predictive Empirical Model

The methodology for placing a waterbody on the verified list of impaired waters involves a demonstration that fish tissue levels are sufficiently high for the Florida Department of Health to issue a fish consumption advisory for the waterbody. For a given aquatic ecosystem, the amount of mercury that bioaccumulates in the tissues of top predators (*e.g.*, largemouth bass) is a function both of mercury loading to the system and its biogeochemistry (*e.g.*, pH, dissolved organic carbon, and trophic state). Therefore, this element of FDEP's mercury TMDL will employ an empirical model that can quantitatively link the bioaccumulation of mercury in fish, not only to mercury loading, but also to waterbody biogeochemistry on a regional and statewide basis. Different models may potentially be developed for lakes, streams, and coastal systems within Florida. Although waterbody biogeochemistry complicates TMDL development, this approach is based on the knowledge that fish tissue concentrations are ultimately driven by mercury inputs and the relationship between mercury loading and fish tissue concentrations within a given class of waterbodies is linear¹.

FDEP currently conducts "status and trends" monitoring for a large number of aquatic ecosystems, and this monitoring includes a suite of water quality parameters (*e.g.*, pH, nutrients) that have previously been determined to be useful predictors of largemouth bass tissue mercury concentrations. The FDEP status and trends monitoring is based on a probabilistic design, and uses a rotating basin approach. Sites are randomly selected within certain categories (*e.g.*, large lakes, small lakes, large streams, small streams), and their locations may be assigned *post-hoc* to one of the sub-ecoregions or lake regions developed for Florida. To develop an appropriately robust statistical model, the waterbodies included in the FDEP status and trends monitoring network will be ranked and subdivided into categories of similarity. Each category will be defined by a narrow range of water quality characteristics across a multidimensional continuum of specific parameters. For example, one category (or "bin") for lakes might include all systems with pH between 4 and 5.6 SU, total phosphorus concentrations between 50 and 100 µg/L, and total organic carbon between 0 and 3 mg/L, whereas a second bin might be identical except that it includes lakes with total phosphorus between 0 and 25 µg/L. If a four-parameter matrix is used in combination with four different concentration ranges, this equates to 64 bins distributed continuously across the sampling space to develop the statistical or empirical model.

Lake chemistry, particularly with respect to pH, tends to be bimodally distributed, and such a bimodal distribution can obscure both the true relationship between pH and mercury

¹ The linearity of the mercury loading-biota concentration relationship is based on both a series of mesocosm studies conducted in the Everglades and mercury dose-response studies such as the METAALICUS study in southern Ontario in which stable isotope additions of mercury to both a whole lake and its watershed were used to quantitatively link mercury uptake by the food chain with loading rates.

concentrations in aquatic biota and the impact of other variables as well. The problem with bimodal distributions is that bivariate relationships between a response variable such as fish tissue concentrations of mercury and the bimodally distributed variable such as pH will appear to be linear (two points, or rather in this case, two clouds of points, define a line). Ensuring that the lakes sampled represent a continuum over the given variable's range of interest will help preclude oversimplifying key relationships between variables. Lakes (or stream systems) will be randomly drawn from each bin, with the same number of systems drawn from each bin, and will then be subsequently sampled for both fish tissue mercury concentrations and water chemistry variables. Ideally, a statistical model based on this approach will be developed for each of the major lake districts or regions of watersheds within Florida. The model will relate mercury concentrations in largemouth bass to water quality variables with the greatest explanatory power (*e.g.*, pH and nutrient status). A subset of the sampled lakes within each region will be used to develop the statistical model, and the remainder will be used to validate the model. The empirical model will then be used to define the distribution of mercury in largemouth bass within the appropriate region or lake district, and an appropriate TMDL calculated based on the current mercury loading rates and the target loading rate.

Use Empirical Model to Predict Magnitude of Requisite Source Reductions to Meet Target Endpoint

The data from the status and trends program will be used in association with the validated empirical statistical model (described above) to predict the cumulative frequency distribution of mercury concentrations in largemouth bass in each sub-ecoregion (or lake region). Once this is accomplished, needed reductions in loading of mercury to each region will then be calculated based on the cumulative frequency distributions (*cf**d*'s), including a margin of safety. The margin of safety will be based on the propagated uncertainty in both the loading estimates and the uncertainty in the empirical model. Comparing the current *cf**d*'s with the target *cf**d*'s will define the relative reduction in loading of mercury that needs to occur. Coupling that reduction with the modeled atmospheric deposition rates for a given district or region thus defines the actual acceptable mercury deposition flux. Next, allocation of the requisite source reductions will be calculated for each region. Regional source reductions will then be aggregated on a statewide basis to develop the overall source reductions necessary to meet the TMDL target fish tissue concentration.

Given this complex array of data collection activities and modeling, TMDL development is targeted for the spring of 2011.

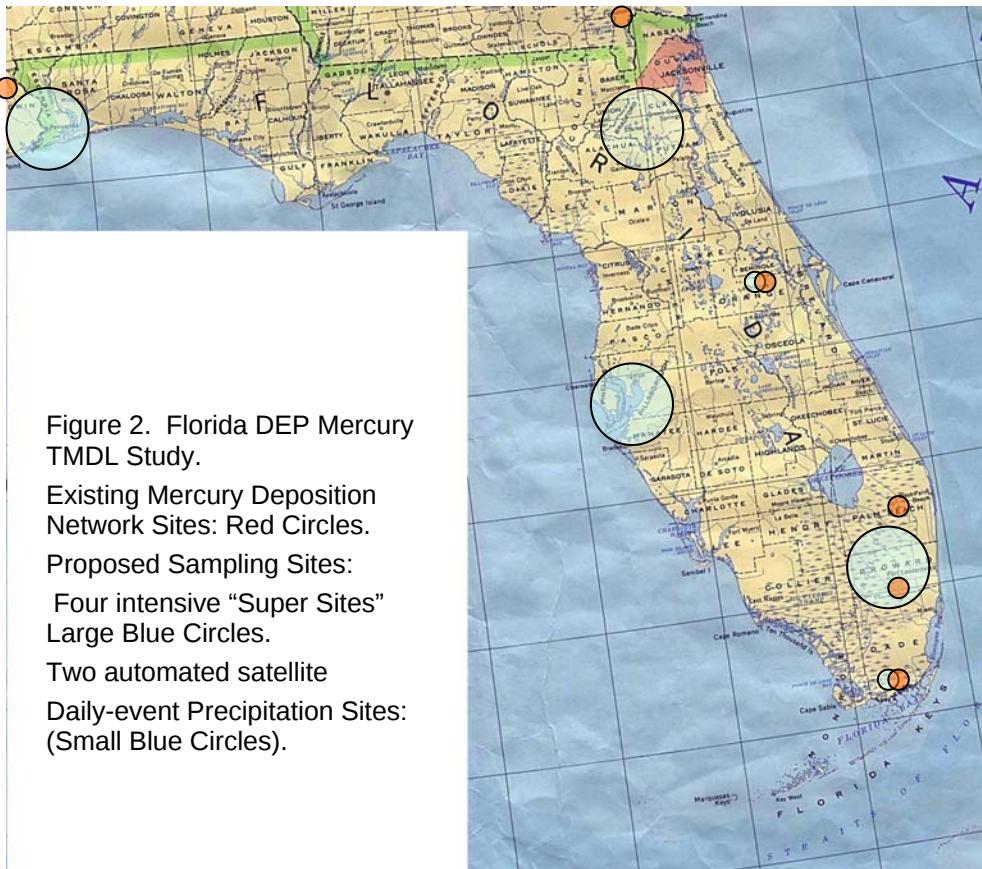


Figure 2. Florida DEP Mercury TMDL Study.

Existing Mercury Deposition Network Sites: Red Circles.

Proposed Sampling Sites:

Four intensive “Super Sites”
Large Blue Circles.

Two automated satellite
Daily-event Precipitation Sites:
(Small Blue Circles).